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Gallium(III) halide complexes with phosphines, arsines and phosphine oxides – a comparative study

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Abstract

The phosphine oxide complexes $[GaX_3(Me_3PO)]$ and $[(GaX_3)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2P(O)Ph_2)_2\}]$ have been prepared and characterised by microanalysis, IR and multinuclear NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{71}Ga) spectroscopy. The structures of $[GaCl_3(Me_3PO)]$, $[(GaBr_3)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2P(O)Ph_2)_2\}]$ and of the ionic product $[GaI_2(Me_3PO)_2][GaI_4]$ have been determined and show that the Lewis acidity of the gallium halides towards phosphinoyl ligands diminishes as the halogen becomes heavier. The $[GaX_3(Ph_3E)]$ (X = Cl, Br or I; E = P or As) and $[(GaX_3)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2PPh_2)_2\}]$ (X = Br or I) have been prepared and their structural and spectroscopic properties compared with those of the phosphinoyl complexes. The results, and competitive solution NMR studies, show that Ga(III) binds the hard R_3PO in preference to the softer phosphine or arsine ligands. Hydrolysis of gallium(III) phosphines is shown to lead to $[R_3PH][GaX_4]$, but in contrast to some other p-block halides, GaX_3 do not promote air-oxidation of R_3P to R_3PO.

Keywords: Gallium; Phosphine oxide; Phosphine; Phosphonium; NMR spectroscopy

1. Introduction

The heavier p-block metals and metalloids have a rich, albeit poorly explored, coordination chemistry, which is significantly different to that of the transition elements [1,2]. The differences arise from the limited range of oxidation states in the p-block and also from the different metal–ligand bonding which utilises only s and p orbitals and where necessary multicentre orbitals or M–X σ^* (X = halogen, etc.) as acceptor orbitals [3–5]. We have recently explored the complexes of Sn(IV) [6–10], Bi(III) [11–13], Tl(I) [14] and Sb(III) [11,15,16] with a variety of P, As, S, Se and Te donor ligands. Here we report a comparative structural and spectroscopic study of gallium(III) halide complexes with soft P or As (R_3E) and hard R_3PO donor ligands. There are limited reports of gallium(III) halide complexes of phosphorus or arsenic donor ligands [17–27], and only one phosphine oxide complex, $[GaCl_3(Ph_3PO)]$, has been thoroughly characterised [28]. We have also explored whether gallium(III) promotes or catalyses air-oxidation of R_3P to R_3PO as established previously for Sn(IV) and Bi(III) halides [29,30].

2. Results and discussion

2.1. Ga(III) phosphine oxides

Reaction of the appropriate GaX_3 (X = Cl, Br or I) with Me_3PO in a 1:1 mol. ratio in CH_2Cl_2 under anhydrous conditions gave the white $[GaX_3(Me_3PO)]$. The diphosphine dioxide complexes $[(GaX_3)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2P(O)Ph_2)_2\}]$ were obtained similarly using a 2:1 GaX_3:$o\text{-}C_6H_4(CH_2P(O)Ph_2)_2$ ratio. The isolated complexes are air-stable in the solid state and easily soluble in a range of organic

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Table 1
Selected bond lengths (Å) and angles (°) for [$GaCl_3(Me_3PO)$]

Ga1–O1	1.828(6)	Ga1–Cl1	2.162(2)
Ga1–Cl2	2.161(2)	Ga1–Cl3	2.159(2)
P1–O1	1.518(7)		
O1–Ga1–Cl3	108.9(3)	O1–Ga1–Cl2	106.5(2)
Cl3–Ga1–Cl2	109.60(11)	O1–Ga1–Cl1	109.9(2)
Cl3–Ga1–Cl1	111.28(10)	Cl2–Ga1–Cl1	110.52(12)
P1–O1–Ga1	147.9(4)		

solvents. Crystals of [$GaCl_3(Me_3PO)$] were obtained from CH_2Cl_2–hexane and showed the expected pseudo-tetrahedral structure (Table 1, Fig. 1). The d(P–O) (1.518(7) Å) is lengthened from the value in Me_3PO itself (1.489(6) Å) [31] and d(Ga–O) 1.828(6) Å is similar to the value in [$GaCl_3(Ph_3PO)$] (1.818(10) Å) [28], although in the latter the phosphine oxide coordination is linear by symmetry (although adp ellipsoids suggest some disorder [28]), compared to the significantly bent geometry in the present complex (angle Ga–O–P = 148°). The three [$GaX_3(Me_3PO)$] complexes show strong ν(P=O) stretches in the IR spectra at ~1100 cm^{-1}, lowered from 1166 cm^{-1} in Me_3PO, and ν(GaX) are typical of tetrahedral Ga(III) (Table 2, Section 6). In chlorocarbon solvents the ^1H NMR spectra show sharp doublets for the Me resonances, and the $^{31}P\{^1H\}$ NMR spectra are sharp singlets with substantial high frequency coordination shifts from Me_3PO ($\delta = 38$). The chemical shifts fall with halogen: $\delta = 73.5$ (Cl), 72.0 (Br), 70.5 (I), suggesting the Lewis acidity of the GaX_3 also falls in this order. All exhibit relatively sharp singlets in the ^{71}Ga NMR spectra[1] at ambient temperatures (Table 2), which will be discussed further below. Although the spectroscopic data on [$GaI_3(Me_3PO)$] showed only the neutral species present, a solution in CH_2Cl_2–hexane produced a small number of colourless crystals which were shown to be the ionic product, [$GaI_2(Me_3PO)_2$][GaI_4]. The structure is shown in Fig. 2 (Table 3) and contains a tetrahedral [GaI_4]$^-$ anion (d(Ga–I) = 2.548(2) Å) and a pseudo-tetrahedral cation with d(Ga–O) = 1.854(8), 1.848(8) Å and d(Ga–I) = 2.488(2), 2.500(2) Å, with Ga–O–P angles of 136.8(6) and 140.6(6)°. The Ga–I distances are somewhat shorter in the cation than the anion as expected, but the notable difference is the longer d(Ga–O) (1.851 (av) Å), compared to the neutral [$GaCl_3(Me_3PO)$] (1.828 Å) (above). In spite of the crystallographic evidence for [$GaI_2(Me_3PO)_2$]$^+$, [$GaCl_2(Me_3PO)_2$]$^+$ could not be prepared from [$GaCl_3(Me_3PO)$], Me_3PO and either $FeCl_3$ or $SbCl_5$ (as chloride abstractors).

The structure of [$(GaBr_3)_2\{\mu$-o-$C_6H_4(CH_2P(O)Ph_2)_2\}$] (Table 4, Fig. 3) shows a bridging diphosphine dioxide coordinated to two pseudo-tetrahedral gallium moieties, which are staggered to minimise steric crowding. The Ga–O distances 1.892(4) and 1.858(4) Å are surprisingly different, but the other parameters seem unexceptional, including the non-linear Ga–O–P angles of 148° and 153°. Spectroscopically the three [$(GaX_3)_2\{\mu$-o-$C_6H_4(CH_2P(O)Ph_2)_2\}$] complexes show similar trends to those with Me_3PO described above, notably the significant fall in ν(PO) on coordination and the high frequency coordination shifts in $\delta(^{31}P)$ which vary with halogen Cl > Br > I (Table 2). Curiously, we were unable to observe a ^{71}Ga NMR resonance for any of the diphosphine dioxide complexes over the temperature range 295–180 K, presumably due to the line broadening resulting from fast relaxation of the quadrupolar gallium nucleus in these large and asymmetric molecules.

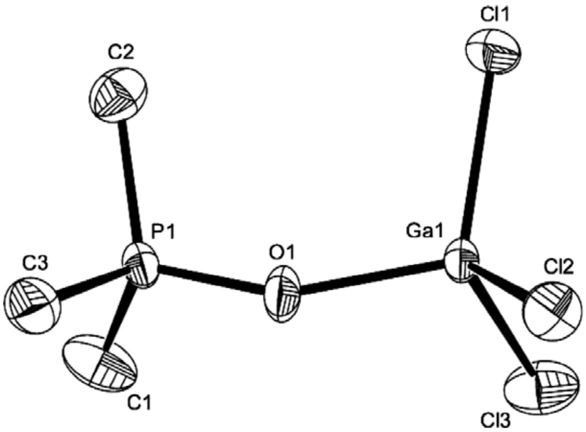

Fig. 1. View of the structure of [$GaCl_3(Me_3PO)$] with atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

2.2. Gallium phosphine and arsine complexes

As indicated in Section 1, it is of interest to compare the spectroscopic and structural consequences of changing the hard R_3PO donor for a soft R_3P or R_3As ligand. Initially [$GaX_3(Me_3P)$] were prepared, but were found to be very poorly soluble in solvents suitable for spectroscopic studies (cf. Ref. [19]), and we have therefore used [$GaX_3(Ph_3P)$] and [$GaX_3(Ph_3As)$] as comparator complexes (the R group is expected to have a minimal effect on the trends). These complexes have been reported previously and some data presented [20–23,26]. The complexes were obtained in high yield by reaction of the appropriate GaX_3 and Ph_3E in anhydrous diethyl ether. X-ray crystal structures were determined for [$GaX_3(Ph_3P)$] (X = Cl or Br) (Table 5, Figs. 4 and 5). There are two reports [20,21,26] of the crystal structure of [$GaI_3(Ph_3P)$] both in the trigonal space group $R\bar{3}$, but with one using hexagonal and the other rhombohedral basis vectors. The Ga–P (2.416(5), 2.413(4) Å) and Ga–I (2.5212(9), 2.518(2) Å) are in excellent agreement, as are the I–Ga–I (ca. 113.8°) and I–Ga–P (ca. 104.6°) angles. [$GaCl_3(Ph_3P)$] and [$GaBr_3(Ph_3P)$] show the expected pseudo-tetrahedral monomer geometry. The Ga–P distances increase along the series Cl (2.372(2)) → Br (2.385(1)) → I (2.416(5) Å) consistent with reduced Lewis

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[1] ^{71}Ga, $I = 3/2$, 39.9%, $\Xi = 30.49$ MHz, $Q = 0.112 \times 10^{-28}$ m^2; ^{69}Ga, $I = 3/2$, 60.1%, $\Xi = 24.00$ MHz, $Q = 0.178 \times 10^{-28}$ m^2 [32].

Table 2
Selected spectroscopic data

Complex	ν(P=O)/cm^{-1}	δ(^{31}P)[a]	δ(^{71}Ga)[b]
[GaCl$_3$(Me$_3$PO)]	1100	73.5	230
[GaBr$_3$(Me$_3$PO)]	1095	72.0	106
[GaI$_3$(Me$_3$PO)]	1102	70.5	−242
[GaCl$_3$(Ph$_3$PO)][c]	1144	45.9	230
[(GaCl$_3$)$_2${μ-*o*-C$_6$H$_4$(CH$_2$P(O)Ph$_2$)$_2$}]	1088, 1070	52.5	n.o.
[(GaBr$_3$)$_2${μ-*o*-C$_6$H$_4$(CH$_2$P(O)Ph$_2$)$_2$}]	1091, 1080	52.0	n.o.
[(GaI$_3$)$_2${μ-*o*-C$_6$H$_4$(CH$_2$P(O)Ph$_2$)$_2$}]	1086, 1076	51.4	n.o.
[GaCl$_3$(Ph$_3$P)]		−5.5(m)	264 (d, $J = 721$ Hz)
[GaBr$_3$(Ph$_3$P)]		−10.7(m)	152 (d, $J = 693$ Hz)
[GaI$_3$(Ph$_3$P)]		−29.7(m)	−151 (d, $J = 466$ Hz)
[GaCl$_3$(Ph$_3$As)]			264
[GaBr$_3$(Ph$_3$As)]			132
[GaI$_3$(Ph$_3$As)]			−203

[a] Relative to external 85% H$_3$PO$_4$, ligand shifts are Me$_3$PO $\delta = 38$, *o*-C$_6$H$_4$(CH$_2$P(O)Ph$_2$)$_2$ $\delta = 30.8$, PPh$_3$ $\delta = -6$.

[b] Relative to [Ga(H$_2$O)$_6$]$^{3+}$ in water at pH = 0, [GaCl$_4$]$^-$ $\delta = 251$, [GaBr$_4$]$^-$ $\delta = 64$, [GaI$_4$]$^-$ $\delta = -455$.

[c] Data from Ref. [28].

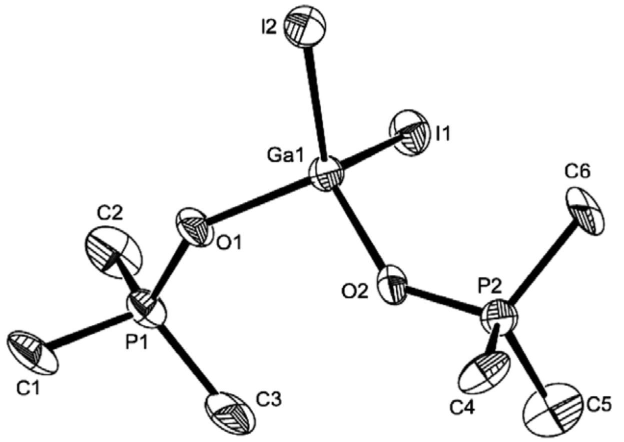

Fig. 2. View of the structure of the cation in [GaI$_2$(Me$_3$PO)$_2$][GaI$_4$] with atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for [GaI$_2$(Me$_3$PO)$_2$][GaI$_4$]

Ga1–O1	1.854(8)	Ga1–O2	1.846(8)
Ga1–I1	2.4997(17)	Ga1–I2	2.4875(16)
Ga2–I3	2.5472(16)	Ga2–I4	2.5482(15)
Ga2–I5	2.5461(15)	Ga2–I6	2.5258(16)
P1–O1	1.523(9)	P2–O2	1.525(8)
O2–Ga1–O1	101.3(4)	O2–Ga1–I2	111.8(3)
O1–Ga1–I2	106.7(3)	O2–Ga1–I1	109.8(3)
O1–Ga1–I1	109.2(3)	I2–Ga1–I1	116.89(6)
Ga1–O1–P1	136.8(6)	Ga1–O2–P2	140.6(6)

acidity of the gallium as the halide becomes less electronegative, whilst the changes in Ga–X follow the changes in covalent radii of X. The literature structure of [GaI$_3$(Ph$_3$As)] [20,21] is isomorphous with the Ph$_3$P analogue ($R\bar{3}$) with a slightly shorter Ga–I (2.509(1) Å) and with Ga–As = 2.490(1) Å. We note that in the series containing the silyl phosphine, [GaX$_3${P(SiMe$_3$)$_3$}] (X = Cl, Br, I), [17] the Ga–P distances decrease Cl → Br → I, which is the reverse of that observed in organophosphine complexes.

The ^{31}P{^{1}H} NMR spectra of [GaX$_3$(Ph$_3$P)] are notable in showing resolved ^{31}P–$^{69/71}$Ga couplings. [GaCl$_3$(Ph$_3$P)] in CH$_2$Cl$_2$ solution shows no ^{31}P{^{1}H} NMR resonance at room temperature, but a broad feature appears on cooling the solution to 273 K, and at 183 K this has resolved into a broad multiplet which approximates to two overlapping quartets due to coupling to the $I = 3/2$ ^{69}Ga and ^{71}Ga. For [GaBr$_3$(Ph$_3$P)] the room temperature ^{31}P{^{1}H} NMR resonance is an ill-defined multiplet, becomes a quartet at 273 K (although the lines are too broad to show resolved couplings to the separate gallium isotopes). For [GaI$_3$(Ph$_3$P)] two superimposed quartet couplings are

Table 4
Selected bond lengths (Å) and angles (°) for [(GaBr$_3$)$_2${μ-*o*-C$_6$H$_4$-(CH$_2$P(O)Ph$_2$)$_2$}]

Ga1–O1	1.892(4)	Ga1–Br1	2.2669(9)
Ga1–Br3	2.2952(8)	Ga1–Br2	2.3133(8)
Ga2–O2	1.858(4)	Ga2–Br5	2.2853(9)
Ga2–Br4	2.2983(8)	Ga2–Br6	2.2990(8)
P2–O2	1.520(4)	P1–O1	1.525(4)
O1–Ga1–Br1	109.11(11)	O1–Ga1–Br3	106.88(10)
Br1–Ga1–Br3	112.50(3)	O1–Ga1–Br2	101.93(11)
Br1–Ga1–Br2	113.99(3)	Br3–Ga1–Br2	111.62(3)
O2–Ga2–Br5	105.55(13)	O2–Ga2–Br4	102.32(11)
Br5–Ga2–Br4	113.41(3)	O2–Ga2–Br6	107.24(12)
Br5–Ga2–Br6	114.01(3)	Br4–Ga2–Br6	113.10(3)
P1–O1–Ga1	148.3(2)	P2–O2–Ga2	153.9(2)

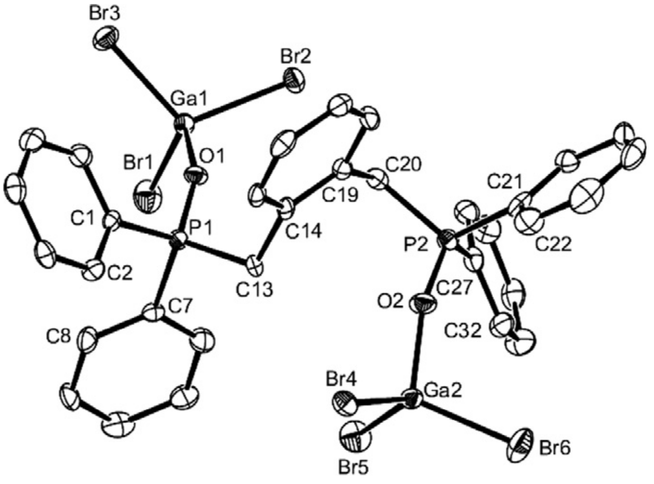

Fig. 3. View of the structure of [(GaBr$_3$)$_2${*o*-C$_6$H$_4$(CH$_2$P(O)Ph$_2$)$_2$}] with the atom numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

Table 5
Selected bond lengths (Å) and angles (°) for [$GaX_3(Ph_3P)$]

	X = Cl	X = Br (Ga1)	X = Br (Ga2)[a]
Ga1–P1	2.3717(16)	2.3848(13)	2.3879(13)
Ga1–X1	2.1677(15)	2.3134(7)	2.3133(7)
Ga1–X2	2.1679(16)	2.3048(7)	2.3212(7)
Ga1–X3	2.1696(15)	2.3225(7)	2.3082(8)
X1–Ga1–P1	104.17(6)	105.83(4)	106.71(4)
X2–Ga1–P1	104.08(6)	107.45(4)	106.88(4)
X3–Ga1–P1	111.46(6)	107.50(4)	105.93(4)
X1–Ga1–X2	112.98(6)	111.79(3)	111.68(3)
X1–Ga1–X3	112.40(6)	114.27(3)	112.39(3)
X2–Ga1–X3	111.24(6)	109.63(3)	112.73(3)

For comparison [$GaI_3(Ph_3P)$] has Ga–I = 2.5212(9) or 2.518(2) Å (Refs. [26,20] respectively), Ga–P = 2.416(5) or 2.413(4) Å and [$GaI_3(Ph_3As)$] has Ga–I = 2.509(1) Å and Ga–As = 2.490(1) Å (Ref. [21]).

[a] For the second molecule the data are for Ga2, P2, X4, X5 and X6.

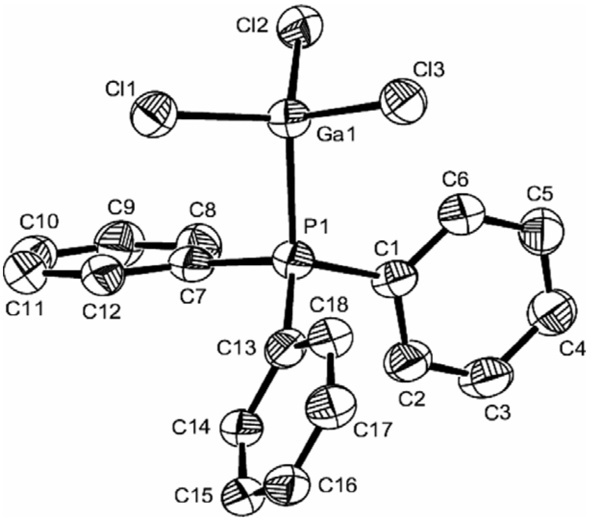

Fig. 4. View of the structure of [$GaCl_3(Ph_3P)$] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

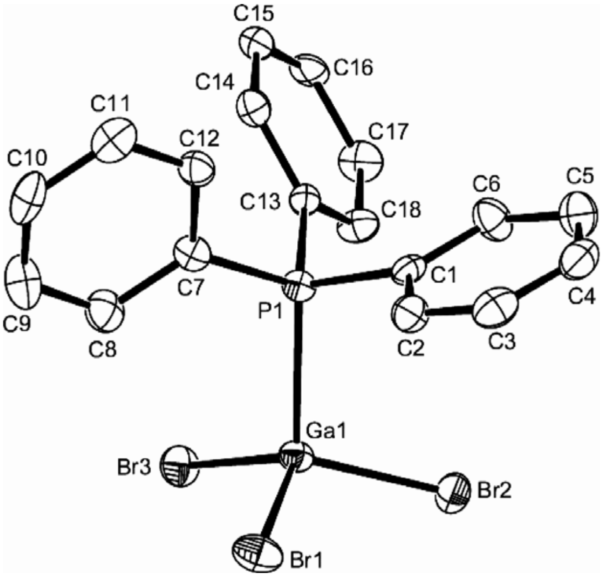

Fig. 5. View of the structure of [$GaBr_3(Ph_3P)$] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The other molecule in the asymmetric unit is very similar.

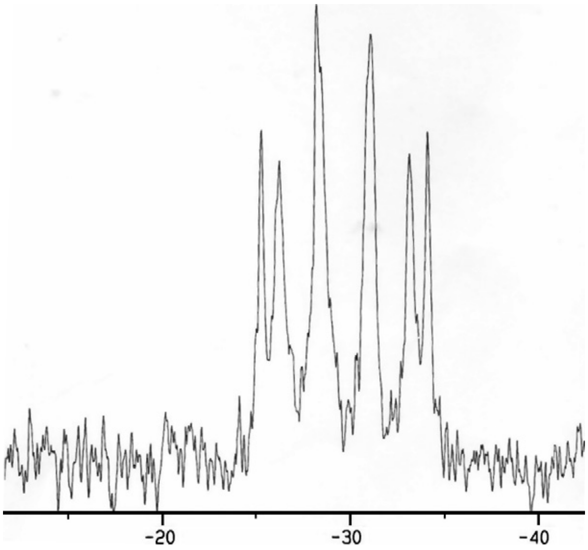

Fig. 6. $^{31}P\{^1H\}$ NMR of [$GaI_3(Ph_3P)$] in CH_2Cl_2 at 273 K.

clearly resolved at ambient temperatures; the lines sharpen on cooling to 273 K (Fig. 6) and then broaden on further cooling. The changes with halide and temperature reflect the different electric field gradients in the three compounds and how these affect the quadrupolar relaxation rates of the gallium nuclei over this temperature range. The ^{71}Ga NMR spectra of all three compounds show clear doublet couplings to ^{31}P (Table 2) with $^1J(^{31}P\text{-}^{71}Ga)$ falling from Cl → Br → I.

The *o*-xylyl diphosphine *o*-$C_6H_4(CH_2PPh_2)_2$ is somewhat pre-organised for chelation by the central *o*-phenylene backbone, and functions as a chelate to many late transition metals, despite forming a seven-membered ring in the process [33]. However, on reaction with GaX_3 it behaves as a bridging bidentate, forming [$(GaX_3)_2$-{*o*-$C_6H_4(CH_2PPh_2)_2$}] as confirmed by the crystal structure of the iodo-complex (Table 6, Fig. 7). The molecule has approximate twofold symmetry and the ligand conformation places the two GaI_3 groups '*anti*' to minimise steric interactions (Ga1–P1···P2–Ga2 = 161°). Spectroscopically these complexes (Table 2) are similar to those of Ph_3P, but provide a useful comparison with the diphosphine dioxide compounds described above.

3. Some comparisons of the effect of donor types on gallium(III)

The spectroscopic and structural data set out in previous sections clearly support the expected conclusion that Lewis acidity decreases in the gallium(III) halides Cl > Br > I,

Table 6
Selected bond lengths (Å) and angles (°) for [$(GaI_3)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2PPh_2)_2\}$]

Ga1–P1	2.3891(9)	Ga2–P2	2.3872(9)
Ga1–I1	2.5312(4)	Ga2–I4	2.5143(4)
Ga1–I2	2.5286(4)	Ga2–I5	2.5211(4)
Ga1–I3	2.5194(4)	Ga2–I6	2.5516(5)
P1–Ga1–I1	111.78(2)	P2–Ga2–I4	109.57(2)
P1–Ga1–I2	102.22(2)	P2–Ga2–I5	109.66(2)
P1–Ga1–I3	105.87(2)	P2–Ga2–I6	99.97(2)
I1–Ga1–I2	112.752(15)	I4–Ga2–I5	111.195(15)
I1–Ga1–I3	111.335(15)	I4–Ga2–I6	115.297(15)
I2–Ga1–I3	112.337(16)	I5–Ga2–I6	110.526(14)

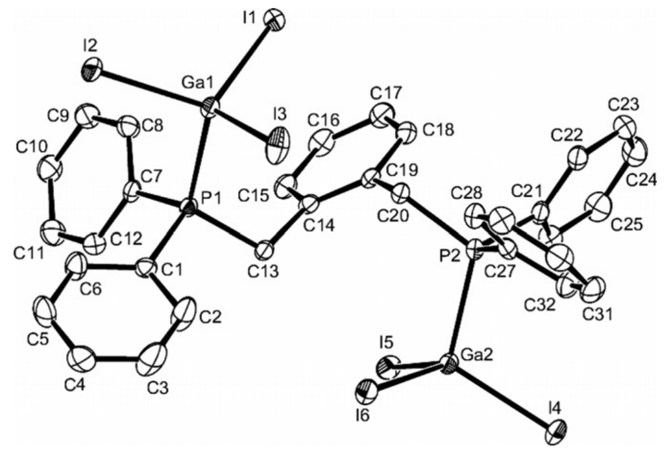

Fig. 7. View of the structure of [$(GaI_3)_2\{o\text{-}C_6H_4(CH_2PPh_2)_2\}$] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

towards both hard and soft donor ligands. The second point to note is the trends in bond lengths about the gallium centre with Ga–Cl (~2.15 Å), Ga–Br (~2.3 Å), Ga–I (~2.5 Å), Ga–O (~1.85 Å), Ga–P (~2.4 Å) and Ga–As (~2.5 Å). It is clear that the Ga–X and the Ga–O bond lengths are *ca.* 0.1 Å shorter than the sum of the covalent radii, [34] whilst the Ga–P(As) are rather longer than expected, suggesting that the softer donors are more weakly bound. Support for this came from *in situ* $^{31}P\{^1H\}$ NMR measurements (CH_2Cl_2 solution) which showed that Me_3PO displaced Ph_3P or Ph_3As (L) from their [$GaCl_3L$] complexes, but that [$GaCl_3(Me_3PO)$] was unaffected by the presence of excess L.

The ^{71}Ga NMR spectra show progressive low frequency shifts with halide Cl → Br → I, but the trends with neutral donor are more variable, giving evidence that several competing factors are involved.

4. Studies on oxidation and hydrolysis of gallium phosphines

In the presence of dioxygen, tin(IV) halides readily convert phosphines to phosphine oxides [8,10,29] and similar behaviour, although less thoroughly explored, is observed with Bi and Sb halides [11,30]. In order to explore whether [$GaX_3(Ph_3P)$] forms Ph_3PO in chlorocarbon solvents, solutions of all three complexes in anhydrous CH_2Cl_2 were placed in 10 mm o.d. NMR tubes, the tubes filled with dry O_2 and the $^{31}P\{^1H\}$ NMR spectra monitored at regular intervals over a three week period. The spectra showed no evidence for phosphine oxide formation (although some [R_3PH][GaX_4] were evident due to trace hydrolysis). We conclude that, in marked contrast to the Group 15 MX_3 and especially the Sn(IV) systems, gallium halides do not promote phosphine oxidation under these conditions.

In rigorously anhydrous chlorocarbons (CH_2Cl_2 or $CHCl_3$ and their deuterated analogues), gallium(III) halide phosphine and diphosphine complexes exhibit $^{31}P\{^1H\}$ NMR spectra consistent with the presence of a single species in each. In favourable cases with the (C_{3v}) $GaPX_3$ donor sets, ^{71}Ga NMR spectra lead to the same conclusions. However, even brief exposure of the solutions of [$GaX_3(R_3P)$] to air resulted in the appearance of new resonances. In the $^{31}P\{^1H\}$ NMR spectra the new features were broad with ill-defined structure and typically to high frequency of that of the gallium complex, and were assigned to the corresponding phosphonium cations $[R_3PH]^+$ both by comparison of their chemical shifts with literature values [35], and from the ^{1}H-coupled ^{31}P NMR spectra which showed doublets due to $^1J_{PH}$ (300–700 Hz).[2] The ^{71}Ga spectra also showed resonances due to the corresponding $[GaX_4]^-$ anion at X = Cl: $\delta = 251$; X = Br: $\delta = 64$; X = I: $\delta = -455$ [32]. All of the complexes we examined showed a tendency to form phosphonium salts, although it is particularly evident with alkyl phosphines, probably because these are the strongest proton bases [36].

Addition of small amounts of water to the solutions resulted in immediate and complete loss of the resonances due to [$GaX_3(R_3P)$] and the only species evident in the ^{71}Ga NMR spectra were the $[GaX_4]^-$ anions. The formation of phosphonium salts was also observed in the gallium–diphosphine complexes, and we note that Sigl et al. [37] identified the hydrolysis product of [$GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$][$GaCl_4$] as [$o\text{-}C_6H_4(PPh_2)(PPh_2H)$][$GaCl_4$] by an X-ray crystal structure.

Final confirmation of the identity of the hydrolysis products comes from the crystal structure of [Me_2PhPH][$GaCl_4$] (Fig. 8). Colourless crystals of which were obtained from a solution shown by NMR spectroscopy to contain mainly [$GaCl_3(Me_2PhP)$], showing the ionic species crystallise preferentially. [$GaCl_3(Ph_3P)$] is quantitatively converted into [Ph_3PH][$GaCl_4$] by treatment with HCl gas in CH_2Cl_2 solution, which provides the most convenient synthesis for these phosphonium species.

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[2] The broad lines arise from incomplete decoupling of the P–H proton under normal broad band decoupling settings.

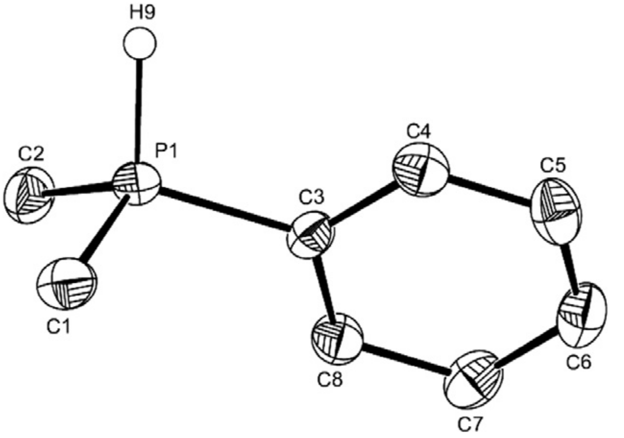

Fig. 8. View of the structure of the cation in $[Me_2PhPH][GaCl_4]$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms (except that on P1) are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.788(4); P1–C2 1.784(3); P1–C3 1.788(3); C–P1–C 110.08(16)–111.50(17); Ga1–Cl 2.1657(11)–2.1770(11).

5. Conclusions

These results show that the Lewis acidity of GaX_3 decreases as the halide becomes heavier and that the maximum coordination number at the gallium in these species is four. With only one exception, all the complexes were neutral with X_3O or X_3E (X = Cl, Br or I; E = P or As) donor sets. Competitive NMR studies on the $GaCl_3$ systems show that R_3PO are preferred to R_3E suggesting that $GaCl_3$ is quite a hard Lewis acid.

6. Experimental

All the reactions and manipulations were performed in an inert atmosphere (N_2) glovebox or using Schlenk techniques. Diethyl ether and hexane were dried by distillation over sodium/benzophenone and dichloromethane was dried by distillation from CaH_2. Infrared spectra were measured as Nujol mulls between CsI plates on a Perkin–Elmer PE983 spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ solution on a Bruker AV300, $^{31}P\{^1H\}$ and ^{71}Ga NMR spectra on a Bruker DPX400 and referenced to 85% H_3PO_4 and $[Ga(H_2O)_6]^{3+}$ respectively. Me_3PO (Aldrich) was freshly sublimed prior to use. $o\text{-}C_6H_4(CH_2P(O)Ph_2)_2$ was obtained as a white solid by stirring a CH_2Cl_2 solution of $o\text{-}C_6H_4(CH_2PPh_2)_2$ in dry air with a catalytic amount of SnI_4 [29] followed by hydrolysis, extraction with CH_2Cl_2 and drying ($MgSO_4$). ^1H NMR ($CDCl_3$): $\delta = 3.90$ (d, [4H], CH_2, $^2J_{PH} = 13.0$ Hz), 6.68 (m, [2H], $o\text{-}C_6H_4$), 6.78 (m, [2H], $o\text{-}C_6H_4$), 7.30–7.67 (m, [20H], Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 35.9$ (d, CH_2, $^1J_{PC} = 66.4$ Hz), 126.6–133.3 (aromatic C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 30.8. IR (Nujol): $v = 1181$ br s (P=O) cm^{-1}.

6.1. *[GaCl₃(Me₃PO)]*

$GaCl_3$ (0.19 g, 1.09 mmol) in CH_2Cl_2 (5 mL) was combined with a CH_2Cl_2 solution (10 mL) of Me_3PO (0.10 g, 1.09 mmol) and the reaction mixture was stirred under N_2 for *ca.* 2 h. The volatiles were then removed *in vacuo* and the white solid rinsed with hexane and dried *in vacuo*. Yield 0.26 g, 88%. *Anal.* Calc. for $C_3H_9Cl_3GaOP$: C, 13.4; H, 3.4. Found: C, 13.7; H, 3.4%. ^1H NMR ($CDCl_3$, 298 K): $\delta = 1.83$ (d, Me, $^2J_{PH} = 12.8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.1$ (d, Me, $^1J_{PC} = 70.6$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 73.5$. ^{71}Ga NMR ($CDCl_3$): $\delta = 230$. IR (Nujol): $v = 1100$ br s (P=O), 387, 358 (Ga–Cl) cm^{-1}.

6.2. *[GaBr₃(Me₃PO)]*

Method as above, but using $GaBr_3$. White solid (62%). *Anal.* Calc. for $C_3H_9Br_3GaOP$: C, 9.0; H, 2.6. Found: C, 9.1; H, 2.0%. ^1H NMR ($CDCl_3$, 298 K): $\delta = 1.85$ (d, Me, $^2J_{PH} = 13.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.3$ (d, Me, $^1J_{PC} = 70.2$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 72.0$. ^{71}Ga NMR ($CDCl_3$): $\delta = 106$. IR (Nujol): $v = 1095$ br s (P=O), 283, 244 (Ga–Br) cm^{-1}.

6.3. *[GaI₃(Me₃PO)]*

Method as above, but using GaI_3. White solid (65%). *Anal.* Calc. for $C_3H_9GaI_3OP \cdot CH_2Cl_2$: C, 7.6; H, 1.8. Found: C, 7.4; H, 1.8%. ^1H NMR ($CDCl_3$, 298 K): $\delta = 1.85$ (d, Me, $^2J_{PH} = 13.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.0$ (d, Me, $^1J_{PC} = 70.5$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 70.5$. ^{71}Ga NMR ($CDCl_3$): $\delta = -242$. IR (Nujol): $v = 1102$ (P=O), 250 (Ga–I) cm^{-1}.

6.4. *[(GaCl₃)₂{μ-o-C₆H₄(CH₂P(O)Ph₂)₂}]*

Method as above, but using a 2:1 $GaCl_3$:diphosphine ratio. White solid (89%). *Anal.* Calc. for $C_{32}H_{28}Cl_6Ga_2O_2P_2 \cdot 0.25CH_2Cl_2$: C, 44.0; H, 3.3. Found: C, 44.1; H, 2.6%. ^1H NMR ($CDCl_3$, 298 K): $\delta = 4.08$ (d, CH_2, 4H, $^2J_{PH} = 12.4$ Hz), 6.51 (m, $o\text{-}C_6H_4$, 2H), 6.98 (m, $o\text{-}C_6H_4$, 2H), 7.50–7.78 (m, Ph, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 33.7$ (d, CH_2, $^1J_{PC} = 68.1$ Hz), 124.3–135.4 (aromatic C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.5$. ^{71}Ga NMR ($CDCl_3$): not observed. IR (Nujol): $v = 1088$ br s, 1070 sh (P=O), 397, 356 (Ga–Cl) cm^{-1}.

6.5. *[(GaBr₃)₂{μ-o-C₆H₄(CH₂P(O)Ph₂)₂}]*

Method as above, but using a 2:1 $GaBr_3$:diphosphine ratio. White solid (94%). *Anal.* Calc. for $C_{32}H_{28}Br_6Ga_2O_2P_2 \cdot CH_2Cl_2$: C, 32.8; H, 2.5. Found: C, 32.4; H, 2.1%. ^1H NMR ($CDCl_3$, 298 K): $\delta = 4.11$ (d, CH_2, 4H, $^2J_{PH} = 12.3$ Hz), 6.50 (m, $o\text{-}C_6H_4$, 2H), 6.95 (m, $o\text{-}C_6H_4$, 2H), 7.50–7.77 (m, Ph, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 34.1$ (d, CH_2, $^1J_{PC} = 68.0$ Hz), 124.2–135.4 (aromatic C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.0$. ^{71}Ga NMR ($CDCl_3$): not observed. IR (Nujol): $v = 1091$ s, 1080 s (P=O), 296, 230 (Ga–Br) cm^{-1}.

6.6. *[(GaI$_3$)$_2${μ-o-C$_6$H$_4$(CH$_2$P(O)Ph$_2$)$_2$}]*

Method as above, but using a 2:1 GaI$_3$:diphosphine ratio. White solid (65%). *Anal.* Calc. for $C_{32}H_{28}Ga_2I_6O_2P_2$: C, 27.3; H, 2.0. Found: C, 27.4; H, 1.7%. ^{1}H NMR (CDCl$_3$, 298 K): $\delta = 4.15$ (d, CH$_2$, 4H, $^2J_{PH} = 12.6$ Hz), 6.50 (m, *o*-C$_6$H$_4$, 2H), 6.95 (m, *o*-C$_6$H$_4$, 2H), 7.50–7.80 (m, Ph, 20H). ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 33.6$ (d, CH$_2$, $^1J_{PC} = 68.1$ Hz), 124.1–135.3 (aromatic C). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 51.4$. ^{71}Ga NMR (CDCl$_3$): not observed. IR (Nujol): $\nu = 1086$ s, 1076 s (P=O), 240 (Ga–I) cm^{-1}.

6.7. *[GaCl$_3$(Ph$_3$P)]*

A solution of Ph$_3$P (0.300 g, 1.14 mmol) in diethyl ether (5 mL) was added dropwise to a stirred solution of GaCl$_3$ (0.201 g, 1.14 mmol) in diethyl ether (4 mL). After stirring at room temperature for 15 h, the resultant white precipitate was filtered off, washed with diethyl ether (2 mL) and dried *in vacuo*. Yield 0.32 g, 65%. *Anal.* Calc. for $C_{18}H_{15}Cl_3GaP$: C, 49.3; H, 3.5. Found: C, 48.7; H, 3.8%. ^{1}H NMR (CDCl$_3$, 295 K): δ 7.69–7.41 (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): 295 K not observed; 273 K $\delta = -5.4$ (m). ^{71}Ga NMR (CDCl$_3$): $\delta = 264$ (br d, $J = 721$ Hz). IR (Nujol): $\nu = 387$ s, 347 m (Ga–Cl) cm^{-1}.

6.8. *[GaBr$_3$(Ph$_3$P)]*

Made similarly to the chloro compound. White solid (64%). *Anal.* Calc. for $C_{18}H_{15}Br_3GaP$: C, 37.8; H, 2.9. Found: C, 38.1; H, 2.8%. ^{1}H NMR (CDCl$_3$, 295 K): δ 7.81–7.38 (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = -10.7$. ^{71}Ga NMR (CDCl$_3$): $\delta = 152$ (d, $J = 693$ Hz). IR (Nujol): $\nu = 289$ s, 234 m (Ga–Br) cm^{-1}.

6.9. *[GaI$_3$(Ph$_3$P)]*

Made similarly to the chloro compound. White solid (66%). *Anal.* Calc. for $C_{18}H_{15}GaI_3P$: C, 30.3; H, 2.1. Found: C, 30.5; H, 2.0%. ^{1}H NMR (CDCl$_3$, 295 K): δ 7.81–7.38 (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = -29.7$. ^{71}Ga NMR (CDCl$_3$): $\delta = -151$ (d, $J = 466$ Hz). IR (Nujol): $\nu = 241$ m (Ga–I) cm^{-1}.

6.10. *[(GaBr$_3$)$_2${o-C$_6$H$_4$(CH$_2$PPh$_2$)$_2$}]*

Made similarly using a 2:1 Ga:ligand mol. ratio. White solid (76%). *Anal.* Calc. for $C_{32}H_{28}Br_6Ga_2P_2$: C, 35.2; H, 2.6. Found: C, 35.5; H, 2.5%. ^{1}H NMR (CDCl$_3$): 3.72 (d, 4H, CH$_2$), 6.53–6.97 (m), 7.45–7.75 (m, aromatic H). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = -14.2$ (s). ^{71}Ga NMR (CDCl$_3$): $\delta = 156$ (br). IR (Nujol): $\nu = 281$ s, 227 m (Ga–Br) cm^{-1}.

6.11. *[(GaI$_3$)$_2${o-C$_6$H$_4$(CH$_2$PPh$_2$)$_2$}]*

Prepared similarly to the previous compound. White solid (75%). *Anal.* Calc. for $C_{32}H_{28}Ga_2I_6P_2$: C, 27.9; H, 2.1. Found: C, 28.2; H, 1.9%. ^{1}H NMR (CDCl$_3$): 3.60 (d, 4H, CH$_2$), 6.97–6.69 (m), 7.63–7.40 (m, aromatic H). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = -33.7$ (s). ^{71}Ga NMR (CDCl$_3$): $\delta = -146$ (s). IR (Nujol): $\nu = 234$ m (Ga–I) cm^{-1}.

6.12. *[GaCl$_3$(Ph$_3$As)]*

A solution of Ph$_3$As (0.220 g, 0.718 mmol) in diethyl ether (10 mL) was added dropwise to a stirred solution of GaCl$_3$ (0.126 g, 0.718 mmol) in diethyl ether (5 mL). After stirring at room temperature for 4 h, removal of Et$_2$O gave a white solid, which was dried *in vacuo*. (Yield 0.32 g, 92%). ^{71}Ga NMR (CDCl$_3$): $\delta = 264$ (s, $W_{1/2} = 4000$ Hz). IR (Nujol): $\nu = 392$ s, 365 m (Ga–Cl) cm^{-1}.

6.13. *[GaBr$_3$(Ph$_3$As)]*

Prepared similarly to the chloro compound. White solid (93%). ^{71}Ga NMR (CDCl$_3$): $\delta = 132$ (s, $W_{1/2} = 3000$ Hz). IR (Nujol): $\nu = 285$ br s, 219 m (Ga–Br) cm^{-1}.

6.14. *[GaI$_3$(Ph$_3$As)]*

Prepared similarly to the chloro compound. White solid (90%). ^{71}Ga NMR (CDCl$_3$): $\delta = -203$ (s, $W_{1/2} = 2500$ Hz). IR (Nujol): $\nu = 244$ m (Ga–I) cm^{-1}.

6.15. *[Me$_2$PhPH][GaCl$_4$]*

Crystals of [PPhMe$_2$H][GaCl$_4$] were isolated from solutions of the corresponding [GaCl$_3$(Me$_2$PhP)] in CH$_2$Cl$_2$ solution by vapour diffusion of *n*-hexane under nitrogen. ^{1}H-coupled ^{31}P NMR (CDCl$_3$): δ −0.47 (d, $^1J = 511$ Hz). ^{71}Ga NMR: $\delta = +251$ (s).

6.16. *X-ray experimental*

Crystallographic parameters are given in Table 7. All the crystals were grown from CH$_2$Cl$_2$ solutions of the complexes by vapour diffusion of *n*-hexane under dinitrogen. Data collections were carried out with a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and with the crystals held at 120 K in a nitrogen gas stream. The structure solutions were straightforward [38–40] except as indicated below with the hydrogen atoms being introduced into the models in calculated positions with default C–H distances. The phosphonium H atom had P–H fixed at 1.40 Å. [GaCl$_3$(Me$_3$PO)] is reported in the space group *Cc* although the 'checkcif' software raised the possibility of missed symmetry. The *Cc*-*C*2/*c* problem is well known [41,42], but with *Z* of 4 a *C*2/*c* solution would require the molecule to have symmetry (or to be disordered). Attempts to find a *C*2/*c* solution failed. [GaI$_2$(Me$_3$PO)$_2$][GaI$_4$] belongs to one of the 11 pairs of enantiomorphous space groups and the fit to the data was slightly improved by the inclusion of a TWIN command. The data for

Table 7
Crystallographic data[a]

Complex	[$GaCl_3(Me_3PO)$]	[$GaI_2(Me_3PO)_2$][GaI_4]	[$(GaBr_3)_2\{o\text{-}C_6H_4(CH_2P(O)Ph_2)_2\}$]	[$(GaI_3)_2\{o\text{-}C_6H_4\text{-}(CH_2PPh_2)_2\}$]	[Me_2PhPH][$GaCl_4$]	[$GaCl_3(Ph_3P)$]	[$GaBr_3\text{-}(Ph_3P)$]
Formula	$C_3H_9Cl_3GaOP$	$C_6H_{18}Ga_2I_6O_2P_2$	$C_{32}H_{28}Br_6Ga_2O_2P_2$	$C_{32}H_{28}Ga_2I_6P_2$	$C_8H_{12}Cl_4GaP$	$C_{18}H_{15}Cl_3GaP$	$C_{18}H_{15}Br_3\text{-}GaP$
Formula weight	268.14	1084.98	1125.38	1375.32	350.67	438.34	571.72
Crystal system	monoclinic	tetragonal	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Cc* (#9)	$P4_32_12$ (#96)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$C2/c$ (#15)	$P2_1/c$ (#14)
a (Å)	8.144(2)	12.259(2)	8.8772(15)	25.401(2)	6.705(2)	16.155(2)	16.193(2)
b (Å)	10.216(3)	12.259(2)	13.6809(15)	8.1399(5)	12.499(4)	14.567(2)	14.3938(12)
c (Å)	12.418(4)	32.976(9)	16.2405(15)	20.094(2)	16.848(4)	15.924(2)	17.779(2)
α (°)	90	90	67.503(7)	90	90	90	90
β (°)	105.577(15)	90	87.495(8)	106.943(5)	99.352(16)	98.249(8)	109.652(4)
γ (°)	90	90	87.788(7)	90	90	90	90
U (Å^3)	995.3(5)	4956.2(18)	1820.0(4)	3974.4(6)	1393.3(6)	3708.6(8)	3902.5(7)
Z	4	8	2	4	4	8	8
μ(Mo Kα) (mm^{-1})	3.664	9.773	8.183	6.118	2.820	1.998	7.631
R_{int}	0.0604	0.0801	0.0730	0.042	0.0525	0.163	0.088
Total number of reflections	4208	37005	36009	46651	16050	53745	43220
Unique reflections	2047	5707	8378	9147	3184	4269	8934
Number of parameters/restraints	86/2	164/13	397/0	379/0	129/0	208/0	415/0
R_1[b] [$I_o > 2\sigma(I_o)$]	0.054	0.054	0.047	0.024	0.042	0.060	0.042
R_1 [all data]	0.073	0.065	0.075	0.028	0.060	0.155	0.108
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.110	0.113	0.090	0.050	0.082	0.130	0.069
wR_2 [all data]	0.121	0.121	0.099	0.052	0.088	0.167	0.086

[a] Common items: temperature = 120 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°.

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

[$GaCl_3(Ph_3P)$] was collected in the triclinic system and yielded a solution with $Z = 4$ in the space group $P\bar{1}$. Inspection of the data and the cell dimensions showed the data could be transformed to a $C2/c$ monoclinic system with $Z = 8$ with one molecule in the asymmetric unit and this is the solution reported.

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Appendix A. Supplementary material

Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 640911 (Cl/O), 640912 (I/O), 640913 (Br/O), 640914 (Cl/P), 640915 (Br/P), 640916 (I/P), 640917 (Cl). The atoms in parentheses denote the atom types bonded to Ga; the final one is the phosphonium salt. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.05.008.

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