

## Adducts of GaI<sub>3</sub> and InI<sub>3</sub> with Ph<sub>3</sub>P and Ph<sub>3</sub>As

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### Abstract

Adducts Ph<sub>3</sub>PGaI<sub>3</sub> and Ph<sub>3</sub>AsGaI<sub>3</sub> obtained by adding the ligands to Et<sub>2</sub>OGaI<sub>3</sub> have been investigated by <sup>71</sup>Ga NMR, IR/Raman spectroscopy and X-ray diffraction. Et<sub>2</sub>OInI<sub>3</sub> with Ph<sub>3</sub>P gives (Ph<sub>3</sub>P)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub>. Ph<sub>3</sub>As yields (Ph<sub>3</sub>As)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O as rhombohedral crystals whose structure was solved by X-ray diffraction. Both these indium complexes contain Ph<sub>3</sub>EInI<sub>3</sub> molecules alongside five-coordinate adducts (Ph<sub>3</sub>E)<sub>2</sub>InI<sub>3</sub> with the Ph<sub>3</sub>E ligands attached in axial sites by long and unequal bonds to a planar InI<sub>3</sub> unit. Vibrational assignments are made for Ph<sub>3</sub>PGaI<sub>3</sub>, Ph<sub>3</sub>AsGaI<sub>3</sub>, Ph<sub>3</sub>EInI<sub>3</sub> and (Ph<sub>3</sub>E)<sub>2</sub>InI<sub>3</sub> (E = P or As). © 1997 Elsevier Science S.A.

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### 1. Introduction

Adducts with neutral or anionic ligands are a major feature of the chemistry of gallium and indium halides [1–3], those of phosphines and arsines being particularly important in relation to III–V semi-conductor materials [4]. The adducts formed by GaI<sub>3</sub> and InI<sub>3</sub> have received fresh attention recently; the molecular structures of (Me<sub>3</sub>Si)<sub>3</sub>AsGaI<sub>3</sub> [5], Ph<sub>3</sub>AsGaI<sub>3</sub> [6] and (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>AsGaI<sub>3</sub> [7] have been determined by X-ray diffraction, and there have been spectroscopic and crystallographic studies on phosphino complexes of indium(III) iodide [8–10], in which earlier work is reviewed.

The reaction of Ph<sub>3</sub>E (E = P or As) with the ether adduct Et<sub>2</sub>OGaI<sub>3</sub> is a convenient route to crystalline products in which triphenylphosphine or triphenylarsine is coordinated to gallium through a Ga–E bond [6]. Extending this observation, we have used Et<sub>2</sub>OInI<sub>3</sub> to prepare the adducts of InI<sub>3</sub> with Ph<sub>3</sub>P and Ph<sub>3</sub>As. Here we present crystallographic investigations of these systems together with IR, Raman and NMR spectroscopic results elucidating the structures of gallium(III) iodide and indium(III) iodide adducts with phosphino and arsino ligands.

### 2. Experimental section

#### 2.1. Preparative work

A solution of Et<sub>2</sub>OGaI<sub>3</sub> was prepared by shaking finely powdered gallium metal with an equivalent amount of I<sub>2</sub> dissolved in dry diethyl ether until the mixture was colourless [11]. Et<sub>2</sub>OInI<sub>3</sub> in Et<sub>2</sub>O was obtained similarly, using freshly cut shavings of indium [11,12].

Ph<sub>3</sub>AsGaI<sub>3</sub> **1** was obtained as colourless crystals which grew slowly in the mixture formed by adding one equivalent of Ph<sub>3</sub>As in Et<sub>2</sub>O to a sample of the Et<sub>2</sub>OGaI<sub>3</sub> solution. The crystals were rinsed with diethyl ether and dried in air without deterioration. Analysis: calculated for C<sub>18</sub>H<sub>15</sub>AsGaI<sub>3</sub>, C 28.6, H 2.00%; found C 28.2, H 2.61%.

Ph<sub>3</sub>PGaI<sub>3</sub> **2** was prepared similarly. Well developed, colourless crystals are obtained within 15 min at ambient temperature from a solution containing Et<sub>2</sub>OGaI<sub>3</sub> plus Ph<sub>3</sub>P. Analysis: calculated for C<sub>18</sub>H<sub>15</sub>PGaI<sub>3</sub>, C 30.3, H 2.12%; found, C 30.7, H 1.80%.

GaI<sub>3</sub> adducts with other phosphine ligands were prepared by reaction of MePh<sub>2</sub>P or Me<sub>2</sub>PhP with Et<sub>2</sub>OGaI<sub>3</sub>, followed by collection of the solid product, which was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> for NMR investigation. Mixed halides were obtained in situ by the action of IBr or ICl on the GaI<sub>3</sub> adducts.

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(Ph<sub>3</sub>P)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub> formed rapidly as pale yellow crystals from a dry ether solution containing Ph<sub>3</sub>P and Et<sub>2</sub>OInI<sub>3</sub> in 2:1 molar proportions. Some of these crystals were heated in cyclohexane to 60°C, whereupon they broke up into a white powder. This product, with small colourless crystals which formed on cooling, was shown by its IR spectrum to be Ph<sub>3</sub>PInI<sub>3</sub>. The two solids Ph<sub>3</sub>PInI<sub>3</sub> and (Ph<sub>3</sub>P)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub> were identified by investigating a single crystal of each sort by X-ray diffraction. The structures thus determined agreed fully with the recently published findings [10].

(Ph<sub>3</sub>As)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub> · H<sub>2</sub>O **3** was produced as pale yellow crystals when a solution containing Et<sub>2</sub>OInI<sub>3</sub> plus Ph<sub>3</sub>As (in equimolar proportions) was allowed to stand for several hours. The crystals were rinsed with ether and dried in air. Analysis: calculated for C<sub>54</sub>H<sub>47</sub>As<sub>3</sub>In<sub>2</sub>I<sub>6</sub>O, C 33.6, H 2.35%; found C 33.8, H 2.07%. The presence of the molecule of H<sub>2</sub>O was revealed by the X-ray analysis. Unlike the triphenylphosphine complex, these crystals dissolved fully in hot cyclohexane and returned on cooling without any change in their appearance or in the IR spectrum of the compound.

## 2.2. Crystallography

Data were collected on a Nonius CAD-4 diffractometer for **1** and **2**, and a Siemens SMART diffractometer for **3**. Unit cell parameters were gained from setting angles of 25 reflections for CAD-4 data, and all reflections with  $I > 10\sigma(I)$  for the SMART data. Intensity data collection on the CAD-4 employed  $\omega/2\theta$  scans with scan width  $0.80 + 0.347\tan\theta$ . For the SMART data, collection covered a nominal hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\phi$  angle for the crystal and each exposure covered 0.3° in  $\omega$ . Crystal alignment and decomposition were monitored throughout the data collection by measuring three reflections on the CAD-4 every 100 measurements, and by repeating the initial frames on the SMART and analysing the duplicate reflections.

The data were corrected for Lorentz and polarisation effects and the empirical absorption corrections were applied using psi scans for the CAD-4 data [13] and employing the method of Blessing [14] for the area collection data. The equivalent reflections for **3** were

Table 1  
Crystal data and refinement parameters

	(1)	(2)	(3)
Formula	C <sub>18</sub> H <sub>15</sub> AsGaI <sub>3</sub>	C <sub>18</sub> H <sub>15</sub> GaI <sub>3</sub> P	C <sub>54</sub> H <sub>47</sub> As <sub>3</sub> I <sub>6</sub> In <sub>2</sub> O
Molecular weight	756.64	712.69	1927.70
Crystal system	Rhombohedral	Rhombohedral	Rhombohedral (Hexagonal axes)
Space group	R-3	R-3	R-3
<i>a</i> (Å)	10.194(4)	10.225(5)	15.5059(1)
<i>c</i> (Å)			42.6060(2)
$\alpha$ (deg.)	93.48(2)	93.83(6)	
<i>V</i> (Å <sup>3</sup> )	1053.2(5)	1062(2)	8871.46(9)
<i>Z</i>	2	2	6
<i>d</i> (calc) (g cm <sup>-3</sup> )	2.386	2.230	2.164
<i>F</i> (000)	692	656	5364
$\mu$ (mm <sup>-1</sup> )	7.259	5.731	5.612
Radiation Mo <i>K</i> $\alpha$ (Monochromatic) $\lambda$ (Å)	0.71069	0.71069	0.71069
Temperature (K)	193	293	293
Diffractometer	Nonius CAD-4	Nonius CAD-4	Siemens SMART
Scan technique	$\omega/2\theta$	$\omega/2\theta$	Area detector
$2\theta$ (min–max) (deg.)	2–60	2–50	3–52
No. of reflections	5326	2058	29613
No. of independent reflections, <i>R</i> (int)	2009, 0.0387	1248, 0.0719	3441, 0.0241
No. of observed reflections $I > 2\sigma(I)$	1842	1065	3084
Crystal size (mm)	0.30 × 0.37 × 0.45	0.35 × 0.45 × 0.50	0.42 × 0.42 × 0.56
<i>A</i> (min–max)	0.69 1.00	0.58 0.98	0.154 0.245
Least squares weights <i>a, b</i>	0.000, 1.336	0.054, 1.244	0.046, 123.50
No. of variables in LS	71	70	199
Goodness of fit on <i>F</i> <sup>2</sup>	1.091	1.093	1.119
Function minimised	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
<i>R</i> and <i>wR</i> <sup>2</sup>	0.0219 0.0432	0.0421 0.1022	0.0438 0.1109
Peak height in final map (min–max) <i>e</i> (Å <sup>-3</sup> )	+ 1.10, - 0.41	+ 0.86, - 1.28	+ 1.24, - 2.10
$R = \sum   F_o  -  F_c   / \sum  F_o $			
weight = $1.0 / [\sigma^2(F_o^2) + a \cdot P^2 + b \cdot P]$		$P = (F_o^2 + 2F_c^2) / 3$	

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	U(eq)
<b>(Ph<sub>3</sub>As)GaI<sub>3</sub> 1</b>				
I(1)	4269(1)	2029(1)	5240(1)	35(1)
Ga(1)	3506(1)	3506(1)	3506(1)	24(1)
As(1)	2001(1)	2001(1)	2001(1)	21(1)
C(1)	266(2)	1754(2)	2613(2)	25(1)
C(2)	-837(2)	1801(2)	1755(3)	31(1)
C(3)	-2081(3)	1635(3)	2225(3)	42(1)
C(4)	-2221(3)	1416(3)	3532(4)	47(1)
C(5)	-1125(3)	1374(3)	4382(3)	46(1)
C(6)	126(3)	1544(3)	3926(3)	36(1)
<b>(PPh<sub>3</sub>)GaI<sub>3</sub> 2</b>				
I(1)	3018(1)	749(1)	-148(1)	65(1)
Ga(1)	1592(1)	1592(1)	1592(1)	46(1)
P(1)	3055(2)	3055(2)	3055(2)	41(1)
C(1)	4679(5)	2455(6)	3234(5)	47(1)
C(2)	5797(6)	3256(7)	3142(6)	55(1)
C(3)	7005(7)	2785(9)	3266(7)	73(2)
C(4)	7114(8)	1463(10)	3490(8)	84(3)
C(5)	6021(8)	662(8)	3571(8)	77(2)
C(6)	4790(7)	1143(7)	3436(7)	64(2)

U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) (Ph<sub>3</sub>As)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, 3

	x	y	z	U(eq)
In(1)	3333	-3333	198(1)	50(1)
I(1)	4761(1)	-1392(1)	184(1)	56(1)
As(1)	3333	-3333	900(1)	35(1)
As(2)	3333	-3333	-489(1)	50(1)
C(1)	3025(5)	-2381(5)	1095(2)	40(2)
C(2)	2241(6)	-2680(6)	1307(2)	48(2)
C(3)	2036(7)	-1981(7)	1432(2)	60(2)
C(4)	2612(8)	-983(8)	1351(2)	68(3)
C(5)	3390(8)	-681(7)	1144(2)	65(2)
C(6)	3598(6)	-1379(6)	1012(2)	51(2)
C(7)	3359(7)	-2189(6)	-687(2)	57(2)
C(8)	2803(10)	-1807(9)	-552(3)	103(5)
C(9)	2869(11)	-953(10)	-678(3)	114(5)
C(10)	3386(9)	-555(8)	-943(3)	84(3)
C(11)	3902(8)	-927(9)	-1078(2)	84(3)
C(12)	3903(9)	-1743(8)	-946(2)	81(3)
In(2)	0	0	1401(1)	43(1)
I(2)	-602(1)	-1904(1)	1541(1)	64(1)
As(3)	0	0	762(1)	34(1)
C(13)	242(5)	1245(5)	581(1)	40(2)
C(14)	-370(6)	1288(6)	353(2)	48(2)
C(15)	-176(8)	2187(7)	229(2)	65(2)
C(16)	640(8)	3044(7)	331(2)	70(3)
C(17)	1275(7)	3015(6)	558(2)	64(2)
C(18)	1060(6)	2115(6)	683(2)	52(2)
O(1)	3333	-3333	-1191(2)	55(2)

U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Table 4

Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for 1 and 2

	(Ph <sub>3</sub> As)GaI <sub>3</sub> 1	(PPh <sub>3</sub> )GaI <sub>3</sub> 2
Ga-I	2.509(1)	2.518(2)
Ga-E	2.490(1)	2.413(4)
C-E	1.919(2)	1.810(5)
I-Ga-E	102.97(2)	104.60(5)
I-Ga-I	115.11(11)	113.87(3)
Ga-E-C	113.21(7)	111.4(2)
C-Ga-C	105.49(8)	107.5(2)

E represents As or P in 1 and 2, respectively.

averaged to give the unique data set. Crystal data, collection parameters and refinement details are given in Table 1.

The structures were solved by direct methods using SHELXS [15]. Refinement was by full-matrix least squares on  $F^2$  using SHELXL-93 [16] with scattering curves for neutral atoms. All non-hydrogen atoms were allowed to refine anisotropically. Hydrogen atoms, except those of the water molecule, were placed geometrically and refined with a riding model and with  $U_{\text{iso}}$  constrained to be 20% greater than  $U_{\text{eq}}$  of the carrier atom. Final atomic coordinates are given in Table 2 for 1 and 2, and in Table 3 for 3. Relevant interatomic distances and angles are given in Tables 4 and 5 for 1 and 2, and 3, respectively. Further details of the crystallographic data for compounds 1–3 are available from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 5

Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for (Ph<sub>3</sub>As)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, 3

In(1)–I(1)	2.7024(5)
In(1)–As(2)	2.926(2)
In(1)–As(1)	2.990(2)
As(1)–C(1)	1.950(7)
As(2)–C(7)	1.947(8)
In(2)–I(2)	2.6811(6)
In(2)–As(3)	2.7238(13)
As(3)–C(13)	1.933(7)
I(1)#1–In(1)–I(1)	119.949(2)
I(1)–In(1)–As(2)	88.70(2)
I(1)–In(1)–As(1)	91.30(2)
C(1)–As(1)–In(1)	115.2(2)
C(7)–As(2)–In(1)	115.7(2)
I(2)#2–In(2)–I(2)	115.22(2)
I(2)–In(2)–As(3)	102.82(2)
C(13)–As(3)–In(2)	113.4(2)

Symmetry transformations used to generate equivalent atoms: #1 -y, x - y - 1, z; #2 -y, x - y, z.

### 2.3. Spectroscopy

NMR measurements were made on a Bruker AM400 spectrometer at 298 K.  $^{31}\text{P}$  and  $^{71}\text{Ga}$  spectra were run using a 10 mm broad-band probe, as described elsewhere [17].

IR spectra were recorded on samples as nujol mulls between CsI plates, or in pressed polythene discs, using Perkin-Elmer Paragon 1000PC and Bio-Rad FTS60V or FTS6000 spectrometers. Raman spectra of crystalline samples were obtained with a Jobin Yvon U1000 spectrometer, employing the green 514 nm line of a Spectra Physics 2016 argon-ion laser at 20 mW.

## 3. Results and discussion

### 3.1. Synthesis

Past preparation of phosphino complexes of gallium trihalides [18] and indium triiodide [7–10] has usually involved the prior synthesis and purification of these highly reactive halides, which were then combined with the chosen ligand in a suitable solvent to yield the adduct. The method employed here makes use of a simple route to  $\text{Et}_2\text{OMI}_3$  [11,12] involving the rapid oxidation of the metal by iodine in anhydrous ether solution. The existence of  $\text{MI}_3$  in ether as the molecular adduct  $\text{Et}_2\text{OMI}_3$  has been proven by NMR in the case of gallium [17], with only a trace of dissociation to the ionic product  $[\text{GaI}_2(\text{Et}_2\text{O})_2]^+[\text{GaI}_4]^-$ . Addition of a ligand L, which is a more powerful donor than diethyl ether, results in the displacement of  $\text{Et}_2\text{O}$  to form  $\text{LMI}_3$ , readily detected in solution by  $^{71}\text{Ga}$  NMR (and  $^{31}\text{P}$  NMR for phosphino complexes). Similar behaviour occurs when indium is used to prepare  $\text{Et}_2\text{OInI}_3$  and then treated with  $\text{Ph}_3\text{P}$  or  $\text{Ph}_3\text{As}$ , although the resulting complex may now contain more than one molecule of the ligand L (see below). The adducts of  $\text{GaI}_3$  and  $\text{InI}_3$  with the phosphine or arsine are only slightly soluble in the ether solution and produce well formed, analytically pure crystals soon after introducing the ligand.

### 3.2. Crystallography

The structure of  $\text{Ph}_3\text{AsGaI}_3$  **1** has been described in our preliminary communication [6].  $\text{Ph}_3\text{PGaI}_3$  **2** is isostructural and isomorphous with **1** whose structure is shown therein [6]. Table 4 compares selected bond lengths and angles of the two compounds. Coordination at Ga and As (or P) is pyramidal. The phenyl substituents are staggered with respect to the iodine atoms. The internal C–C bond lengths and angles in the phenyl rings of both compounds are within the expected ranges and the C–As or C–P bond distances agree with those of kindred systems [19–22]. The Ga–I distance of

2.518(2) Å in  $\text{Ph}_3\text{PGaI}_3$  is slightly longer than that of  $\text{Ph}_3\text{AsGaI}_3$  (2.509(1) Å).

The Ga–P bond length in  $\text{Ph}_3\text{PGaI}_3$  is 2.413 Å. This value is bracketed by 2.35 Å in  $\text{Me}_3\text{PGaCl}_3$  [23] and 2.45 Å in  $(\text{Me}_3\text{Si})_3\text{PGaClPh}_2$  [24]. The Ga–As bond distance of 2.490 Å in  $\text{Ph}_3\text{AsGaI}_3$  may be compared with 2.423 Å in  $(\text{Me}_3\text{Si})_3\text{AsGaI}_3$  [5] and 2.509 Å in  $(p\text{-MeOC}_6\text{H}_4)_3\text{AsGaI}_3$  [7]. Other Ga–As distances in adducts are 2.55 Å in  $\text{R}_3\text{AsGa}(\text{C}_6\text{F}_5)_3$  [25], 2.57 Å in  $\text{R}_3\text{AsGaPh}_3$  [25], and 2.63 Å in  $\text{R}_3\text{AsGaCl}(\text{neo-pentyl})_2$  [26] ( $\text{R} = \text{Me}_3\text{Si}$ ). The mean of these six values is 2.53 Å, whereas the Ga–As covalent radius sum is 2.45 Å [2].

We examined both of the crystalline  $\text{InI}_3 + \text{Ph}_3\text{P}$  adducts by X-ray diffraction. A recent study [10] matches ours and therefore we need only to summarise the main findings. Colourless  $\text{Ph}_3\text{PInI}_3$  exists as a simple 1:1 adduct in which the In–P distance is 2.603 Å. Its precursor is a pale yellow solid in which both  $\text{Ph}_3\text{PInI}_3$  and  $(\text{Ph}_3\text{P})_2\text{InI}_3$  are present. The latter component has a bipyramidal structure comprising planar  $\text{InI}_3$  with weakly attached ligands forming In–P bonds of 2.86(1) and 2.99(1) Å. We have not found the separate 2:1 adduct of  $\text{Ph}_3\text{P}$  with  $\text{InI}_3$  mentioned in some reports [27–29].

The behaviour of  $\text{InI}_3$  with triphenylarsine is akin to that with triphenylphosphine, but there are significant differences. A pale yellow product is obtained on adding  $\text{Ph}_3\text{As}$  to  $\text{Et}_2\text{OInI}_3$ , and this can be recrystallised from cyclohexane without change. The yellow crystals **3** possess equal numbers of  $\text{Ph}_3\text{AsInI}_3$  and  $(\text{Ph}_3\text{As})_2\text{InI}_3$  molecules, and also contain a single, adventitious molecule of  $\text{H}_2\text{O}$  which is not attached to either of the indium species. Fig. 1 shows the structures concerned and Table 5 gives the important bond lengths and angles. Within  $\text{Ph}_3\text{AsInI}_3$  the indium atom has distorted tetrahedral coordination.  $(\text{Ph}_3\text{As})_2\text{InI}_3$  has a bipyramidal skeleton consisting of a trigonal planar  $\text{InI}_3$  unit with the arsine ligands in axial positions. The In–I

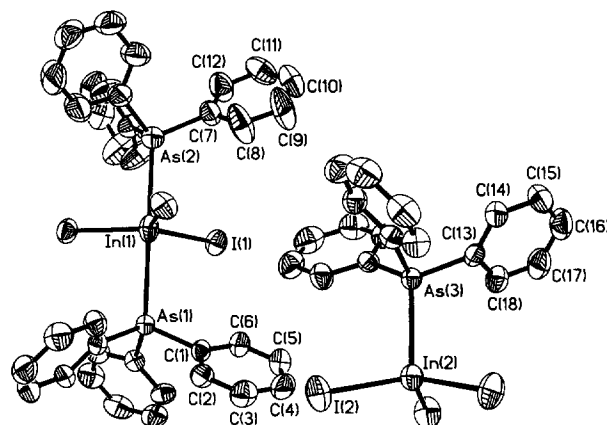


Fig. 1. The molecular structures of the 2:1 and 1:1 adducts of  $\text{Ph}_3\text{As}$  with  $\text{InI}_3$  which co-crystallise in **3**.

bonds of 2.702 Å are slightly less than in the kindred phosphine adduct (2.707 Å [10]). Once again, the distances from indium to the donor ligands are unequal being 2.926(2) and 2.990(2) Å for the Ph<sub>3</sub>As–In links. The In–As bond of the discrete Ph<sub>3</sub>AsInI<sub>3</sub> molecule is much shorter and measures 2.724 Å, which is close to the In–As covalent radius sum (2.70 Å) [2]. Similarly, the In–I bonds of Ph<sub>3</sub>AsInI<sub>3</sub> which measure 2.681 Å are shorter than in (Ph<sub>3</sub>As)<sub>2</sub>InI<sub>3</sub>.

### 3.3. NMR studies

We have investigated the formation of gallium(III) halide adducts by NMR, employing both <sup>71</sup>Ga and <sup>31</sup>P resonances [30,31]. The <sup>71</sup>Ga spectrum of an ether solution of Et<sub>2</sub>OGaI<sub>3</sub>, with added Ph<sub>3</sub>P, was recorded after removal of the crystals of Ph<sub>3</sub>PGaI<sub>3</sub>. Two signals were observed; a broad feature at –228 ppm due to unreacted Et<sub>2</sub>OGaI<sub>3</sub> [17], and a doublet at –157.8 ppm which is attributable to Ph<sub>3</sub>PGaI<sub>3</sub>. The splitting (450 Hz) arises from coupling to phosphorus and its existence shows that the Ga–P bond is long-lived. Similarly, the <sup>31</sup>P spectrum contains a quartet at –30.2 ppm due to the attachment of phosphorus to quadrupolar gallium, both <sup>69</sup>Ga and <sup>71</sup>Ga nuclei having I = 3/2. This phosphorus shift is close to the value of –28.2 ppm recently deduced for Ph<sub>3</sub>PInI<sub>3</sub> during an investigation of the dissociation of (Ph<sub>3</sub>P)<sub>2</sub>InI<sub>3</sub> [10]. In solutions subject to hydrolysis, for example by atmospheric moisture, we observed an additional <sup>31</sup>P resonance as a doublet at 4.8 ppm (split by 510 Hz), which is due to [Ph<sub>3</sub>PH]<sup>+</sup>. A further signal at 45 ppm was sometimes present and this probably belongs to [Ph<sub>3</sub>PI]<sup>+</sup>. The counter-ion to these species is [GaI<sub>4</sub>]<sup>–</sup>, revealed by a sharp signal at –458 ppm in the <sup>71</sup>Ga spectrum.

NMR data for the adducts of GaI<sub>3</sub> with Ph<sub>3</sub>P, MePh<sub>2</sub>P and Me<sub>2</sub>PhP are summarised in Table 6. Addition of PhPCl<sub>2</sub> to Et<sub>2</sub>OGaI<sub>3</sub> gave no evidence of adduct formation. The <sup>71</sup>Ga resonance of Ph<sub>3</sub>AsGaI<sub>3</sub> is detected as a very broad signal with w<sub>1/2</sub> = 3400 Hz, owing to unresolved coupling with the quadrupolar <sup>75</sup>As nucleus. This signal occurs at –220 ppm, compared

Table 6  
NMR data for GaI<sub>3</sub> adducts in CH<sub>2</sub>Cl<sub>2</sub> solution

Adduct	δ( <sup>71</sup> Ga) (ppm)	<sup>1</sup> J( <sup>71</sup> Ga– <sup>31</sup> P) (Hz)	δ( <sup>31</sup> P) (ppm)
Ph <sub>3</sub> PGaI <sub>3</sub>	–157.9	452	–30.2
MePh <sub>2</sub> PGaI <sub>3</sub> <sup>a</sup>	–141.5	464	–28
Me <sub>2</sub> PhPGaI <sub>3</sub>	–126.6	476	–42
Ph <sub>3</sub> PGaBrI <sub>2</sub>	–43.1	549	–30
Ph <sub>3</sub> PGaClI <sub>2</sub>	11.9	586	–30
Ph <sub>3</sub> AsGaI <sub>3</sub>	–220 broad		
Ph <sub>3</sub> AsGaBrI <sub>2</sub>	–106 broad		
Ph <sub>3</sub> AsGaClI <sub>2</sub>	–35 broad		

<sup>a</sup> In Et<sub>2</sub>O solution.

Table 7  
IR and Raman bands (below 600 cm<sup>–1</sup>) of 1:1 Ph<sub>3</sub>EMI<sub>3</sub> adducts

Ph <sub>3</sub> PGaI <sub>3</sub>		Ph <sub>3</sub> AsGaI <sub>3</sub>		Ph <sub>3</sub> PInI <sub>3</sub>		Assignment <sup>a</sup>
IR	Raman	IR	Raman	IR	Raman	
				45 m	43 s	δ <sub>as</sub> (InI <sub>3</sub> )
				54 s	54 m	δ <sub>s</sub> (InI <sub>3</sub> )
60 m	64 w	55 m	59 w			δ <sub>as</sub> (GaI <sub>3</sub> )
70 m	75 m	68 w	72 m	72 m	67 m	bending
83 m	89 s	86 w	84 s			δ <sub>s</sub> (GaI <sub>3</sub> )
				85 w	85 m	bending
100 w	98 w	95 vw	92 sh	96 w	94 s	modes
				145 w	145 vs	ν <sub>s</sub> (In–I)
144 m	148 vs	142 w	141 vs			ν <sub>s</sub> (Ga–I)
		175 m	176 vw	157 s	158 m	ν(In–P)
		185 w	183 w	185 w	190 vw	x
187 m	185 m	202 m	198 w			x
198 m	197 m			202 vs	203 m	ν <sub>as</sub> (In–I)
216 m	211 m	232 w	234 w	215 w	213 m	u
				245 w	247 w	u
246 vs	245 s	246 s	249 m			ν <sub>as</sub> (Ga–I)
266 w	265 m			266 w	266 w	u
		310 w				t(Ph <sub>3</sub> As)
		331 m	333 vw			t(Ph <sub>3</sub> As)
397 w	395 vw	397 w	392 w	397 w	395 vw	w
421 w	423 w			421 w	420 w	t(Ph <sub>3</sub> P)
442 w	441 w			439 w	441 w	t(Ph <sub>3</sub> P)
		445 w				y(Ph <sub>3</sub> As)
		462 s	464 w			y(Ph <sub>3</sub> As)
496 s	498 w			493 s	495 vw	y(Ph <sub>3</sub> P)
525 s	520 w			519 s	523 m	y(Ph <sub>3</sub> P)
545 w	545 vw			540 w	545 vw	y(Ph <sub>3</sub> P)

<sup>a</sup> Phenyl ring modes are assigned according to Whiffen's notation (see text).

with –158 ppm for Ph<sub>3</sub>PGaI<sub>3</sub>, demonstrating that arsenic has a greater shielding influence upon gallium than does phosphorus.

Mixed halide data in Table 6 were obtained by introducing a chloride or bromide ligand to the gallium complex through the addition of IBr or ICl to the solution of Ph<sub>3</sub>PGaI<sub>3</sub> or Ph<sub>3</sub>AsGaI<sub>3</sub>. The observed trend in <sup>71</sup>Ga chemical shift to a more positive value as iodine is replaced by bromine or chlorine is normal for such complexes of gallium, for example, the diethyl ether adducts [17].

### 3.4. Vibrational spectra

Far IR data for adducts of GaI<sub>3</sub> [18,32,33] and InI<sub>3</sub> [28,29] are of long standing. We have extended these and have also recorded the Raman spectra of the various crystalline products of GaI<sub>3</sub> and InI<sub>3</sub> with Ph<sub>3</sub>P or Ph<sub>3</sub>As as ligands. Structure-sensitive bands occur particularly in the region below 600 cm<sup>–1</sup> and are presented in Tables 7 and 8, where internal modes of the ligands are assigned according to Whiffen's notation [34].

Table 8  
IR and Raman Bands (below 600 cm<sup>-1</sup>) of 3:2 Ph<sub>3</sub>E/MI<sub>3</sub> adducts

(Ph <sub>3</sub> P) <sub>2</sub> InI <sub>3</sub> :Ph <sub>3</sub> PIInI <sub>3</sub>		(Ph <sub>3</sub> As) <sub>2</sub> InI <sub>3</sub> :Ph <sub>3</sub> AsInI <sub>3</sub>		Assignment <sup>a,b</sup>
IR	Raman	IR	Raman	
46 m	45 w	48 w	46 w	$\delta_{as}(\text{InI}_3) C_{3v}$
58 m	55 m	58 m	56 w	$\delta_s(\text{InI}_3) C_{3v}$
66 w	64 m	63 m	63 m	$\delta(\text{InI}_3) D_{3h}$
80 vw	82 w	85 vw	85 w	bending
105 w	104 w	100 w	100 w	modes
		124 m	125 sh	$\nu(\text{In-As})$
	133 vs		133 vs	$\nu_s(\text{In-I}) D_{3h}$
148 m	148 sh	152 s	154 s	$\nu_s(\text{In-I}) C_{3v}$
160 s	160 w			$\nu(\text{In-P})$
		185 sh	187 w	x
191 vs	197 s	195 vs	197 s	$\nu_{as}(\text{In-I}) D_{3h}$
		205 sh	202 m	$\nu_{as}(\text{In-I}) C_{3v}$
216 w	215 w			u
		230 w	237 w	u
246 w	250 w	245 vw	248 vw	u
		308 w	309 w	t (Ph <sub>3</sub> As)
		323 m	325 w	t (Ph <sub>3</sub> As)
397 vw	394 w	397 vw	395 vw	w
415 vw	417 m			t (Ph <sub>3</sub> P)
434 m	435 vw			t (Ph <sub>3</sub> P)
442 w	443 w			t (Ph <sub>3</sub> P)
		464 s	465 w	y (Ph <sub>3</sub> As)
		475 m	475 vw	y (Ph <sub>3</sub> As)
492 s	495 vw			y (Ph <sub>3</sub> P)
514 m				y (Ph <sub>3</sub> P)
520 s	519 s			y (Ph <sub>3</sub> P)
537 s				y (Ph <sub>3</sub> P)

<sup>a</sup> Phenyl ring modes are assigned according to Whiffen's notation (see text).

<sup>b</sup> The InI<sub>3</sub> group has C<sub>3v</sub> symmetry in Ph<sub>3</sub>EInI<sub>3</sub> and D<sub>3h</sub> symmetry in (Ph<sub>3</sub>E)<sub>2</sub>InI<sub>3</sub>.

Table 7 contains IR and Raman spectra of the 1:1 adducts Ph<sub>3</sub>EGaI<sub>3</sub> (E = P or As) and Ph<sub>3</sub>PIInI<sub>3</sub>. The GaX<sub>3</sub> modes of gallium trihalide complexes with O, S and N ligands were located by Greenwood in early work [32]. For Et<sub>2</sub>OGaI<sub>3</sub>, symmetric stretching appears at 165 cm<sup>-1</sup> and antisymmetric stretching at 252 cm<sup>-1</sup>, and similar  $\nu(\text{Ga-I})$  frequencies were found with the ligands Me<sub>2</sub>S, Et<sub>2</sub>S or pyridine. For Me<sub>3</sub>PGaI<sub>3</sub> the values are 157 and 252 cm<sup>-1</sup> [18,35]. The present findings are 148 and 246 cm<sup>-1</sup> for the Ph<sub>3</sub>P adduct, or 141 and 248 cm<sup>-1</sup> for the Ph<sub>3</sub>As adduct, which extend the series, showing the influence of the nature of the ligand especially upon the symmetric mode. The 246 cm<sup>-1</sup> band of Ph<sub>3</sub>PGaI<sub>3</sub> was reported and assigned by Carty [33] in an IR study of the spectra of GaX<sub>3</sub> complexes with triarylphosphine ligands covering the range 600–200 cm<sup>-1</sup>. This band was unaltered in dichloromethane solution, but shifted to 226 cm<sup>-1</sup> in acetone, which calls into question the integrity of the complex in this solvent. For Ph<sub>3</sub>PIInI<sub>3</sub>, we see  $\nu_{as}(\text{In-I})$  at 202 cm<sup>-1</sup> (in agreement with a previous report of the IR spectrum [29]) and find a strong Raman signal at 145 cm<sup>-1</sup>, which is naturally assigned to  $\nu_s(\text{In-I})$ . The IR

spectrum attributed elsewhere to the 2:1 adduct (Ph<sub>3</sub>P)<sub>2</sub>InI<sub>3</sub>, with a strong band at 184 cm<sup>-1</sup> and broad features at 132 and 121 cm<sup>-1</sup> [29], has not been observed in our investigations.

A mode of particular interest in coordination complexes is that of metal–ligand stretching. Such M–L modes can prove difficult to locate, but fortunately a recent study of trimethylphosphine–gallium halide complexes provides secure ground [35]. For Me<sub>3</sub>PGaI<sub>3</sub>, the Ga–I stretching mode occurs at 355 cm<sup>-1</sup> and shifts to 326 cm<sup>-1</sup> upon deuteration of the methyl groups. Using this behaviour as a model, and assuming the Ga–P force constant remains approximately the same, the change in mass from Me<sub>3</sub>P to Ph<sub>3</sub>P might be expected to lower the Ga–L frequency by a factor of (262/78)<sup>1/2</sup> or 1.83, which leads to a predicted value of 194 cm<sup>-1</sup> for Ph<sub>3</sub>PGaI<sub>3</sub>. Accordingly, we assign the band at 187 cm<sup>-1</sup>, which has medium intensity in both IR and Raman spectra, to gallium–phosphorus stretching,  $\nu(\text{Ga-PPh}_3)$ . Internal vibrations of the Ph<sub>3</sub>P ligand occur in this vicinity, but are normally rather weak. For indium–phosphorus stretching,  $\nu(\text{In-PPh}_3)$ , there is a plausible band of Ph<sub>3</sub>PIInI<sub>3</sub> at 157 cm<sup>-1</sup>, although its closeness to the band at 145 cm<sup>-1</sup> attributed to In–I symmetric stretching means that the designation is somewhat arbitrary. The corresponding assignment for Ga–AsPh<sub>3</sub> stretching involves a band at 175 cm<sup>-1</sup> with a weak Raman counterpart. Otherwise, this moderately strong band of Ph<sub>3</sub>AsGaI<sub>3</sub> has no obvious origin, since  $\nu_s(\text{Ga-I})$  is assigned at 141 cm<sup>-1</sup> and  $\nu_{as}(\text{Ga-I})$  at 246 cm<sup>-1</sup> for this complex. Bands at lower frequency can be assigned to the bending modes of GaI<sub>3</sub> or InI<sub>3</sub> in the Ph<sub>3</sub>EMI<sub>3</sub> series, using the prior knowledge of the spectra of LMX<sub>3</sub> and [MX<sub>4</sub>]<sup>-</sup> [18,36,37] for guidance.

The IR and Raman spectra of the complexes (Ph<sub>3</sub>P)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub> and (Ph<sub>3</sub>As)<sub>3</sub>(InI<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O are given in Table 8. For the former, our results are in agreement with the limited data previously available [28]. The internal ligand bands associated with Ph<sub>3</sub>P or Ph<sub>3</sub>As present a similar picture to those of the 1:1 adducts, although the pattern is more complicated owing to the presence of both strongly and weakly coordinated ligands. Other bands will be due to the InI<sub>3</sub> moieties and here the situation appears relatively straightforward. The very intense Raman band at 133 cm<sup>-1</sup> is likely to be that of symmetric In–I stretching of the planar InI<sub>3</sub> unit in the five-coordinate species. It has the same frequency in each case, which is not surprising since the phosphine or arsine ligands are only weakly attached. This mode is inactive in the infrared. The antisymmetric In–I stretching mode is allowed in IR and Raman spectra and is assumed to produce the strong 195 cm<sup>-1</sup> band. For comparison, the free InI<sub>3</sub> molecule in the gas phase exhibits  $\nu_s$  at 151 and  $\nu_{as}$  at 200–230 cm<sup>-1</sup> [37]. Other bands in the 100–200 cm<sup>-1</sup> region can be plausibly associated with the four-coordinate Ph<sub>3</sub>EInI<sub>3</sub>

molecules which crystallise alongside those of the five-coordinate kind. The appropriate assignments are given in Table 8. These include the  $\nu(\text{In-I})$  modes shown, along with  $\nu(\text{In-As})$  at  $124\text{ cm}^{-1}$  and  $\nu(\text{In-P})$  at  $160\text{ cm}^{-1}$  (to be compared with  $157\text{ cm}^{-1}$  for  $\text{Ph}_3\text{PInI}_3$  in the pure crystalline 1:1 compound). Assignments of the  $\text{InI}_3$  bending modes of both planar and pyramidal species are included, although these can only be tentative because of complications due to other bending and possible lattice modes. Overall, the spectroscopic data form a useful complement to the X-ray findings. These results provide further evidence of the structural diversity which is a feature of the coordination chemistry of the Group 13 elements, especially indium.

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