Spectroscopic and crystallographic studies of phosphino adducts of gallium(III) iodide

Martyn A. Brown, Jesus A. Castro, and Dennis G. Tuck

Abstract: The solid state structures of the compounds $GaI_3 \cdot PPh_3$ and $Ga_2I_6 \cdot dppe$ (dppe = 1,2-bis(diphenylphosphino)ethane) have been determined. For the former, in which the GaI_3P core has C_{3v} symmetry, the structure is trigonal, with a = 14.961(2) Å, c = 16.509(3) Å, V = 3199.5(4) Å^3, Z = 6, space group $R\bar{3}$. In $Ga_2I_6 \cdot dppe$, the ligand bridges two GaI_3P centres; the structure is monoclinic, a = 10.196(7) Å, b = 15.363(1) Å, c = 23.027(9) Å, β = 98.735(4)°, V = 3565.1(3.2) Å^3, Z = 4, space group $P2_{1/n}$. The use of ^{31}P NMR spectroscopy shows that $GaI_3 \cdot PPh_3$ is slightly dissociated in nonaqueous solution, and the effect of adding Ph_3P or I^- has been investigated. Similar studies with $Ga_2I_6 \cdot dppe$ are also reported. In each system, four-coordination at gallium is dominant; an equally important factor is the dimerization of uncomplexed GaI_3 to Ga_2I_6 in these solutions.

Key words: gallium(III) iodide, complexes, phosphorus, NMR, crystallography.

Résumé : On a déterminé les structures des composés $GaI_3 \cdot PPh_3$ et $Ga_2I_6 \cdot dppe$ (dppe = 1,2-bis(diphénylphosphino)éthane) à l'état solide. Dans le cas du premier composé, dans lequel la symétrie du groupe GaI_3P fondamental est C_{3v}, la structure est trigonale, groupe d'espace $R\bar{3}$, avec a = 14,961(2) et c = 16,509(3) Å, V = 3199,5(4) Å^3 et Z = 6. Dans le composé $Ga_2I_6 \cdot dppe$, le coordinat fait le pont entre deux centres GaI_3; la structure est monoclinique, groupe d'espace $P2_{1/n}$, avec a = 10,196(7), b = 15.363(1) et c = 23.027(9) Å , β = 98,735(4)°, V = 3565,1(3.2) Å^3 et Z = 4. La spectroscopie RMN du ^{31}P permet de démontrer que le $GaI_3 \cdot PPh_3$ est légèrement dissocié en solution non aqueuse et d'étudier l'effet de l'addition de PPh_3 ou de I^- sur cette dissociation. On a aussi effectué des études semblables avec le $Ga_2I_6 \cdot dppe$. Dans chacun de ces systèmes, le gallium tétracoordinant est dominant; un facteur qui est aussi important est la dimérisation du GaI_3 non-complexé en Ga_2I_6 dans ces solutions.

Mots clés : iodure de gallium(III), complexes, phosphore, RMN, cristallographie.

[Traduit par la rédaction]

Introduction

The adducts formed by the trihalides of the Group III elements (B, Al, Ga, In, Tl) with neutral or anionic donors have played a fundamental role in the overall development of coordination chemistry, and a variety of investigations have established the basic features of both the solid state and solution chemistry. In a recent paper (1), we used multinuclear NMR spectroscopy and X-ray crystallography to extend the understanding of the behaviour of the InI_3/Ph_3P system, and showed that the 1:1 and 1:2 complexes are closely related in their solution and crystal chemistry, and that both four- and five-coordinate adducts can be formed. With InI_3/dppe (dppe = bis(diphenylphosphino)ethane) the 1:1 adduct is a five-coordinate linear polymer, but four-coordinate species are important in solution.

In addition to the intrinsic interest of such complexes, their solution chemistry is germane to that of *ortho*- and *para*-quinone complexes, currently under investigation in this laboratory. An important factor in all of these studies is the effect of the size, and hence maximum coordination number, of the metallic elements in question, and it therefore seemed reasonable to investigate the chemistry of gallium compounds analogous to the indium species discussed in ref. 1. We have identified significant differences in the behaviour of these two groups of compounds in both the solid and solution state.

Two earlier investigation of GaI_3/Ph_3P and GaI_3/dppe systems have been reported. Balls, Greenwood, and Straughan (2) prepared a number of phosphino derivatives of the gallium(III) halides, and analysed the infrared spectra, while Carty (3, 4) used both infrared and conductivity measurements in attempts to identify the structures of these compounds in the solid state and in solution.

Experimental section

General techniques

Gallium(III) iodide was prepared by reacting gram quantities of the elements in refluxing xylene. Triphenylphosphine and bis(diphenylphosphino)ethane (Aldrich) were recrystallized before use. Solvents were distilled from suitable drying agents, and stored over molecular sieves.

Phosphorus-31 NMR spectra were recorded on a Bruker 300 instrument, operating at 81.0 MHz, with 85% H_3PO_4 = 0. Infrared spectra were run on a Nicolet 4DX instrument, and the Raman spectra of finely ground solids were recorded with a Jobin Yvon S3000 spectrometer. Microanalysis was by Canadian Microanalytical Services Ltd.

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M.A. Brown, J.A. Castro,[1] and D.G. Tuck.[2] Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON N9B 3P4, Canada.

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[1] Permanent address: Departamento de Quimica Pura y Aplicada, Universidade de Vigo, 36200 Vigo, Galicia, Spain.

[2] Author to whom correspondence may be addressed. Telephone: (519) 253-4232, ext. 3541. Fax: (519) 973-7098. E-mail: DGTuck@uwindsor.ca

Table 1. Summary of crystal data, intensity collection, and structural refinement.

	1	**2**
Chemical formula	$C_{18}H_{15}GaPI_3$	$C_{26}H_{24}Ga_2P_2I_6$
M	712.72	1299.29
Crystal system	Trigonal	Monoclinic
Space group	$R\bar{3}$ (No.148)	$P2_{1/n}$ (No. 14)
a/Å	14.961(2)	10.196(7)
b/Å	14.961(6)	15.363(11)
c/Å	16.509(3)	23.027(9)
β (deg)	90.00	98.735(54)
V/Å^3	3199.5(4)	3565.1(3.2)
Z	6	4
F(000)	1968	2160
D_c/g cm^{-3}	2.22	2.42
Crystal dimensions/mm	0.1 × 0.1 × 0.1	0.1 × 0.2 × 0.3
Absorption coeff/cm^{-1}	57.05	68.14
2θ° (max)	50	50
Total reflections measured	1379	6938
Unique data used	1253	6545
T/°C	23	23
No. of parameters	71	196
R	0.040	0.063
R_w	0.034	0.058
Max. shift/error in final cycle	0.16	0.07
Max., min. peaks in final difference map/e Å^{-3}	+0.67, –0.67	+1.47, –1.54

Preparative

Triphenylphosphine adduct: the procedure involved mixing solutions of GaI_3 and PPh_3 in toluene, following the method of Carty (3). The precipitate was recrystallized from toluene. Anal. calcd. for $C_{18}H_{15}GaPI_3$: C 30.3, H 2.12; found: C 30.7, H 2.17.

Immediate precipitation occurred when ethyl acetate solutions of GaI_3 (0.45 g, 1 mmol) and dppe (0.20 g, 0.5 mmol) were mixed, and the product, Ga_2I_6·dppe, was collected, washed, and recrystallized from the same solvent. Anal. calcd. for $C_{26}H_{24}Ga_2P_2I_6$: C 24.0, H 1.86; found: C 24.2, H 2.01.

Crystallographic analysis

(*i*) In the study of GaI_3·PPh_3, **1**, a colourless crystal mounted on a glass fibre was sited in a Rigaku AFC6S diffractometer, equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a rotating anode generator. Cell constants, and orientation matrices for data collection, were obtained from least-squares refinements, using 20 carefully centred reflections in the range $8.59° < 2\theta < 16.07°$. Based on the systematic absences *hkl*: $-h + k + l \neq 3n$, the space group was uniquely identified as $R\bar{3}$ (No. 148), and this was confirmed by subsequent solution and refinement of the structure. Details of the intensity collection are given in Table 1.

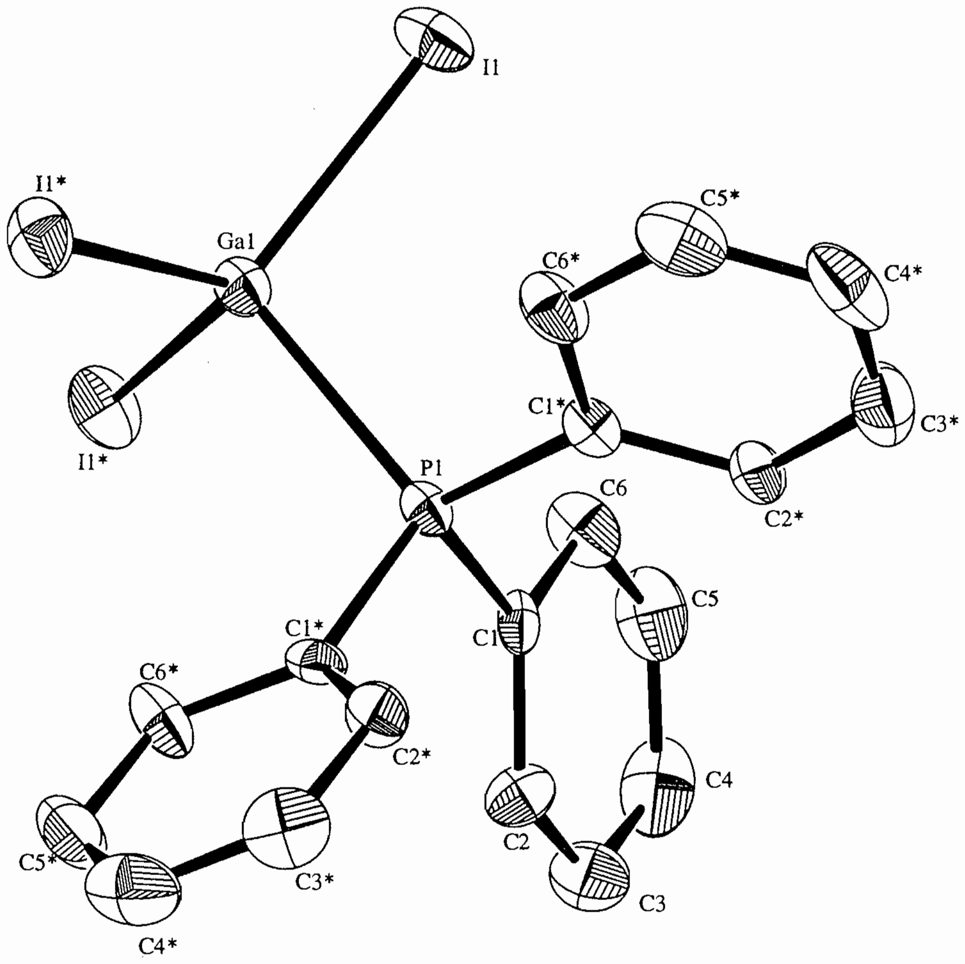
The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standard increased 1%, and a linear correction factor was applied to the results. The linear absorption coefficient (57.05 cm^{-1}) required an absorption correction, using PSI Scan, with transmission factors between 0.80 and 1.00. The results were also corrected for Lorentz and polarization effects. The structure was solved by direct methods, and expanded using Fourier techniques. The non-hydrogen atoms were refined isotropically; hydrogen atoms on carbon were included in ideal positions but were not refined. The final cycle of full-matrix least-squares refinement was based on 761 observed reflections ($I > 3\sigma(I)$) and 71 variable parameters, and the solution converged at $R = 0.040$ and $R_w = 0.034$. A final Fourier difference map calculation showed no peaks of chemical significance; the maximum and minimum peaks corresponded to + and − 0.67 e Å^{-3}, respectively.

(*ii*) The structural study of crystals of Ga_2I_6·dppe, **2**, followed essentially the same procedure. The space group was identified as $P2_{1/n}$ (No. 14). The data were corrected for decay absorption, Lorentz and polarization effects, and the structure was again solved by direct methods. The final Fourier calculation showed no peaks of chemical significance; the maximum and minimum peaks corresponded to 1.47 and −1.54 e Å^{-3}, respectively. The solution converged at $R = 0.063$ and $R_w = 0.058$.

In both sets of calculations, neutral-atom scattering factors were taken from Cromer and Waber (5). Anomalous dispersion effects were included in the calculations (6); the values for $\Delta f'$ and $\Delta f''$ were those published by Cromer (7). All calculations were performed using the TEXSAN (8) crystallographic software package. The structure of the molecules are shown in Figs. 1 and 2; the positional parameters are in Tables 2 and 4, and important bond distances and angles in Tables 3 and 5.

Tables of hydrogen-atom coordinates and thermal parameters, anisotropic thermal parameters for other atoms, and bond

Fig. 1. The molecular structure of $GaI_3 \cdot PPh_3$, **1**, showing the numbering system. ORTEP diagram, with 30% probability ellipsoids.



lengths and angles other than those in Tables 3 and 5, are available as supplementary data.[3]

Results and discussion

Crystallographic studies

The triphenylphosphine adducts of GaI_3 (**1**) and InI_3 are, not surprisingly, isostructural, with the stereochemistry at metal and phosphorus being essentially C_{3v} in each case. The complex **2** shows the same structural features at the metal centre, and differs from **1** only in the sense that the ligand is effectively $P(C_6H_5)_2CH_2^-$. This structure represents a departure from $InI_3 \cdot$dppe, in which an infinite chain of planar InI_3 units is linked by bridging dppe to give five-coordinate indium. The Ga—I bond distance in **1** is 2.5212(9) Å, to be compared with the range of 2.533(5)–2.481(5) Å in **2**, for which the average r(Ga—I) is 2.513 Å. The average Ga—P bond distances in **1** (2.416(5) Å) and **2** (2.407(9) Å) are also identical within the experimental error, all of which emphasizes the close relationship in the structural chemistry of the gallium centres in these two molecules in the solid state, and the predominance of four-coordination, in contrast to the analogous indium complexes.

Preparative

The first point to note is that the preparative chemistry of the GaI_3/PPh_3 system appears much simpler than for the indium analogue, in which both 1:1 and 1:2 adducts were characterized and shown to readily interconvert in nonaqueous solution (1). None of the previous workers reported such behaviour in the gallium system, and our results are in keeping with their findings (2–4). Similarly, the reaction with dppe gives a single species, whereas with indium triiodide and dppe, both $[InI_3(dppe)]_\infty$ and $(InI_3)_3(dppe)_2$ have been identified crystallographically (1, 9). These comparisons and contrasts emphasize that here, as in other parts of this paper, the maximum coordination number for gallium in these systems is four, and the apparent inability to exceed this underlies the differences between gallium and indium.

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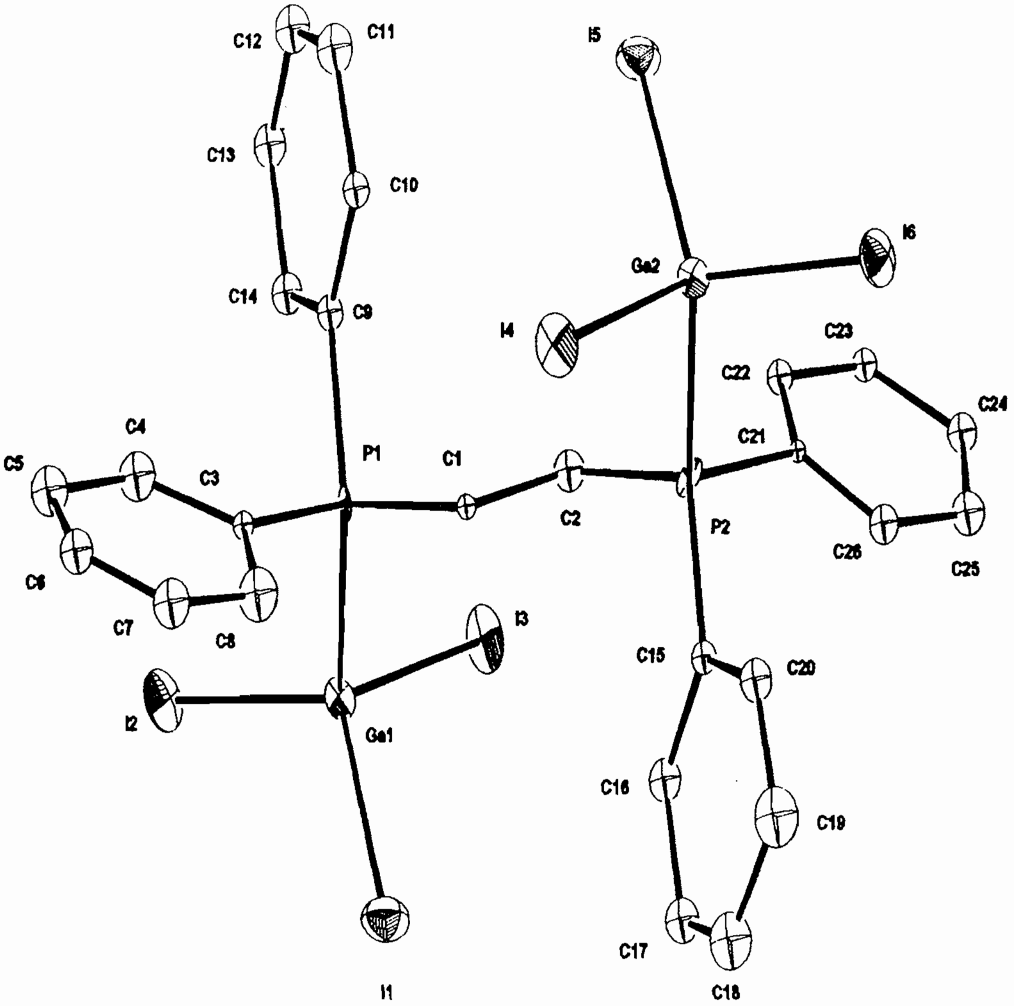
[3] Copies of material on deposit can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. The tables of H-atom coordinates have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Fig. 2. The molecular structure of Ga_2I_6·dppe, **2**, showing the numbering system. ORTEP diagram, with 30% probability ellipsoids.



^{31}P NMR studies of $GaI_3 \cdot PPh_3$

A solution of $GaI_3 \cdot PPh_3$ in acetone (0.1 M) at 23°C has two ^{31}P resonances, at 28.35 ppm, half-width 10.1 Hz, and −3.91 ppm, half-width 46.5 Hz. Since triphenylphosphine in the same solvent gives a signal at −4.77 ppm, $w_{1/2}$ = 9 Hz, this spectrum establishes immediately that the 1:1 complex, for which $\delta(^{31}P)$ = 28.35 ppm, undergoes partial dissociation, with the simplest equilibrium being

$$[1] \quad GaI_3 \cdot PPh_3 \rightleftharpoons GaI_3 + PPh_3$$

The ratio of the peak heights for complex:PPh_3 is 12.0, so that the equilibrium constant for eq. [1] is ca. 0.08 mol L^{-1}. The rather large half-width for Ph_3P in this solution suggests a relatively slow exchange process in eq. [1], which is at first sight surprising, since adduct formation is presumed to be fast (but see below). There is a smooth change in the ratio of the peak heights for the complex and free PPh_3 as PPh_3 is added (Fig. 3*a*) and the half-width for free PPh_3 also decreases over the range studied (Fig. 3*b*).

Figure 4 shows the effect of adding iodide ion (as *n*-Bu_4NI) to the solution. At low I^-:complex ratios, PPh_3 is released as the result of the reaction

$$[2] \quad GaI_3 \cdot PPh_3 + I^- \rightarrow GaI_4^- + PPh_3$$

but beyond an I^-:complex mole ratio of 0.6, a sharp rise in the amount of free PPh_3 is detected. The interpretation of these results is complicated by the presence of a small quantity of PPh_3 in the solution due to the dissociation described in eq. [1], and clearly the quantity of $GaI_3 \cdot PPh_3$ is also lowered by the effect of eq. [2]. At I^- = 0, the quantity of PPh_3 from dissociation of $GaI_3 \cdot PPh_3$ is ca. 8% (see above), which accounts for the point at −4.7 ppm, peak height = 0.1, in Fig. 4. At added I^- = 0.05 M, the quantity of free PPh_3 is more than 10 times greater, and the correction for eq. [1] is of the order of 1% and therefore negligible. The dotted line in Fig. 4 is an approximate correction to allow for PPh_3 arising via eq. [1] rather than eq. [2].

With or without this correction, Fig. 4 shows a linear dependence up to a mole ratio of approx. 0.5, followed by a steep rise in the quantity of Ph_3P released, reaching a maximum at the equimolar point. Further addition of iodide beyond this

Table 2. Positional parameters for non-hydrogen atoms in $GaI_3 \cdot PPh_3$ (**1**).

Atom	*x*	*y*	*z*	*B*(eq)
I(1)	0.18102(6)	0.04565(6)	0.62089(5)	4.49(2)
Ga(1)	0	0	0.6595(1)	2.86(3)
P(1)	0	0	0.8058(3)	2.4(6)
C(1)	−0.0216(7)	−0.1211(7)	0.8462(6)	2.7(2)
C(2)	−0.0927(8)	−0.1722(8)	0.9061(6)	3.6(3)
C(3)	−0.108(1)	−0.265(1)	0.9340(7)	5.3(3)
C(4)	−0.054(1)	−0.310(1)	0.9022(9)	6.0(4)
C(5)	0.015(1)	−0.258(1)	0.8409(8)	5.1(4)
C(6)	0.0330(9)	−0.1645(8)	0.8128(7)	4.1(3)
I(1*)	−0.13537(6)	−0.18102(6)	0.62089(5)	4.49(2)
I(1*)	−0.04565(6)	0.13537(6)	0.62089(5)	4.49(2)
C(1*)	0.1211(7)	0.0994(7)	0.8462(6)	2.7(2)
C(1*)	−0.0944(7)	0.0216(7)	0.8462(6)	2.7(2)
C(2*)	0.1722(8)	0.0795(8)	0.9061(6)	3.6(3)
C(2*)	−0.0795(8)	0.0927(8)	0.9061(6)	3.6(3)
C(3*)	0.2852(10)	0.157(1)	0.934(7)	5.3(3)
C(3*)	0.01574(10)	0.108(1)	0.934(7)	5.3(3)
C(4*)	0.31(1)	0.2556(10)	0.9022(9)	6.0(4)
C(4*)	−0.256(1)	0.054(10)	0.9022(9)	6.0(4)
C(5*)	0.258(1)	0.2737(10)	0.8409(8)	5.1(4)
C(5*)	−0.274(1)	−0.0153(10)	0.8409(8)	5.1(4)
C(6*)	0.1645(9)	0.1976(8)	0.8128(7)	4.1(3)
C(6*)	−0.01978(9)	−0.033(8)	0.8128(7)	4.1(3)

Table 3. (*a*) Bond distances (Å) and (*b*) angles (deg) in $GaI_3 \cdot PPh_3$ (**1**).

(*a*)

Atom	Atom	Distance	Atom	Atom	Distance
I(1)	Ga(1)	2.5212(9)	C(1)	C(2)	1.37(1)
Ga(1)	P(1)	2.416(5)	C(1)	C(6)	1.39(1)
P(1)	C(1)	1.801(9)	C(2)	C(3)	1.37(1)
			C(3)	C(4)	1.38(2)
			C(4)	C(5)	1.37(2)
			C(5)	C(6)	1.37(1)

(*b*)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
I(1)	Ga(1)	I(1)	113.85(4)	C(1)	P(1)	C(1)	107.1(3)
I(1)	Ga(1)	P(1)	104.62(5)	C(2)	C(1)	C(6)	120(1)
Ga(1)	P(1)	C(1)	111.7(3)	C(1)	C(2)	C(3)	120(1)
P(1)	C(1)	C(2)	121.8(8)	C(2)	C(3)	C(4)	121(1)
P(1)	C(1)	C(6)	118.2(8)	C(3)	C(4)	C(5)	118(1)
				C(4)	C(5)	C(6)	122(1)
				C(1)	C(6)	C(5)	119(1)

point produces no change. The half-width of the ^{31}P resonance of the complex is constant at 12.3 ± 0.1 Hz throughout this series, whereas the value for the free ligand changes monotonically from a value of 46.5 Hz for $I^- = 0$ to 15.5 Hz at the equimolar point; this latter is characteristic of free Ph_3P in acetone (see above).

These results, and those for the addition of Ph_3P, suggest a set of equilibria more complicated than eqs. [1] and [2]. The

Table 4. Positional parameters for non-hydrogen atoms in $Ga_2I_6\cdot$dppe (**2**).

Atom	*x*	*y*	*z*	*B*(eq)
I(1)	0.4443(3)	−0.1022(2)	0.3537(1)	4.8(2)
I(2)	0.3215(2)	0.0745(2)	0.4771(1)	3.8(1)
I(3)	0.1371(2)	0.0747(2)	0.3036(1)	3.9(1)
I(4)	0.8561(2)	0.1597(2)	0.1904(1)	4.0(1)
I(5)	0.5479(3)	0.3426(2)	0.1503(1)	4.2(1)
I(6)	0.6520(2)	0.1766(2)	0.0185(1)	3.7(2)
Ga(1)	0.3478(3)	0.0431(2)	0.3739(2)	2.0(2)
Ga(2)	0.6406(3)	0.1977(3)	0.1256(2)	1.9(2)
P(1)	0.5155(7)	0.1379(6)	0.3462(4)	1.1(4)
P(2)	0.4751(7)	0.0999(6)	0.1526(4)	1.2(4)
C(1)	0.556(3)	0.112(2)	0.275(1)	1.0(6)
C(2)	0.441(3)	0.128(2)	0.223(1)	2.3(7)
C(3)	0.668(3)	0.127(2)	0.394(1)	1.0(6)
C(4)	0.771(4)	0.076(2)	0.384(2)	4(1)
C(5)	0.896(3)	0.070(2)	0.422(2)	3.3(8)
C(6)	0.906(3)	0.116(2)	0.472(2)	2.9(8)
C(7)	0.805(3)	0.166(3)	0.493(2)	3.5(9)
C(8)	0.684(3)	0.171(2)	0.451(1)	2.5(8)
C(9)	0.477(3)	0.254(2)	0.347(1)	1.6(7)
C(10)	0.550(3)	0.314(2)	0.318(1)	2.1(7)
C(11)	0.522(3)	0.402(2)	0.325(2)	3.3(8)
C(12)	0.428(3)	0.429(3)	0.355(2)	3.2(8)
C(13)	0.354(3)	0.374(2)	0.380(1)	2.6(7)
C(14)	0.374(3)	0.283(2)	0.377(1)	2.1(7)
C(15)	0.518(3)	−0.012(2)	0.153(1)	1.6(7)
C(16)	0.463(3)	−0.071(2)	0.185(1)	2.4(7)
C(17)	0.487(3)	−0.156(2)	0.183(1)	2.5(7)
C(18)	0.568(4)	−0.185(3)	0.152(2)	5(1)
C(19)	0.627(4)	−0.127(3)	0.112(2)	4(1)
C(20)	0.603(3)	−0.042(2)	0.114(2)	2.9(8)
C(21)	0.320(3)	0.112(2)	0.100(1)	1.1(6)
C(22)	0.224(3)	0.168(2)	0.114(1)	1.8(7)
C(23)	0.111(3)	0.171(2)	0.073(1)	1.5(6)
C(24)	0.089(3)	0.120(2)	0.023(1)	1.8(7)
C(25)	0.187(3)	0.062(2)	0.018(2)	2.9(8)
C(26)	0.302(3)	0.056(2)	0.056(1)	2.4(7)

most important factor is that the dimerization of gallium(III) halides is an important process in nonaqueous solution, and that ligand addition, and hence dissociation, must go via this dimer (10–12). We therefore rewrite eq. [1], and add the successive processes

[3] $$2\,GaI_3\cdot PPh_3 \rightleftharpoons 2\,GaI_3 + 2PPh_3$$

[4] $$2\,GaI_3 \rightleftharpoons Ga_2I_6$$

[5] $$Ga_2I_6 + PPh_3 \rightleftharpoons Ga_2I_6\cdot PPh_3$$

[6] $$Ga_2I_6\cdot PPh_3 \rightleftharpoons GaI_3 + GaI_3\cdot PPh_3$$

The sum of eqs. [3]–[6] is of course eq. [1]. We postulate that the equilibria [3] and [4] are rapidly established, and that [4] lies strongly to the right. In the presence of added PPh_3, eq. [5] becomes important, since this step accounts for the uptake of the ligand to yield the complex $GaI_3\cdot PPh_3$ via eqs. [5] + [6]. We further suggest that eq. [5] is the rate-controlling step in the sequence, and that the decreasing ^{31}P line width shown in Fig. 3*b* is caused by increasingly rapid exchange between PPh_3 as the quantity of free ligand is increased.

Similar equilibria can also be used to understand the processes implicit in the addition of I^- (Fig. 4). Equations [3] and [4] are here followed by

[7] $$Ga_2I_6 + I^- \rightleftharpoons Ga_2I_7^-$$

[8] $$Ga_2I_7^- \rightleftharpoons GaI_4^- + GaI_3$$

[9] $$GaI_3 + I^- \rightleftharpoons GaI_4^-$$

The addition of I^- to a solution of $GaI_3\cdot PPh_3$, already in equilibrium via eqs. [1] and [2] with Ga_2I_6 and PPh_3, leads via eq. [7] to $Ga_2I_7^-$, which is the anionic analogue of $Ga_2I_6\cdot PPh_3$ (eq. [5]). If eq. [7] lies to the right, then the formation of a steady concentration of $Ga_2I_7^-$ will occur at the mole ratio

Table 5. (*a*) Bond distances (Å) and (*b*) angles (deg.) in $Ga_2I_6\cdot$dppe (**2**).

(*a*)

Atom	Atom	Distance	Atom	Atom	Distance
I(1)	Ga(1)	2.512(5)	P(1)	C(1)	1.80(3)
I(2)	Ga(1)	2.481(5)	P(1)	C(3)	1.78(3)
I(3)	Ga(1)	2.533(5)	P(1)	C(9)	1.82(3)
I(4)	Ga(2)	2.530(4)	P(2)	C(2)	1.76(3)
I(5)	Ga(2)	2.518(5)	P(2)	C(15)	1.78(3)
I(6)	Ga(2)	2.506(5)	P(2)	C(21)	1.85(3)
Ga(1)	P(1)	2.404(9)	C(1)	C(2)	1.56(3)
Ga(2)	P(2)	2.410(9)			

(*b*)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
I(1)	Ga(1)	I(2)	116.9(2)	I(5)	Ga(2)	P(2)	101.0(2)
I(1)	Ga(1)	I(3)	111.7(2)	I(6)	Ga(2)	P(2)	108.2(2)
I(1)	Ga(1)	P(1)	100.1(2)	Ga(1)	P(1)	C(1)	112(1)
I(2)	Ga(1)	I(3)	111.8(2)	Ga(1)	P(1)	C(3)	112(1)
I(2)	Ga(1)	P(1)	108.8(2)	Ga(1)	P(1)	C(9)	115(1)
I(3)	Ga(1)	P(1)	106.4(2)	C(1)	P(1)	C(3)	104(1)
I(4)	Ga(2)	I(5)	113.1(2)	C(1)	P(1)	C(9)	108(1)
I(4)	Ga(2)	I(6)	112.7(2)	C(3)	P(1)	C(9)	105(1)
I(4)	Ga(2)	P(2)	106.4(3)	Ga(2)	P(2)	C(2)	109(1)
I(5)	Ga(2)	I(6)	114.3(2)	Ga(2)	P(2)	C(15)	115(1)
Ga(2)	P(2)	C(21)	109(1)	P(1)	C(3)	C(4)	125(3)
C(2)	P(2)	C(15)	109(2)	P(1)	C(3)	C(8)	119(2)
C(2)	P(2)	C(21)	108(1)	P(1)	C(9)	C(10)	121(2)
C(15)	P(2)	C(21)	106(1)	P(1)	C(9)	C(14)	119(2)
P(1)	C(1)	C(2)	115(2)	P(2)	C(15)	C(16)	122(3)
P(2)	C(2)	C(1)	116(2)	P(2)	C(15)	C(20)	119(3)
				P(2)	C(21)	C(22)	119(2)
				P(2)	C(21)	C(26)	116(2)

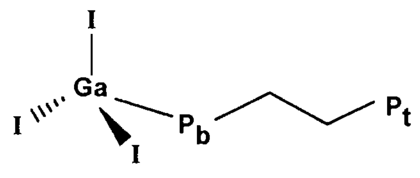
Phenyl rings, average values

C3–C8	1.41(4)	120(3)
C9–C14	1.38(4)	120(3)
C15–C20	1.37(5)	120(4)
C21–C26	1.37(4)	120(4)

$I^-:GaI_3\cdot PPh_3 = 0.5$, and only beyond that point can further uptake of I^- (and hence further dissociation of $GaI_3\cdot PPh_3$) occur by eqs. [8] and [9]. This mechanism accepts that direct nucleophilic attack of I^- on $GaI_3\cdot PPh_3$ via a five-coordinate intermediate cannot be important, and in this context the molecular structure of $Ga_2I_6\cdot$dppe, in which gallium prefers four-coordination to the alternative GaI_3P_2 mode, is significant. An important conclusion of these studies is that four-coordination at gallium(III) is predominant in the solution chemistry of $GaI_3/PPh_3/I^-$ systems.

We also investigated the effect of temperature change on the ^{31}P spectra of $GaI_3\cdot PPh_3$, in the hope of identifying some of the kinetic parameters. For a 0.1 M solution in acetone at 283 K, the only resonance observed is at 27.4 ppm, with $w_{1/2} = 15$ Hz. Over the temperature range 283–323 K, the resonance of free PPh_3 appears at −5.7 ppm, but we did not observe any signs of coalescence, and therefore chose not to extend these studies.

Scheme 1.



^{31}P NMR studies of $GaI_3\cdot$dppe

The ^{31}P spectrum of a solution of $Ga_2I_6\cdot$dppe in acetone (0.1 M) at 23°C consists of two sharp doublets at 33.61, 33.46 and −(11.87, 11.52) ppm. The half-width for each is ca. 75 Hz. These resonances are assigned to the bound and terminal

Table 6. Vibrational spectra (in cm^{-1}) of $GaI_3\cdot PPh_3$ and $Ga_2I_6\cdot$dppe in the metal–ligand region.

Molecule	Core symmetry	Spectra	Assignment
GaI_4^{-a}	T_d	ν_1 145, ν_2 52, ν_3 222, ν_4 73	
$GaI_3\cdot PPh_3$	C_{3v}	ν_1 395 (w) (IR)	ν(Ga–P)
		ν_3 264 (m), 245(s)(R)	
		266 (w), 245(s) (IR)	ν(Ga–I)
$Ga_2I_6\cdot$dppe	C_{2v}	ν_1 350 (m)(R)	ν(Ga–P)
		ν_3 260 (w), 250 (w), 238 (m) (R)	
		257(s), 246(s), 233(s) (IR)	ν(Ga–I)

[a]Values from ref. 13.

Fig. 3. Effect of adding PPh_3 to a solution of $GaI_3\cdot PPh_3$, 0.1 M in acetone; (*a*) change in ^{31}P peak height ratio, (*b*) change in line width at half-height for PPh_3 resonance.

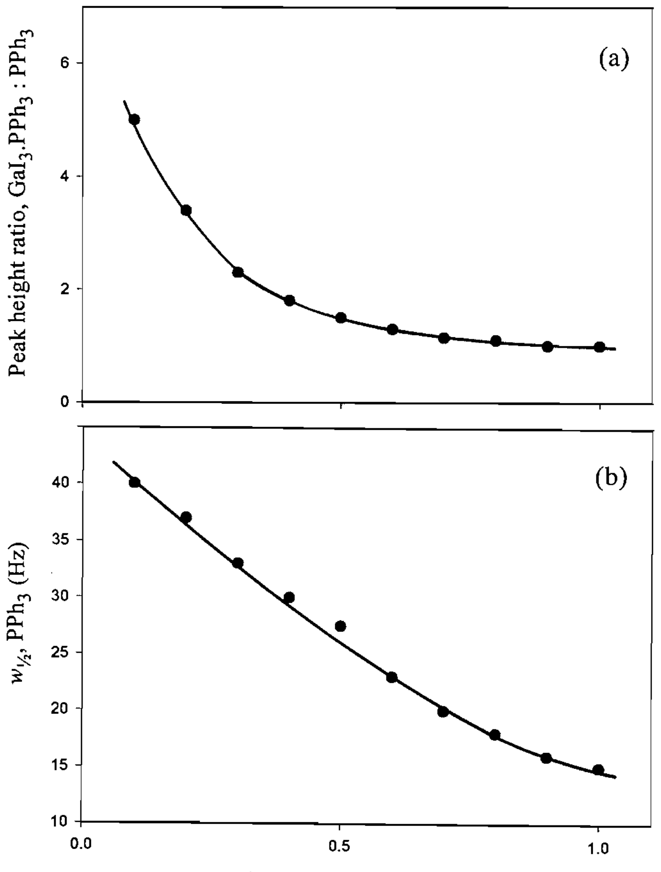
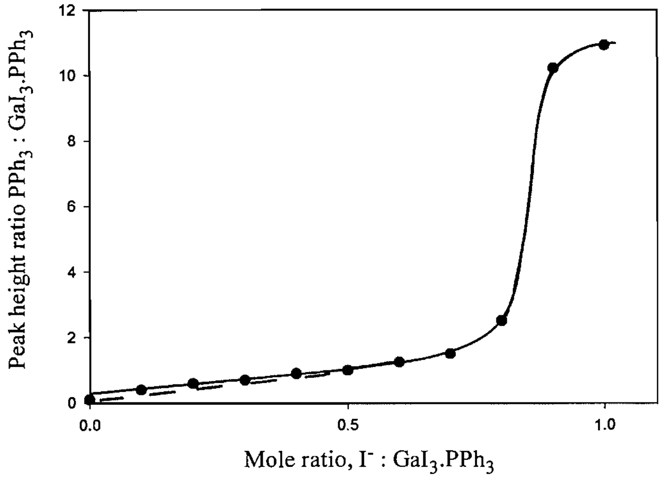


Fig. 4. Effect of adding I^- to a solution of $GaI_3\cdot PPh_3$, 0.1 M in acetone; change in ^{31}P peak height ratio.



phosphorus atoms of the species based on the ^{31}P resonance of dppe in acetone, at −12.45 ppm, $w_{1/2}$ = 14 Hz, and the positive shift observed for this ligand, and for PPh_3, on coordination (ref. 1, and above). This pair of doublets is observed in all experiments in which $Ga_2I_6\cdot$dppe is present in solution, and the average value of J = 42 Hz is ascribed to long-range P–P coupling. The four-coordinate complex of Scheme 1 arises from the processes

[10] $Ga_2I_6\cdot dppe \rightleftharpoons GaI_3\cdot dppe + GaI_3$

[11] $GaI_3 \rightleftharpoons \frac{1}{2}\, Ga_2I_6$

in which all the species are undergoing exchange. The addition of dppe causes no initial change in the ^{31}P NMR spectrum, since the process

[12] $\frac{1}{2}\, Ga_2I_6 + dppe \rightleftharpoons GaI_3\cdot dppe$

removes free ligand. As more dppe is added, the ^{31}P spectrum remains essentially constant, but at the mole ratio dppe:$Ga_2I_6\cdot$dppe = 1.0, a new signal appears at −12.1 ppm, indicating the presence of free dppe, and the absence of uncomplexed GaI_3 (or Ga_2I_6). Beyond this point, the addition of dppe (up to a mole ratio of 1.8) causes an increased intensity of the resonance at −12.15 ppm, which masks that assigned to P_t (Scheme 1); the doublet at ca. 34 ppm remains throughout this sequence. Similarly the addition of Ga_2I_6 causes the gradual disappearance of the P_t resonance, which is completely absent beyond the equimolar point. In this region, the ^{31}P spectrum consists of a doublet at 33.71, 33.38, establishing the presence of $I_3Ga{\cdot}dppe{\cdot}GaI_3$ (i.e., the solid state structure **2**) in the solution. We conclude that although $GaI_3{\cdot}dppe$ does not give rise to a crystalline 1:1 adduct under the preparative conditions used in this, and earlier (2–4), work, this molecule can exist in nonaqueous solution, as described by eq. [10]. Equally, the solid state species in which dppe bridges two four-coordinate gallium(III) entities can also be formed in solution in the presence of excess gallium(III) iodide. These results provide yet another example of the effect of differing solution and solid state stabilizing factors on the properties, and especially the stoichiometry, of such adducts.

Following eqs. [10] and [11], the addition of I^- to a solution of $Ga_2I_6{\cdot}dppe$ in fact involves the interaction of I^- with $GaI_3{\cdot}dppe$ and (or) Ga_2I_6. At low I^-:complex mole ratios, there is no change in the ^{31}P spectrum, since the dominant process is

$$[13] \quad \tfrac{1}{2}\,Ga_2I_6 + I^- \rightleftharpoons GaI_4^-$$

When sufficient I^- has been added to complex all the Ga_2I_6 as the stable GaI_4^- anion, displacement of dppe from $GaI_3{\cdot}dppe$ occurs

$$[14] \quad GaI_3{\cdot}dppe + I^- \rightleftharpoons GaI_4^- + dppe$$

and this release of dppe results in the growth of the resonance at −12.2 ppm. The continued addition of I^- causes an increase in the height of this signal relative to that for bound dppe; at the mole ratio $I^-:Ga_2I_6 = 1.4$, approximately 48% of the dppe has been displaced, and at a mole ratio of 2.0, this rises to 96%. Beyond this ratio, only free dppe is detected in the ^{31}P spectrum since all the gallium is present as GaI_4^-. The half-width of the ^{31}P resonance is almost constant at 80 Hz throughout.

Vibrational spectroscopy

The earlier investigations of the phosphino complexes of gallium(III) iodide depended in large measure on infrared spectroscopy for the elucidation of the solid state structures (2–4). We have recorded the Raman and far infrared spectra of both $GaI_3{\cdot}PPh_3$ and $Ga_2I_6{\cdot}dppe$, with the results shown in Table 6. Given the similarities in the coordination kernels of the two complexes, it is not surprising that the vibrational spectra are very similar in the metal–ligand stretching region. This conclusion is easily reached in the light of the crystallographic results not available to the earlier workers.

General conclusions

It is useful to compare and contrast the behaviour of gallium and indium in terms of the complexation of MI_3 with PPh_3 and dppe. Four-coordination is an exclusive feature of gallium chemistry in such systems, and this factor also accounts for the significance of Ga_2I_6 in nonaqueous solution. For indium, four-coordination is important, but five-coordinate species are also found in crystalline $InI_3(PPh_3)_2$ and $[InI_3(dppe)]_\infty$. The bisphosphino adduct of InI_3 dissociates completely in nonaqueous solution to the 1:1 adduct, but this process can be reversed somewhat by the addition of excess ligand. The preparative chemistry of InI_3–PPh_3 and InI_3–dppe systems is therefore complicated to an extent which is not apparent in the analogous gallium chemistry. The spectroscopic investigations of these various species in nonaqueous solution provide an explanation in terms of the different equilibria involved. No doubt comparable dissimilarities will be found in further investigations of related systems.

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