Synthetic, Spectroscopic and X-Ray Crystallographic Studies on Complexes formed between Indium(III) Iodide and Phosphine Ligands†

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The 1:1 adducts of InI_3 with various phosphine ligands [PR_3; R_3 = Bu^i_3, HPh_2, HBu^t_2 or $H(C_6H_{11})_2$ (C_6H_{11} = cyclohexyl)] have been prepared and characterised, and their solution properties, as examined by ^1H, ^{31}P and ^{115}In NMR and conductivity measurements, indicate the presence of only neutral species. Infrared and Raman data have been recorded for the adducts in the solid state and compared with other published data. X-Ray studies on $InI_3 \cdot PHR_2$ (R = Ph or Bu^t) confirm the presence of neutral compounds containing four-co-ordinate indium atoms, but reveal that significant intermolecular interactions (In–I–In, P–H–I, In–I–I–In) are present.

The co-ordination chemistry of the indium(III) halides is of continuing interest due in part to the use of such compounds as intermediates in the preparation of the Group 13–Group 15 semiconductors (InP, *etc.*). Reactions with a variety of ligands have been studied,[1,2] and in general monodentate donors [*e.g.* L = PPh_3, Et_2O, pyridine(py)] form compounds of the type $InX_3 \cdot nL$ (X = Cl, Br or I; *n* = 1, 2 or 3), although from results obtained so far the stoichiometry of the adducts cannot be predicted with any degree of certainty. Also very little structural information on the solid state is available, and that which has been obtained (*e.g.* from IR, Raman and X-ray data) shows that both ionic and neutral species are possible. It does appear that the complexes of InI_3 have a greater tendency towards the formation of ionic species than do the lighter halides. For example, with dimethyl sulfoxide (dmso) the iodide forms a 1:2 (ratio InI_3:ligand) ionic dimer $[InI_2(dmso)_4][InI_4]$,[3] while the chloro- and bromo-derivatives afford octahedral (*fac*) neutral 1:3 compounds $[InX_3(dmso)_3]$ (X = Cl or Br).[4,5]

Surprisingly there is no report of an X-ray study on any of the 1:1 adducts, but a trigonal-pyramidal structure has been established for several 1:2 adducts, namely $InCl_3 \cdot 2L$ [L = PPh_3,[6] NMe_3,[7] PMe_3[8] and hexamethylphosphoramide $PO(NMe_2)_3$[9]], and more recently $[InX_3(ESMe_3)_2]$ (X = Cl or Br, E = P or As).[10] In addition to the dmso adducts noted above, crystal structures are available for other derivatives of $InCl_3$ and $InBr_3$ with oxo ligands such as $POMe_3$ and $AsOMe_3$ which form 1:3 adducts [*e.g.* $InCl_3(POMe_3)_3$] with *mer* or *fac* octahedral structures,[4] or the ligand-bridged $[(InCl_3)_2(AsOMe_3)_3]$ respectively.[11] The only other known structures are for the 1:4 adducts with pyridine ($InX_3 \cdot 4py$, X = Cl or Br), which show *mer*-octahedral geometry with one of the pyridine ligands remaining unco-ordinated in the lattice.[12,13]

We now report the results of a study of reactions between the easily accessible indium(III) iodide and a series of phosphine ligands, together with X-ray crystal structures of two 1:1 adducts. The structures obtained reveal some interesting features as discussed below and indicate the caution which must sometimes be exercised in deducing structures from spectroscopic data. Previously reported derivatives with phosphines show two different compositions, namely 1:1 adducts $InI_3 \cdot PR_3$ [R = Ph,[5] $4\text{-}MeOC_6H_4$[14] or C_6H_{11};[15] R_3 = $(CH{=}CH_2)Ph_2$;[16] PR_3 = $(Ph_2PCH_2)_2$[5]], and 1:2 adducts $InI_3 \cdot 2PR_3$ [R = Ph,[5] Me[15,17] or Et;[15] R_3 = Me_2Ph,[16] $(CH_2CH_2CH{=}CH_2)Ph_2$[16] or $Ph_2(4\text{-}MeC_6H_4)$[16]]. While Raman spectral data of the 1:1 adduct with $P(C_6H_{11})_3$ have been interpreted in terms of an ionic product $[InI_2\{P(C_6H_{11})_3\}_2][InI_4]$,[15] corresponding spectra of the 1:2 adducts $InI_3 \cdot 2PR_3$ (R = Me or Et) are more complicated and no conclusions could be drawn about their structures.[15,17] However the Raman spectra of the corresponding chloro- and bromo-derivatives $[InX_3(PR_3)_2]$ (X = Cl or Br, R = Me or Et) are simpler, and these compounds were suggested to be neutral with a trigonal-bipyramidal geometry around the metal atom.[14] This is the structure found in the only reported X-ray studies on any indium halide–phosphine adduct, namely $InCl_3 \cdot 2PR_3$ (R = Ph or Me), as mentioned above.

Results and Discussion

The addition of the phosphine ligands [$PHBu^t_2$, $PH(C_6H_{11})_2$, $PHPh_2$ or PBu^i_3] to a diethyl ether solution of indium(III) iodide, using a 1:1 molar ratio, leads to the precipitation of a series of 1:1 complexes as colourless crystalline solids. While this stoichiometry may appear to be not unexpected, it is not always the case. For example, with PPh_3 it is the 1:2 complex, $InI_3 \cdot 2PPh_3$ which is first obtained, even when a 1:1 molar ratio of reactants is used, and the 1:1 complex has to be obtained by recrystallisation of the 1:2 compound.[5] However, in the present examples when a 1:2 molar ratio was used only the 1:1 complex was obtained, with the excess phosphine remaining unreacted. The adducts, which could be recrystallised from toluene or hexane, were all slightly moisture sensitive, decomposing over a period of several hours in air. Their ^1H NMR spectra ($CDCl_3$ solution) were unremarkable, simply confirming the presence of the phosphine ligand. However, the $^{31}P\text{-}\{^1H\}$ NMR spectra of the four adducts in $CDCl_3$, together with that of the previously reported $InI_3 \cdot PPh_3$, did show some points of interest in that, apart from the adduct with $PHPh_2$, all the resonances were very broad ($\Delta\nu_{\frac{1}{2}}$ 800–2200 Hz at 293 K) as shown in Table 1. The linewidths decrease at low temperatures (*e.g.* $\Delta\nu_{\frac{1}{2}}$ for $InI_3 \cdot PBu^i_3$ at 193 K is 350 Hz), rather than broaden and split into two or more resonances as would be expected for any dissociation/exchange process. We have been unable to find any reports of ^{31}P NMR spectra of indium trihalide–phosphine adducts for comparison, but we have observed that the $\Delta\nu_{\frac{1}{2}}$ values for adducts $InMe_xI_{3-x} \cdot L$ (L = PPh_3 or $PHBu^t_2$, *x* = 1 or 2) are 50 Hz or less.

We have also studied the ^{115}In NMR spectra (^{115}In,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Phosphorus-31{hydrogen-1} and ^{115}In NMR data of the $InI_3{\cdot}PR_3$ complexes in $CDCl_3$ showing the chemical shifts and the half-height linewidths ($\Delta\nu_{\frac{1}{2}}$)

	^{31}P		^{115}In	
Complex	δ^a	$\Delta\nu_{\frac{1}{2}}$/Hz	δ^b	$\Delta\nu_{\frac{1}{2}}$/Hz
$InI_3{\cdot}PBu^i_3$	−34	2200	−94	3400
$InI_3{\cdot}HPBu^t_2$	3	1300	−228	3800
$InI_3{\cdot}HP(C_6H_{11})_2$	−33	800	−185	6100
$InI_3{\cdot}PPh_3$	−22	800	—	—
$InI_3{\cdot}HPPh_2$	−48	50	Not observed^c	

^{a} Relative to H_3PO_4 (external). ^{b} Relative to $[In(H_2O)_6]^{3+}$, 0.5 mol dm^{-3} in D_2O. ^{c} The resonance was too broad to be observed.

Table 2 Raman spectra (100–400 cm^{-1}) of 1:1 InI_3–phosphine adducts, and the $[InI_4]^-$ anion

L = PBu^i_3	$PHPh_2$	$PH(C_6H_{11})_2$	$PHBu^t_2$	$P(C_6H_{11})_3$^{a}	$[InI_4]^-$ ^{b}
125m			117m		
138vs	145vs	136vs		138vs	139vs
150w		154s	151vs		
158w	165vw		161m	162m	
			184w	185w(sh)	185w
192w			195w	191w	
	205w	198m		198w(sh)	
372vw		233vw			

^{a} Data from ref. 15. ^{b} Data from ref. 22, recorded from aqueous solution.

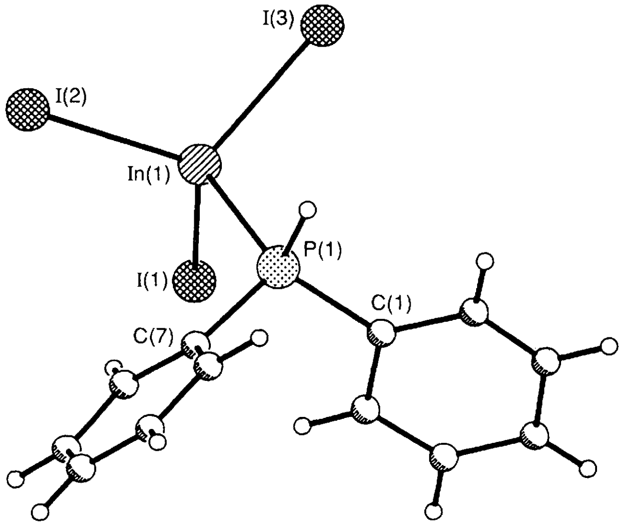

Fig. 1 View of one molecule of the $InI_3{\cdot}PHPh_2$ adduct, showing atomic numbering

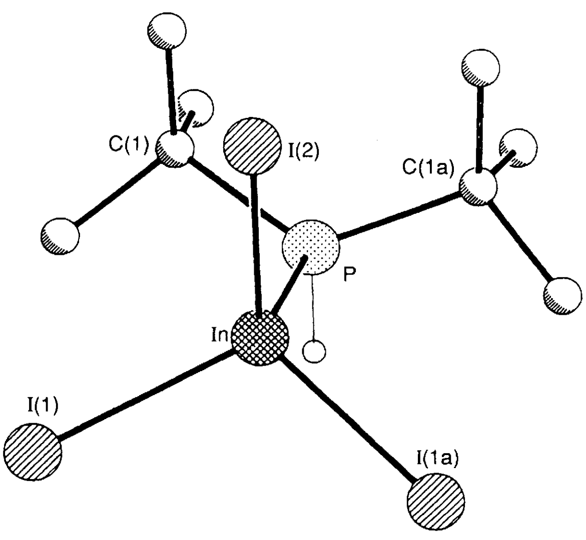

Fig. 2 View of the $InI_3{\cdot}PHBu^t_2$ adduct, showing atomic numbering

abundance 95%, $I = \frac{9}{2}$) of these complexes to obtain more information on the species present in solution, and to try to resolve the question of the relatively narrow linewidth observed in the ^{31}P NMR spectrum of the $InI_3{\cdot}PHPh_2$ adduct. The ^{115}In NMR spectra for the present compounds have broad resonances as shown in Table 1, and although the shifts vary there is a clear trend in the $\Delta\nu_{\frac{1}{2}}$ values which is opposite to that observed in the ^{31}P NMR spectra. The resonances observed in the present work are broad (> 3400 Hz), and occur below δ −228 (Table 1). In view of the above data we suggest that the phosphorus resonance is broadened by coupling to the ^{115}In nucleus. A coupling constant $^1J_{InP}$, of the order of 2 kHz, is anticipated by analogy with $^1J_{FIn} \approx 10$ kHz.[18] This coupling would give rise to a ten-line multiplet in the ^{31}P spectrum, which would partially collapse to a broad singlet if the ^{115}In relaxation rate were to exceed $^1J_{InP}$. As the observed indium linewidths are 3400 Hz and upwards, the corresponding relaxation rates exceed 10 kHz, for in such cases the width at half height (≥3400 Hz) equals $1/\pi T_2$ and $T_1 = T_2$. Thus even the narrowest indium resonance will undergo relaxation sufficiently rapidly to ensure partial decoupling of the ^{31}P resonance. Also, as the indium linewidth increases, the phosphorus linewidth should decrease by approximately the same factor. The data in Table 1 are consistent with this proposal. The possibility that the compounds as used here afford ionic dimers in solution according to equation (1)

$$2InI_3{\cdot}L \rightleftharpoons [InI_2L_2]^+[InI_4{}^-] \qquad (1)$$

appears unlikely, since previous studies have shown that the presence of the $[InI_4]^-$ ion gives a characteristic narrow (400 Hz) resonance near δ −580 {relative to $[In(H_2O)_6]^{3+}$, δ 0}.[14,19–21]

Also since the spectra were recorded from $CDCl_3$ solutions we have measured the molar conductivity of the $InI_3{\cdot}PHPh_2$ adduct in chloroform solution to determine whether any significant dissociation occurs under these conditions. Using concentrations of approximately 10^{-3} mol dm^{-3} the conductivity values were very low (2.6–2.8 ohm^{-1} cm^2 mol^{-1}) indicating that little dissociation occurs in this solvent, consistent with the above discussion.

In a separate series of experiments we have confirmed that the addition of excess phosphine to a solution of a 1:1 adduct does result in exchange between the free and bound ligand. Thus the ^{31}P-{^{1}H} NMR spectrum at 298 K of a 1:1 molar mixture of $InI_3{\cdot}PHBu^t_2$ and $PHBu^t_2$ in $CDCl_2$ solution shows only a single resonance. On cooling the solution the resonance broadens and eventually splits into two resonances at 183 K; one of these resonances corresponds to the free phosphine (δ +17) and the other at δ −1 is very close to that for the 1:1 adduct. The spectra also confirm that no 1:2 adduct, $InI_3{\cdot}2PHBu^t_2$ is formed in this solution.

Attempts to define the structures of the adducts in the solid state using spectroscopic methods proved only partially successful. Other workers have experienced similar difficulties.[15,17] The infrared spectra of the four complexes as Nujol mulls in the region 4000–250 cm^{-1} (see Experimental section) indicate the presence of the phosphine ligands,[15] with weak absorptions at 2364 and 2355 cm^{-1} from the P–H bonds of the co-ordinated $PHBu^t_2$ and $PH(C_6H_{11})_2$ ligands respectively, the corresponding band of the adduct with $PHPh_2$ being undetected. A previous report of the Raman spectrum of solid $InI_3{\cdot}P(C_6H_{11})_3$ has indicated that, although the spectrum was complex, bands occur at 138 and 185 cm^{-1} which may arise from the ν_1 and ν_3

Table 3 Selected bond distances (Å) and angles (°) for $InI_3 \cdot PHPh_2$ and $InI_3 \cdot PHBu^t{}_2$

$InI_3 \cdot PHPh_2$			
In(1)–I(1)	2.674(5)	I(1)–In(1)–I(2)	114.3(1)
In(1)–I(2)	2.676(5)	I(1)–In(1)–I(3)	114.3(1)
In(1)–I(3)	2.672(5)	I(1)–In(1)–P(1)	102.8(2)
In(1)–P(1)	2.605(9)	I(2)–In(1)–I(3)	113.1(1)
In(2)–I(4)	2.674(4)	I(2)–In(1)–P(1)	108.1(2)
In(2)–I(5)	2.665(5)	I(3)–In(1)–P(1)	102.8(2)
In(2)–I(6)	2.676(5)	I(4)–In(2)–I(5)	113.0(1)
In(2)–P(2)	2.592(9)	I(4)–In(2)–I(6)	103.7(2)
P(1)–C(1)	1.800(26)	I(4)–In(2)–P(2)	103.7(2)
P(1)–C(7)	1.813(20)	I(5)–In(2)–I(6)	113.5(1)
P(2)–C(13)	1.785(27)	I(5)–In(2)–P(2)	111.8(2)
P(2)–C(19)	1.812(30)	I(6)–In(2)–P(2)	99.3(2)
$InI_3 \cdot PHBu^t{}_2$*			
In–I(1)	2.668(2)	I(1)–In–I(2)	107.7(1)
In–I(2)	2.679(3)	I(1)–In–P	113.7(1)
In–P	2.586(6)	I(1)–In–I(1a)	107.0(1)
P–C(1)	1.870(25)	I(2)–In–P	106.7(1)
		In–P–C(1)	111.8(7)

* Position a: $x, \frac{1}{2} - y, z$.

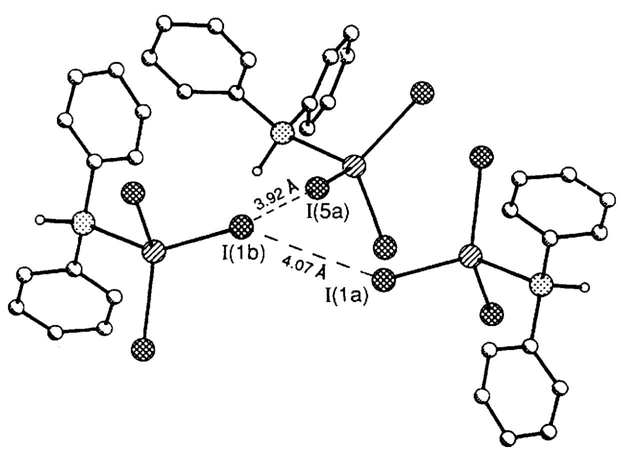

Fig. 3 Intermolecular interactions for $InI_3 \cdot PHPh_2$

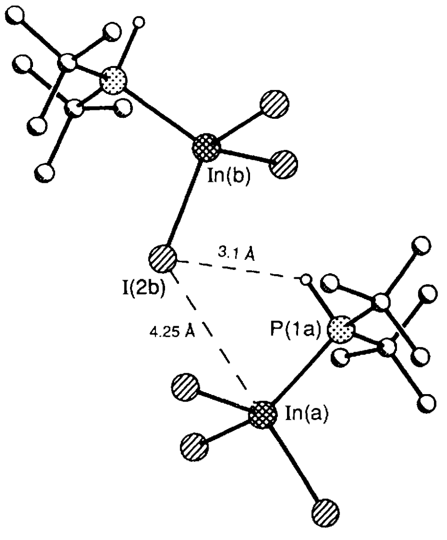

Fig. 4 Intermolecular interactions for $InI_3 \cdot PHBu^t{}_2$

vibrations of the $[InI_4]^-$ ion,[22] and on this basis it was suggested that a dimeric formulation $[InI_2\{P(C_6H_{11})_3\}_2][InI_4]$ was possible.[15] We have recorded the Raman spectra of the 1:1 adducts reported here using powder samples. The bands observed are shown in Table 2, and compared with those for $InI_3 \cdot P(C_6H_{11})_3$.

It can be seen that there are similarities between the spectra of the adducts with $PHPh_2$, $PH(C_6H_{11})_2$ and $PBu^i{}_3$. These spectra also show some resemblance to the spectrum of $InI_3 \cdot P(C_6H_{11})_3$ in having the strongest absorption near 140 cm^{-1}, although the band at 185 cm^{-1} of $InI_3 \cdot P(C_6H_{11})_3$ (and InI_4^-) is shifted slightly to between 192 and 205 cm^{-1} in the three adducts. The spectrum of the adduct with $PHBu^t{}_2$ is also generally similar to that of $InI_3 \cdot P(C_6H_{11})_3$, but while this does show a band at 184 cm^{-1} the strongest absorption is shifted from 138 cm^{-1} up to 151 cm^{-1}. Bands in the 100–200 cm^{-1} region have been assigned to the In–I vibrations, but it is clear that overall the spectra neither allow an unambiguous assignment of the solid-state structures nor do they define whether the solid adducts are best represented by an ionic or neutral formulation. X-Ray studies were therefore undertaken on the adducts with $PHPh_2$ and $PHBu^t{}_2$ to determine the precise structures.

X-Ray Structural Analyses.—Both compounds show monomeric primary structures, with tetrahedral geometry at In (Figs. 1 and 2), though each also forms weak intermolecular interactions. The two independent molecules of the $PHPh_2$ complex are essentially identical. Most of the principal dimensions (Table 3) of the two complexes are almost equal, with mean In–I and In–P distances of 2.673 and 2.590 Å respectively. Both correspond to values in similar compounds, *e.g.* terminal In–I of 2.64 Å in In_2I_6[23] and In–P of 2.576(3) Å in $InCl_3 \cdot 2PMe_3$,[8] though it should be noted that In–P distances vary from 2.576 up to 2.810 Å in $[(InI_3)_2(Ph_2PCH_2CH_2PPh_2)_3]$.[8]

The P–C bonds of the compounds do differ significantly with the P–C of the adduct with $PHBu^t{}_2$ being 1.87(3) Å, while the P–C of the $PHPh_2$ adduct is 1.82(2) Å (mean). As well as the normal lengthening due to the presence of $sp^3(Bu^t)$ and $sp^2(Ph)$ carbon atoms the first value also probably reflects the steric effect of the bulky *tert*-butyl group. The phenyl derivative $InI_3 \cdot PHPh_2$ contains weak I···I contacts of 3.92(5) and 4.07(5) Å (Fig. 3); these are considerably longer than the interactions in solid I_2 (3.50 Å), and close to twice the van der Waals radius for iodine (3.96 Å). However, they provide the principal intermolecular contacts in the structure, linking the molecule into pairs themselves more weakly linked into sets of four. The intermolecular interaction in $InI_3 \cdot PHBu^t{}_2$ is more significant (Fig. 4). It is formed between In and I(2) in a glide-plane related molecule with length 4.25(2) Å. Although this is not much shorter than the estimated van der Waals distance (about 1.5 Å greater than the covalent In–I distance, *i.e.* 4.3 Å),[24] there are two detectable effects on the primary geometry of the complex. The In–I bond *trans* to the interaction is slightly but significantly longer than the other two such bonds [2.679(3) with two at 2.668(2) Å respectively]; such lengthening is expected to occur when a three-centre four-electron secondary bond is formed. In addition the I–In–I angles are also smaller than in the $PHPh_2$ complex (mean 107.5 and 113.9° respectively). This might seem more easily explained through the steric effect of the Bu^t groups, were it not for the pattern of I–In–P angles. That involving I(2) is *gauche* to both butyl groups and must be most affected by their steric effects, yet it is the smaller angle [106.7(1) compared to 113.7(1)° for the other iodine atoms]. There also appears to be a very weak interaction between the hydrogen atom on the phosphorus and one of the iodine atoms on a neighbouring molecule with an estimated distance of 3.1 Å which is slightly less than the sum of the van der Waals radii for the two atoms of 3.2 Å.[24]

The different types of secondary interactions that are found in the two structures can be used to account for the very different Raman spectra of the complexes. The frequency of a vibrational mode involving the iodide ligands would be strongly affected if those iodides were involved in secondary bonding with neighbouring molecules. Such interactions would give rise to a

Table 4 Unit-cell and data collection parameters

Compound	InI_3·$PHPh_2$	InI_3·$PHBu^t_2$
Formula	$C_{12}H_{11}I_3InP$	$C_8H_{19}I_3InP$
M	681.5	641.8
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnma*
Absences	None	$0kl, k + l = 2n + 1; hk0, h = 2n + 1$
a/Å	12.454(9)	9.411(6)
b/Å	12.773(18)	12.479(8)
c/Å	14.158(12)	14.719(11)
α/°	102.58(9)	
β/°	107.48(6)	
γ/°	114.69(10)	
U/Å^3	1792	1729
D_c/g cm^{-3}	2.53	2.46
Z	4	4
F(000)	1224	1160
T/K	298	293
Angular range (2θ)/°	3–45	3–50
Scan range (2θ)/°	−0.5; +0.55	−0.5; +0.6
Index ranges	0–14, −14 to 14, −16 to 16	0–12, 0–15, 0–18
μ(Mo-Kα)/cm^{-1}	23.2	67.1
Crystal size/mm	0.27 × 0.20 × 0.24	0.32 × 0.14 × 0.40
Transmission factor range	0.31–0.55	0.20–0.41
Total no. reflections	4949	1774
No. unique reflections	4692	1588
No. reflections with $I/\sigma(I) \geqslant 2.0$	3304	1165
R_{int}	0.033	
Parameters refined	307	65
Weight parameter (g)	0.019	0.0006
Shift/σ (last cycle)	0.02	0.12
δF max. peak/e Å^{-3}	+1.6; −1.4	±3.0
Final R	0.070	0.082
Final R'	0.076	0.093
S (goodness of fit)	1.58	2.85

change in the In–I bond strength but equally they would also lead to a lowering of the symmetry of the molecule. Hence, the differing interactions in InI_3·$PHPh_2$ and InI_3·$PHBu^t_2$ would be expected to give rise to variations in the Raman spectra. Also, since the adducts with $PHPh_2$, $PH(C_6H_{11})_2$ and PBu^i_3 show similar absorptions in the range 100–200 cm^{-1} it is not unreasonable to suggest that these adducts possess closely related structures in the solid state. It is evident that caution is required in assigning structures of such adducts in the solid state from spectroscopic data, especially when using such data to infer the presence of the corresponding $[InX_4]^-$ ion. As more X-ray structures become available the relevance of the intermolecular interactions especially towards spectral data recorded from the same phase will no doubt become clearer.

Experimental

Compounds were handled either in a nitrogen-filled glove-box, or using Schlenk line techniques as appropriate. Solvents were dried prior to use, and freshly distilled from sodium–benzophenone or calcium hydride. The NMR spectra were recorded using a Perkin Elmer R34 (^1H, 220 MHz) or a Bruker WH400 spectrometer (^{31}P, 161.92 MHz; ^{115}In, 87.61 MHz). The ^1H, ^{31}P and ^{115}In shifts are quoted relative to $SiMe_4$, H_3PO_4 and $[In(H_2O)_6]^{3+}$ as 0.5 mol dm^{-3} solutions in D_2O, respectively, as external standards. Infrared spectra (4000–250 cm^{-1}) were recorded using a Perkin Elmer 580B spectrophotometer, and the Raman spectra were recorded from finely ground solid samples sealed in capillary tubes. Conductivity measurements were carried out using a Phillips PW9527 conductivity meter. Spectroscopic grade chloroform was dried over CaH_2 and distilled under nitrogen prior to use, its specific conductivity being 1.8×10^{-8} ohm^{-1} cm^{-1}. Solutions ($\approx 10^{-3}$ mol dm^{-3}) were made up in the dry-box and loaded into the conductivity cell equipped with polished platinum electrodes.

Indium analyses were carried out on dilute nitric acid solutions (*ca.* 1 mol dm^{-3}) of the compounds using a Varian Techtron AA6 atomic absorption spectrometer. Carbon, H and I analyses were performed by Butterworth Laboratories, Teddington. Dicyclohexylphosphine and diphenylphosphine were obtained from Strem Chemicals, and tri-isobutylphosphine from Maybridge Chemicals. Di-*tert*-butylphosphine and the 1:1 complex In_3I·PPh_3 were prepared by the methods previously reported.[5,25]

Preparation of Compounds.—Indium triiodide. A reported method[26] was modified as follows. Indium foil (5 g, 43.6 mmol) was added to an ethereal solution of iodine (16.4 g, 64.6 mmol). The mixture was stirred at 0 °C until the iodine colour had disappeared. After filtering off the small amount of unreacted indium the ether was removed under reduced pressure. The yellow powder was then heated at 100 °C to remove the last traces of ether. After washing with hot toluene the bright yellow powder was dried *in vacuo* for 3 h. Yield of InI_3: 19 g (90%).

The 1:1 complexes were prepared by the same method, and that used for InI_3·$PHBu^t_2$ is quoted in more detail as an example.

InI_3·$PHBu^t_2$. Di-*tert*-butylphosphine (0.84 g, 5.6 mmol) in diethyl ether (10 cm^3) was added slowly to a solution of InI_3 (2.85 g, 5.75 mmol) in ether (50 cm^3). The adduct precipitated as a colourless crystalline solid; it was filtered off and recrystallised from hot toluene, and after a further filtration was dried *in vacuo*. Yield 3.35 g (91%), m.p. 126–132 °C (Found: C, 14.90; H, 3.10; In, 17.2. $C_8H_{19}I_3InP$ requires C, 14.95; H, 2.95; In, 17.9%). NMR: ^1H ($CDCl_3$), δ 1.64 (18 H, d, CH_3), 3.98 and 5.57 (1 H, d, PH). IR: 2364vw, 1410w, 1310w, 1211w, 1179s, 1028s, 945m, 867w, 813w, 767vs and 468m cm^{-1}. Crystals of the complex suitable for the X-ray study were grown from hexane solution at −5 °C.

InI_3·PBu^i_3. Using the above method triisobutylphosphine (2.37 g, 11.7 mmol) was added to InI_3 (5.81 g, 11.7 mmol) in

Table 5 Atomic coordinates ($\times 10^4$) for $\text{InI}_3\cdot\text{PHPh}_2$

Atom	*x*	*y*	*z*
In(1)	4 885(2)	27(2)	8 029(1)
In(2)	3 125(2)	3 217(2)	3 024(1)
I(1)	4 337(2)	129(2)	6 087(1)
I(2)	7 425(2)	872(2)	9 215(2)
I(3)	3 251(2)	−2 165(2)	8 007(2)
I(4)	1 163(2)	1 827(2)	1 029(1)
I(5)	3 558(2)	1 841(2)	4 088(2)
I(6)	5 320(2)	5 037(2)	3 140(1)
P(1)	4 285(6)	1 545(5)	8 974(4)
P(2)	2 366(6)	4 579(6)	3 937(4)
C(1)	2 740(22)	1 329(19)	8 130(16)
C(2)	1 613(26)	799(21)	8 294(18)
C(3)	486(25)	679(26)	7 650(25)
C(4)	367(34)	992(27)	6 778(20)
C(5)	1 510(32)	1 551(26)	6 634(19)
C(6)	2 677(22)	1 709(22)	7 268(17)
C(7)	5 566(22)	3 183(20)	9 511(17)
C(8)	5 764(29)	4 005(24)	10 432(19)
C(9)	6 661(30)	5 243(29)	10 825(22)
C(10)	7 358(30)	5 663(24)	10 332(27)
C(11)	7 211(27)	4 882(24)	9 394(23)
C(12)	6 302(22)	3 599(23)	8 977(19)
C(13)	1 260(21)	3 878(22)	4 478(15)
C(14)	1 283(27)	4 538(24)	5 381(18)
C(15)	339(32)	3 960(37)	5 744(23)
C(16)	−574(30)	2 736(31)	5 224(24)
C(17)	−570(30)	1 990(26)	4 297(22)
C(18)	359(27)	2 588(24)	3 968(20)
C(19)	1 701(22)	5 220(22)	3 063(16)
C(20)	440(23)	4 426(23)	2 194(18)
C(21)	−58(30)	4 929(31)	1 497(24)
C(22)	601(31)	6 178(32)	1 778(26)
C(23)	1 819(28)	6 934(26)	2 564(20)
C(24)	2 416(27)	6 469(24)	3 264(23)

Table 6 Atomic coordinates ($\times 10^4$) for $\text{InI}_3\cdot\text{PHBu}^t{}_2$

Atom	*x*	*y*	*z*
In	316.4(14)	2500.0	2147.4(16)
I(1)	420.8(21)	1043.3(13)	3827.9(18)
I(2)	−1611(2)	2500	895(2)
P	1724(5)	2500	131(6)
C(1)	1722(19)	1404(18)	−875(23)
C(2)	1906(40)	685(15)	253(39)
C(3)	2659(24)	1329(19)	−1935(26)
C(4)	625(30)	1368(34)	−1689(51)

diethyl ether (50 cm^3). The product was a colourless crystalline solid. Yield 6.21 g (76%), m.p. 176–179 °C (Found: C, 20.65; H, 3.95; I, 54.35; In, 16.2. $\text{C}_{12}\text{H}_{27}\text{I}_3\text{InP}$ requires C, 20.65; H, 3.90; I, 54.55; In, 16.5%). NMR: ^{1}H (CDCl_3), δ 0.84 (6 H, d, CH_3), 1.53 (2 H, m, CH_2), 1.93 (1 H, m, CH). IR: 1402w, 1345w, 1307w, 1250m, 1165m, 1100m, 1074m, 972m(br), 848m and 820m cm^{-1}.

$\text{InI}_3\cdot\text{PH(C}_6\text{H}_{11})_2$. Dicyclohexylphosphine (1.13 g, 5.71 mmol) was added to InI_3 (2.83 g, 5.72 mmol) in diethyl ether (20 cm^3). The adduct was a colourless crystalline solid. Yield 3.64 g, (91%), m.p. 127–129 °C (Found: C, 21.30; H, 3.50; In, 16.0. $\text{C}_{12}\text{H}_{23}\text{I}_3\text{InP}$ requires C, 20.75; H, 3.30; In, 16.6%). NMR: ^{1}H (CDCl_3), δ 1.37, 1.90, 2.56 (22 H, m, C_6H_{11}), 3.75 and 5.36 (1 H, d, PH). IR: 2355vw, 1447s, 1360m, 1347m, 1330m, 1300s, 1270s, 1208s, 1200s, 1184s, 1178s, 1124s, 1116s, 1086m, 1080m, 1047m, 1031m, 1009s, 1003s, 939m, 922m, 910m, 892m, 870m, 851m, 826w, 793s, 782s, 739m, 699w, 511m, 463m, 439m, 379w, 364w, 307w and 285w cm^{-1}.

$\text{InI}_3\cdot\text{PHPh}_2$. Diphenylphosphine (1.81 g, 9.73 mmol) was added to InI_3 (4.82 g, 9.73 mmol) in diethyl ether (30 cm^3). The product was a colourless crystalline solid. Yield 4.91 g (72%), m.p. 214–218 °C (Found: C, 20.95; H, 1.65; In, 17.2. $\text{C}_{12}\text{H}_{11}\text{I}_3\text{InP}$ requires C, 21.10; H, 1.60; In, 16.8%). NMR: ^{1}H (CDCl_3), δ 5.76 and 7.48 (1 H, d, PH) and 7.7 (10 H, m, C_6H_5). IR: 3060w, 1573m, 1438s, 1332m, 1307w, 1184w, 1159w, 1108m, 1100m, 1069w, 1026w, 999w, 918w, 875m, 787s, 748s, 740s, 691s, 507s, 457m, 430m, 402w and 345w cm^{-1}. Crystals for the X-ray study were grown from a hexane solution at −5 °C.

Crystal Structure.—Crystal data and refinement parameters are given in Table 4. In the following comments, information for $\text{InI}_3\cdot\text{PHBu}^t{}_2$ is given in parentheses. Data were collected with a Siemens R3m ($P2_1$) four circle diffractometer in ω–2θ mode. Scan speed was 2(1.5)–15°(ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time.

Three standard reflections were monitored every 200 reflections, and showed a slight decrease (3% for each) during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22°$). Reflections were processed using profile analysis; those with $I/\sigma(I) \geqslant 2.0$ were considered observed. They were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method).

Anisotropic thermal parameters were used for all non-H atoms. Final refinement was on *F* by least-squares methods. All large positive and negative peaks on final Fourier difference syntheses were near I or In atoms. Weighting schemes of the form $w = 1/[\sigma^2(F) + gF^2]$ were used and shown to be satisfactory by a weight analysis. Computing with SHELXTL PLUS[27] (SHELXTL)[28] on a DEC MicroVax-II. Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 29. Final atomic coordinates are given in Tables 5 and 6 and selected bond lengths and angles in Table 3.

For $\text{InI}_3\cdot\text{PHPh}_2$ space group $P\bar{1}$ was selected and shown to be correct by the successful refinement. The structure was solved by direct methods using SHELXTL (TREF), locating two independent molecules. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2. They were inserted at calculated positions and not refined.

For $\text{InI}_3\cdot\text{PHBu}^t{}_2$, the systematic absences indicate either space group *Pnma* or $Pn2_1a$; the former was initially selected and shown to be correct by the successful refinement. Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found by successive Fourier syntheses. The molecule has crystallographic mirror symmetry. Hydrogen atoms were not included, but that attached to P has been inserted in a calculated position in Fig. 2.

Additional material available from the Cambridge Crystallographic Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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