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

Martyn A. Brown, Dennis G. Tuck, and Edward J. Wells

Abstract: Indium(III) iodide forms both 1:1 and 1:2 adducts with triphenylphosphine, depending on the reaction conditions, and especially on the solvent used. The complex InI₃·PPh₃ involves four-coordination at indium; the structure is trigonal, with a = 15.105(4) Å, c = 16.769(7) Å, V = 3313(2) Å³, Z = 6, and space group $R\overline{3}$. Crystals were also obtained in which InI₃·PPh₃ and InI₃(PPh₃)₂ are present in a 1:1 ratio; these are also trigonal, a = 15.473(4) Å, c = 41.701(7) Å, V = 8646.1(1.8) Å³, Z = 3 + 3 and space group $R\overline{3}$. The 1:2 adduct has approximately D_{3h} symmetry in the InI₃P₂ kernel. The bond distances and angles are discussed; in particular, the In—P bonds are extremely weak in the 1:2 adduct. This compound has been shown by ³¹P NMR to undergo complete dissociation in solution to InI₃·PPh₃ and PPh₃. The addition of R₄NI (R = n-C₃H₇, n-C₄H₉) causes quantitative conversion to InI₄⁻ and free Ph₃P. Similar experiments are reported for the compound InI₃(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane), whose structure is an infinite chain of InI₃ units linked through In-P-C₂H₄-P-In coordination. The crystal structure showed that InI₃(dppe) cocrystallizes with an equimolar quantity of dppe; these crystals are cubic, a = 41.445(14) Å, b = 15.944(8) Å, c = 16.533(11) Å, $\beta = 102.02(4)^\circ$, V = 10.685(9) Å³, Z = 4 + 4, space group C_2/c . Solid state and solution phase results are discussed in terms of the coordination chemistry of indium(III).

Key words: indium, phosphorus, coordination chemistry, multinuclear NMR, X-ray crystallography.

Résumé : L'iodure d'indium(III) réagit avec la triphénylphosphine pour former, suivant les conditions expérimentales et particulièrement du solvant utilisé, des adduits 1 : 1 ou 1 : 2. Le complexe $InI_3 \cdot PPh_3$ implique un tétracoordination au niveau de l'indium; la structure est trigonale, groupe d'espace $R\overline{3}$, avec a = 15,104(4) et c = 16,769(7) Å, V = 3313(2) Å³ et Z = 6. On a aussi obtenu des cristaux dans lesquels $InI_3 \cdot PPh_3$ et $InI_3(PPh_3)_2$ sont présents dans un rapport de 1 : 1; ces cristaux sont trigonaux, groupe d'espace $R\overline{3}$, avec a = 15,473(4) et c = 41,701(7) Å, V = 8646.1(1,8) Å³ et Z = 3 + 3. La symétrie de l'adduit 1 : 2 est approximativement D_{3h} et elle comporte un noyau InI_3P_2 . On discute des longueurs et des angles des liaisons; dans l'adduit 1 : 2, on note, en particulier, que les liaisons In—P sont extrêmement faibles. Faisant appel à la RMN du ³¹P, il a été démontré que, en solution, ce composé subit une dissociation complète en $InI_3 \cdot PPh_3$ et en PPh_3 . L'addition de R_4NI ($R = n-C_3H_7$, $n-C_4H_9$) provoque une conversion quantitative en InI_4^- et de PPh_3 libre. Des expériences semblables ont été effectuées avec le composé $InI_3(dppe)$ (dppe = 1,2-bis(diphénylphosphino)éthane) dont la strcture correspond à une chaîne infinie d'unités InI_3 liées par une coordination $P-C_2H_4$ -P-In. La structure cristalline montre que le $InI_3(dppe)$ cocristallise avec une quantité équimolaire de dppe; ces cristaux sont cubiques, groupe d'espace C_2/c , avec a = 41,445(14), b = 15,944(8) et c = 16,533(11) Å, $\beta = 102,02(4)^\circ$, V = 10 685(9) Å³ et Z = 4 + 4. On discute des résultats obtenus à l'état solide et en solution en termes de la chimie de coordination de l'indium.

Mots clés : indium, phosphore, chimie de coordiantion, RMN multinoyaux, cristallographie, rayons X.

[Traduit par la rédaction]

Introduction

The formation of adducts with neutral or anionic donor ligands is an important feature of the chemistry of the elements of Group III (or 13), with both applied and fundamental implications (1). The behaviour of derivatives of indium(III) halides and pseudo-halides has been of especial interest in this laboratory. The features of the problem which are most closely rele-

Received September 29, 1995.¹

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¹ Revision received April 29, 1996.

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 E-mail: dgtuck@uwindsor.ca vant to this paper are the range of coordination numbers that is possible, and the dissociation which can occur in nonaqueous solvents, involving loss of either halide or neutral ligand (2). Each of these processes is strongly affected by the nature of both halide and neutral donor atom, and by the solvent. Halide effects are also clearly seen in both the solid state and solution chemistry of anionic indium(III) complexes (1).

The present paper reexamines some of the early work (2) on triphenylphosphine and bis(diphenylphosphino)ethane (dppe) adducts of indium(III) iodide, using the experimental techniques of X-ray crystallography and multinuclear magnetic resonance which were not previously available. The new information on the solution phase behaviour of these substances is relevant to other work in this laboratory on adduct formation and dissociation of the derivatives of Group III and IV halides with ortho- and paraquinones.³

³ M.A. Brown, D. Boucher, and D.G. Tuck. Unpublished results.

Experimental section

General techniques

Indium(III) iodide was prepared by reacting gram quantities of the elements in refluxing xylene (3). Triphenylphosphine and bis(diphenylphospino)ethane (Aldrich) were recrystallized before use. Solvents were distilled from suitable drying agents, and stored over molecular sieves.

Microanalysis was by Guelph Chemical Laboratories Ltd. Phosphorus-31 and indium-115 NMR spectra were recorded on Bruker AC 200L and 300L instruments, operating at 81.0 and 43.8 MHz, respectively. The reference standards for these nuclei were, for ³¹P, 85% H₃PO₄ = 0 and, for ¹¹⁵In, $InCl_4^- = 0$ (4). Infrared spectra were run on a Nicolet 4DX instrument. Raman spectra of finely ground solids were recorded with a Jobin Yvon S3000 spectrometer. Mass spectrometry involved heated samples in a Shimadzu 14-B spectrometer operating in the EI mode, with Sun Sparc software.

Conductivity measurements were made on a YSI 3400 model 31 conductivity bridge, using a YSI cell with Pt-Ir alloy electrodes coated with platinum black. Solutions were approximately 1 mmol L^{-1} . The cell constant was checked with a 1 mM aqueous solution of KCl after conditioning the electrodes for ca. 5 min.

Preparative

(i) Triphenylphosphine adducts

A solution of InI_3 (0.99 g, 2 mmol) in ethyl acetate (50 mL) was added dropwise to a stirred solution of Ph_3P (1.20 g, 4.6 mmol) in the same solvent. The yellow solid which precipitated was collected after 1 h, washed with ethyl acetate, and dried in vacuo. This solid is $InI_3(PPh_3)_2$, yield 1.56 g, 77%. Anal. calcd. for $C_{36}H_{30}P_2InI_3C$ 42.4, H 2.96; found: C 42.2, H 2.80. The mass spectrum of this compound (sample temp. 100°C) showed important ions based on *m/e* 262 (Ph₃P⁺), 183 (Ph₂P⁺-2), and 108 (PhP⁺), but no peaks attributable to InI_3 or its derivative ions were observed.

When this product was recrystallized from cyclohexane, colourless crystals of the 1:1 adduct $InI_3 \cdot PPh_3$ were obtained. Anal. calcd. for $C_{18}H_{15}PInI_3$: C 28.5, H 2.00; found: C 28.5, H 1.90. The mass spectrum again has significant peaks at *m/e* 262, 183, and 108, but no ions derived from InI_3 .

Recrystallization from ethyl acetate gave yellow crystals, whose analysis corresponded to an equimolar mixture of InI_3 ·PPh₃ and InI_3 (PPh₃)₂. Anal. calcd. for $C_{54}H_{45}P_3In_2I_6$ C 36.5, H 2.55: found: C 37.5, H 2.61. The composition of these crystals was confirmed by X-ray crystallography (see below).

(ii) Bis(diphenylphosphino)ethane adduct

The procedure followed that for triphenylphosphine, using ethyl acetate as solvent; the white powdery product was $InI_3(dppe)$, yield 1.05 g, 59%. Anal. calcd. for $C_{26}H_{24}P_2InI_3$: C 34.9, H 2.71; found: C 34.7, H 2.80. The mass spectrum had important features at *m/e* 398 (diphos⁺), 262, 183, and 108 (Ph₃P⁺ and derivatives). The molar conductivity of this compound in dichloromethane was 3.8 ohm⁻¹ mol⁻¹ cm².

Recrystallization from a mixture of ethyl acetate and toluene (50:50, v/v) gave, on cooling, crystals suitable for X-ray study. This study, and the results of elemental analysis, showed that these crystals contained equimolar quantities of $InI_{3}(dppe)$ and dppe. Anal. calcd. for $C_{52} H_{48} P_{4} InI_{3}$, C 48.3, H 3.74; found: C 48.8, H 3.83.

Crystallographic analysis

(*i*) In the study of $InI_3 \cdot PPh_3$, 1, a colourless crystal mounted on a glass fibre was sited in a Rigaku AFC6S diffractometer, equipped with graphite monochromated Mo-K α 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 $8.59 < 2\theta < 16.07^\circ$. Based on the systematic absences hkl: $-h + k + 1 \neq 3n$, the space group was uniquely identified as $R\overline{3}$ (No. 148), and this was confirmed by subsequent solution and refinement of the structure. Details of the intensity collection for all substances studied are given in Table 1.

The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards increased 1%, and a linear correction factor was applied to the results. The linear absorption coefficient (53.3 cm^{-1}) was such that an absorption correction using PSI Scan was applied, with transmission factors ranging from 0.80 to 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 anisotropically; 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 555 observed reflections $(I > 3\sigma(I))$ and 71 variable parameters, and the solution converged at R = 0.034 and $R_w =$ 0.029. A final Fourier difference map calculation showed no peaks of chemical significance; the maximum and minimum peaks corresponded to 0.68 and -0.45 e Å⁻³, respectively.

(*ii*) The structural study of crystals of $InI_3 \cdot PPh_3 + InI_3(PPh_3)_2$, **2**, followed essentially the same procedure. The space groups are identical. No decay correction was applied, since the intensities of three representative reflections remained constant throughout the data collection, indicating crystal and electronic stability. The data were corrected for absorption, Lorentz, and polarization effects. The structure was solved by direct methods. The indium, iodine, and phosphorus atoms were refined anisotropically, and carbon atoms were refined isotropically; hydrogen atoms on carbon were initially included in ideal positions, and subsequently refined isotropically. After several cycles of refinement, the structure converged to R = 0.047 and $R_w = 0.036$. A final Fourier difference map calculation showed no peaks of chemical significance.

(*iii*) Similar methods were used in the characterization of $InI_3(dppe) + dppe$, **3**. Corrections were made for decay (-0.4%), Lorentz and polarization effects, and for absorption (range 0.747–1.000). Indium, iodine, and phosphorus atoms were refined anisotropically, and carbon atoms isotropically. The structural refinement converged at R = 0.060, $R_w = 0.060$. The maximum and minimum peaks in the final Fourier map were +0.43 and -0.72 e Å⁻³, and there were no peaks of chemical significance.

In each set 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) crystallo-

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Table 1.	Summary	of crystal	data, inte	nsity collect	ion, and struc	tural refinement.
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	1	2	3
Chemical formula	$C_{18}H_{12}I_{3}PIn$	$C_{18}H_{15}I_{3}PIn + C_{30}H_{30}I_{3}P_{2}In$	$C_{26}H_{24}P_2 + C_{26}H_{24}I_3P_2In$
Μ	757.82	757.82 + 1020.13	398.43 + 893.96
Crystal system	Trigonal	Trigonal	Cubic
Space group	R3(No. 148)	$R\overline{3}$ (No. 148)	C_2/c
a/Å	15.105(4)	15.473(4)	41.445(14)
b/Å	—	_	15.944(8)
c/Å	16.769(7)	41.701(7)	16.533(11)
β/°		_	102.02(4)
V/Å ³	3313(2)	8646.1(1.8)	10685.3(9.5)
Ζ	6	3 + 3	4 + 4
<i>F</i> (000)	2076	4980	4992
$D_{\rm calc}/{\rm g~cm^{-3}}$	2.28	2.05	1.60
Crystal dimensions/mm	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$
Abs. coeff./cm ⁻¹	53.3	41.3	23.3
$2\theta^{\circ}$ (max)	50	50	50
Total reflections measured	1428	3661	8704
Unique data used	1297	3408	8536
T/°C	23	23	23
No. of parameters	71	131	282
R	0.034	0.047	0.060
R_{w}	0.029	0.036	0.060
Max. shift/error in final cycle	0.03	4.7	0.02
Max., min. peaks in final difference map /e $Å^{-3}$	0.68, -0.45	1.05, -1.41	0.43, -0.72

Table 2. Positional parameters and isotropic thermal parameters for non-hydrogen atoms in InI_3 ·PPh₃ (1).

Atom	x	у	Z	B(eq)
I(1)	0.14273(8)	-0.04921(8)	0.38241(7)	5.71(3)
I(1*)	0.04921(8)	0.19194(8)	0.38241(7)	5.71(3)
I(1*)	-0.19194(8)	-0.14273(8)	0.38241(7)	5.71(3)
In(1)	0.0000	0.0000	0.3465(1)	3.66(3)
P(1)	0.0000	0.0000	0.1913(4)	3.31(9)
C(1)	0.0206(9)	-0.1006(10)	0.1508(8)	3.5(4)
C(2)	0.091(1)	-0.080(1)	0.0922(9)	4.5(4)
C(3)	0.105(1)	-0.157(1)	0.0651(9)	5.9(5)
C(4)	0.052(1)	-0.255(1)	0.098(1)	6.6(6)
C(5)	-0.018(1)	-0.273(1)	0.156(1)	5.5
C(6)	-0.032(1)	-0.196(1)	0.1829(9)	4.6(4)
C(1*)	0.1006(9)	0.1212(10)	0.1508(8)	3.5(4)
C(1*)	-0.1212(9)	-0.0206(10)	0.1508(8)	3.5(4)
C(2*)	0.080(1)	0.170(1)	0.0922(9)	4.5(4)
C(6 ⁺).	-0.0164(1)	0.032(1)	0.1829(9)	4.6(4)
C(3*)	0.157(1)	0.263(1)	0.0651(9)	5.9(5)
C(5*)	0.273(1)	0.256(1)	0.156(1)	5.5(5)
C(3*)	-0.263(1)	-0.105(1)	0.0651(9)	5.9(5)
C(5*)	-0.256(1)	0.018(1)	0.156(1)	5.5(5)
C(4*)	0.255(1)	0.306(1)	0.098(1)	6.6(6)
C(4*)	-0.306(1)	-0.052(1)	0.098(1)	6.6(6)

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Table 3. (a) Bond distance (Å) and (b) angles (deg) in InI_3 PPh₃ (1). (a)

Atom	Atom	Distance	A	tom	Atom	Distance		
 I(1)	In(1)	2.677(1)	(C(1)	C(6)	1.36(2)		
In(1)	P(1)	2.603(7)	(C(2)	C(3)	1.38(2)		
P(1)	C(1)	1.83(1)	(C(3)	C(4)	1.37(2)		
P(1)	C(1)*	1.83(1)	(2(4)	C(5)	1.36(2)		
P(1)	C(1)*	1.83(1)	(C(5)	C(6)	1.37(2)		
C(1)	C(2)	1.36(2)	_		_			
(b)								
Atom	Atom	Atom	Angle		Atom	Atom	Atom	Angle
I(1)	In(1)	I(1)*	115.11(3)			P(1)	C(1)*	107.0(5)
I(1)	In(1)	I(1)*	115.11(4)		C(1)	P(1)	C(1)	107.0(5)
I(1)*	In(1)	P(1)	102.98(5)		P (1)	C(1)	C(2)	120(1)
I(1)*	In(1)	I(1)*	115.11(3)		P (1)	C(1)	C(6)	118(1)
I(1)*	In(1)	P(1)	102.98(5)		C(2)	C(1)	C(6)	120(1)
I(1)*	In(1)	P(1)	102.98(5)		C(1)	C(2)	C(3)	118(1)
In(1)	P(1)	C(1)	111.8(5)		C(2)	C(3)	C(4)	121(1)
In(1)	P(1)	C(1)*	111.8(5)		C(3)	C(4)	C(5)	119(1)
In(1)	P(1)	C (1)*	111.8(5)		C(4)	C(5)	C(6)	119(1)
C(1)	P(1)	C(1)*	106.6(5)		C(1)	C(6)	C(5)	119(1)

Table 4. Positional parameters and isotropic thermal parameters for nonhydrogen atoms in $InI_3 \cdot PPh_3 + InI_3(PPh_3)_2$ (2).

Atom	<i>x</i>	у	z	B(eq)
I(1)	0.1946(1)	0.1443(1)	0.14870(4)	4.08(6)
I (2)	0.1423(1)	0.6020(1)	0.01395(4)	4.66(7)
In(1)	0	0	0.14793(7)	4.1(1)
In(2)	1/3	2/3	0.03016(6)	3.03(8)
P(1)	0	0	0.2164(2)	4.1(3)
P(2)	0	0	0.0763(2)	2.6(3)
P(3)	1/3	2/3	0.0929(2)	2.5(3)
C(1)	0.112(1)	0.009(1)	0.2337(5)	3.5(4)
C(2)	0.161(2)	0.064(2)	0.2610(6)	5.4(6)
C(3)	0.243(2)	0.065(2)	0.2741(6)	6.1(6)
C(4)	0.275(2)	0.009(2)	0.2600(6)	5.4(6)
C(5)	0.232(2)	-0.046(2)	0.2336(6)	7.5(7)
C(6)	0.147(2)	-0.052(2)	0.2209(5)	6.0(6)
C(7)	0.037(1)	0.123(1)	0.0583(4)	2.6(4)
C(8)	-0.022(1)	0.167(1)	0.0669(4)	3.5(4)
C(9)	0.003(1)	0.259(1)	0.0538(5)	3.8(5)
C(10)	0.078(1)	0.303(1)	0.0332(5)	3.9(5)
C(11)	0.137(1)	0.263(1)	0.0235(4)	3.0(4)
C(12)	0.113(1)	0.173(1)	0.0366(4)	3.5(4)
C(13)	0.457(1)	0.695(1)	0.1082(4)	2.4(4)
C(14)	0.541(1)	0.777(1)	0.0982(4)	3.3(4)
C(15)	0.633(1)	0.799(1)	0.1107(5)	3.6(4)
C(16)	0.639(1)	0.736(1)	0.1315(5)	3.9(5)
C(17)	0.557(2)	0.651(1)	0.1420(5)	4.4(5)
C(18)	0.460(1)	0.626(1)	0.1312(4)	3.2(4)

Table 5. (a) Bond distances (Å) and (b) angles (deg) in $InI_3 \cdot PPh_3 + InI_3(PPh_3)_2$ (2). (a)

Atom	Atom	Distance	Atom	Atom	Distance		
I(1)	In(1)	2.707(1)	C(2)	C(3)	1.38(3)		
I(2)	In(2)	2.691(2)	C(3)	C(4)	1.33(3)		
In(1)	P(1)	2.86(1)	C(4)	C(5)	1.35(3)		
In(1)	P(2)	2.99(1)	C(5)	C(6)	1.37(3)		
In(2)	P(3)	2.616(9)	C(7)	C(8)	1.45(2)		
P(1)	C(1)	1.82(2)	C(7)	C(12)	1.37(2)		
P(1)	C(1)	1.82(2)	C(8)	C(9)	1.39(2)		
P(1)	C(1)	1.82(2)	C(9)	C(10)	1.33(2)		
P(2)	C(7)	1.85(2)	C(10)	C(11)	1.40(2)		
P(2)	C(7)	1.85(2)	C(11)	C(12)	1.36(2)		
P(2)	C(7)	1.85(2)	C(13)	C(14)	1.36(2)		
P(3)	C(13)	1.85(2)	C(13)	C(18)	1.45(2)		
P(3)	C(13)	1.85(2)	C(14)	C(15)	1.38(2)		
P(3)	C(13)	1.85(2)	C(15)	C(16)	1.34(2)		
C(1)	C(2)	1.40(2)	C(16)	C(17)	1.37(2)		
C(1)	C(6)	1.40(3)	C(17)	C(18)	1.42(2)		
(<i>b</i>)							
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
I(1)	In(1)	I(1)*	119.99(1)	C(7)	P(2)	C(7)	105(2)
I(1)	In(1)	I(1)*	119.986(7)	C(7)	P(2)	C(7)	105(2)
I(1)	In(1)	P(1)	89.31(3)	In(2)	P(3)	C(13)	110.184(5)
I(1)	In(1)	P(2)	90.69(3)	In(2)	P(3)	C(13)	110.184(1)
I(1)*	In(1)	I(1)*	119.986(7)	In(2)	P(3)	C(13)	110.1838(7)
I(1)	In(1)	P(1)	89.31(3)	C(13)	P(3)	C(13)	108.749(9)
I(1)*	In(1)	P(2)	90.69(3)	C(13)	P(3)	C(13)	108.750(8)
I(1)	In(1)	P(1)	89.31(3)	C(13)	P(3)	C(13)	108.75(1)
I(1)*	In(1)	P(2)	90.69(3)	P(1)	C(1)	C(2)	124.62(5)
P(1)	In(1)	P(2)	180.00	P(1)	C(1)	C(6)	117(1)
I(2)	In(2)	I(2)*	113.89(8)	C(2)	C(1)	C(6)	118(1)
I(2)	In(2)	I(2)*	113.89(8)	C(1)	C(2)	C(3)	123.08
I(2)*	In(2)	P(3)	104.6(1)	C(2)	C(3)	C(4)	116.44
I(2)*	In(2)	I(2)*	113.89(8)	C(3)	C(4)	C(5)	123.08
I(2)	In(2)	P(3)	104.6(1)	C(4)	C(5)	C(6)	121.96
I(2)	In(2)	P(3)	104.6(1)	C(1)	C(6)	C(5)	116.96
In(1)	P(1)	C(1)	113.18(1)	P(2)	C(7)	C(8)	116(3)
In(1)	P(1)	C(1)	113.18(1)	P(2)	C(7)	C(12)	126(2)
In(1)	P(1)	C(1)	113.18(1)	C(8)	C(7)	C(12)	118(3)
C(1)	P(1)	C(1)	105.52(1)	C(7)	C(8)	C(9)	117(3)
C(1)	P(1)	C(1)	105.52(2)	C(8)	C(9)	C(10)	120(1)
C(1)	P(1)	C(1)	105.52(2)	C(9)	C(10)	C(11)	124.602(9)
In(1)	P(2)	C(7)	114(2)	C(10)	C(11)	C(12)	115.848(5)
In(1)	P(2)	C(7)	114(2)	C(7)	C(12)	C(11)	124(1)
ln(1)	P(2)	C(7)	114(2)	C(13)	C(14)	C(15)	119(13)
C(7)	P(2)	C(7)	105(2)	C(14)	C(13)	C(18)	122.1(7)
C(14)	C(15)	C(16)	120.25	C(15)	C(16)	C(17)	124.09
C(16)	C(17)	C(18)	119.26	P(3)	C(13)	C(14)	120.05(1)
C(13)	C(18)	C(17)	115.37	P(3)	C(13)	C(18)	117.9(7)

graphic software package. The structure of the molecules are shown in Figs. 1, 2, and 3; the positional parameters are in Tables 2, 4, and 6 and important bond distances and angles in Tables 3, 5, and 7.

Tables of hydrogen-atom coordinates and thermal parameters, and anisotropic thermal parameters for other atoms, are available as supplementary data.⁴

⁴ These data can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. The data fro 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.

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Table 6. Positional parameters and isotropic thermal parameters for non-hydrogen atoms in $InI_3(dppe) + dppe$ (3).

Atom	x	у	z	B(eq)
I(1)	0.09986(6)	0.2821(1)	0.7034(1)	4.9(1)
I(2)	0.05413(5)	0.0080(1)	0.6535(1)	4.9(1)
I(3)	0.16547(5)	0.0223(1)	0.7242(1)	4.1(1)
In(1)	0.10715(5)	0.1123(1)	0.6969(1)	2.85(8)
P(1)	0.1096(2)	0.1259(4)	0.5314(4)	3.0(3)
P(2)	0.1098(2)	0.1026(4)	0.8647(4)	2.9(3)
P(3)	0.6173(2)	0.0217(5)	0.6591(4)	4.2(4)
P(4)	0.7235(2)	-0.0048(5)	0.7861(4)	4.5(4)
C(1)	0.1128(5)	0.020(1)	0.492(1)	2.5(5)
C(2)	0.0744(6)	0.171(2)	0.467(1)	3.3(6)
C(3)	0.0705(7)	0.257(2)	0.459(2)	4.6(7)
C(4)	0.0425(8)	0.297(2)	0.410(2)	5.4(7)
C(5)	0.0179(7)	0.247(2)	0.370(2)	4.9(7)
C(6)	0.0204(7)	0.163(2)	0.377(2)	4.0(6)
C(7)	0.0466(7)	0.123(2)	0.428(2)	4.6(7)
C(8)	0.1436(6)	0.188(1)	0.508(1)	3.1(5)
C(9)	0.1669(6)	0.222(1)	0.571(1)	3.2(5)
C(10)	0.1918(7)	0.272(2)	0.555(2)	5.0(7)
C(11)	0.1945(7)	0.289(2)	0.000(2)	4 5(6)
C(12)	0.1910(7)	0.269(2)	0.113(2) 0.413(2)	4 6(7)
C(12)	0.1445(6)	0.200(2)	0.427(1)	2.7(5)
C(14)	0.1132(6)	-0.007(1)	0.901(1)	31(5)
C(15)	0.0740(6)	0.007(1)	0.901(1)	3.1(5)
C(16)	0.0418(8)	0.140(1) 0.151(2)	0.890(1)	6 1(8)
C(17)	0.0158(8)	0.131(2) 0.186(2)	0.044(2)	7 1(9)
C(18)	0.0138(0)	0.100(2)	0.000(2)	5 A(7)
C(10)	0.0100(7)	0.200(2)	1.003(1)	3 2(5)
C(20)	0.0769(6)	0.200(1)	0.980(1)	2.2(5)
C(21)	0.1435(6)	0.171(1) 0.159(2)	0.930(1)	3 2(6)
C(22)	0.1745(0)	0.139(2) 0.119(2)	0.924(1)	4 2(6)
C(22)	0.1745(7)	0.119(2) 0.162(2)	1.000(2)	4.2(0) 5.8(8)
C(24)	0.2010(8)	0.102(2)	1.000(2)	5.6(8)
C(24)	0.1970(8)	0.240(2)	1.009(2)	2.0(8)
C(25)	0.1094(0) 0.1415(7)	0.230(1)	0.977(1)	2.8(5)
C(20)	0.1413(7)	0.244(2)	0.932(2)	3.8(0)
C(21)	0.0009(0)	0.025(2)	0.544(1)	5.3(3)
C(20)	0.5801(7)	0.080(2)	0.303(2)	5.5(7)
C(29)	0.3803(7)	0.080(2)	0.410(2)	4.7(7)
C(30)	0.3922(8)	0.024(2)	0.374(2)	5.0(7)
C(31)	0.0111(0)	-0.033(2)	0.413(2)	5 2(7)
C(32)	0.0213(7)	-0.032(2)	0.300(2)	3.2(7)
C(33)	0.01/2(0)	0.134(1)	0.080(2)	3.7(0)
C(34)	0.3691(7)	0.103(2)	0.714(2)	4.9(7)
C(35)	0.5880(7)	0.254(2)	0.727(2)	5.0(7)
C(30)	0.0132(7)	0.303(2)	0.709(2)	J.2(7)
C(37)	0.0393(7)	0.270(2)	0.074(1)	4.1(0)
C(38)	0.0408(0)	0.194(2)	0.002(1)	3.0(0)
C(39)	0.0398(7)	-0.001(2)	0.079(2)	5.3(7)
C(40)	0.6803(7)	0.012(2)	0.771(2)	5.7(7)
C(41)	0.7271(6)	-0.119(1)	0.783(1)	3.1(5)
C(42)	0.7040(6)	-0.174(1)	0.793(1)	2.9(5)
C(43)	0.7095(7)	-0.259(2)	0.793(2)	5.1(7)

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 Table 6 (concluded).

Atom	x	у	Ζ	B(eq)
C(44)	0.7381(7)	-0.292(2)	0.783(2)	5.6(7)
C(45)	0.7613(7)	-0.235(2)	0.767(2)	5.2(7)
C(46)	0.7575(7)	-0.148(2)	0.769(2)	4.1(6)
C(47)	0.7369(6)	0.011(2)	0.898(1)	3.9(6)
C(48)	0.7194(8)	-0.025(2)	0.957(2)	6.2(8)
C(49)	0.7308(8)	-0.011(2)	1.042(2)	5.8(7)
C(50)	0.7594(8)	0.036(2)	1.065(2)	5.7(7)
C(51)	0.7755(9)	0.074(2)	1.010(2)	8(1)
C(52)	0.7631(8)	0.062(2)	0.927(2)	5.2(7)

Table 7. (a) Bond distances (Å) and (b) angles (deg) in $InI_3(dppe) + dppe$ (3). (a)

Atom	Atom	Distance	Atom	Atom	Distance	
I(1)	In(1)	2.729(2)	C(9)	C(10)	1.37(3)	
I(2)	In(1)	2.730(3)	C(10)	C(11)	1.35(3)	
I(3)	In(1)	2.766(3)	C(11)	C(12)	1.40(3)	
In(1)	P(1)	2.769(7)	C(12)	C(13)	1.35(3)	
In(1)	P(2)	2.758(6)	C(15)	C(16)	1.45(4)	
P(1)	C(1)	1.82(2)	C(15)	C(20)	1.39(3)	
P(1)	C(2)	1.77(3)	C(16)	C(17)	1.33(4)	
P(1)	C(8)	1.83(2)	C(17)	C(18)	1.37(3)	
P(2)	C(14)	1.85(2)	C(18)	C(19)	1.33(3)	
P(2)	C(15)	1.83(2)	C(19)	C(20)	1.43(3)	
P(2)	C(21)	1.77(3)	C(21)	C(22)	1.44(3)	
P(3)	C(27)	1.86(2)	C(21)	C(26)	1.37(3)	
P(3)	C(33)	1.83(2)	C(22)	C(23)	1.37(3)	
P(3)	C(39)	1.76(3)	C(23)	C(24)	1.40(3)	
P(4)	C(40)	1.78(3)	C(24)	C(25)	1.34(3)	
P(4)	C(41)	1.83(2)	C(25)	C(26)	1.44(3)	
P(4)	C(47)	1.84(2)	C(27)	C(28)	1.34(3)	
C(1)	C(14)	1.52(3)	C(27)	C(32)	1.37(3)	
C(2)	C(3)	1.38(3)	C(28)	C(29)	1.41(3)	
C(2)	C(7)	1.42(3)	C(29)	C(30)	1.30(3)	
C(3)	C(4)	1.43(3)	C(30)	C(31)	1.28(4)	
C(4)	C(5)	1.36(3)	C(31)	C(32)	1.42(3)	
C(5)	C(6)	1.34(3)	C(33)	C(34)	1.46(3)	
C(6)	C(7)	1.38(3)	C(33)	C(38)	1.45(3)	
C(8)	C(9)	1.38(3)	C(34)	C(35)	1.47(3)	
C(8)	C(13)	1.38(3)	C(35)	C(36)	1.38(3)	
C(36)	C(37)	1.39(3)	C(37)	C(38)	1.33(3)	
C(39)	C(40)	1.60(3)	C(41)	C(42)	1.33(3)	
C(41)	C(46)	1.40(3)	C(42)	C(43)	1.36(3)	
C(43)	C(44)	1.34(3)	C(44)	C(45)	1.39(3)	
C(45)	C(46)	1.40(3)	C(47)	C(48)	1.45(3)	
C(47)	C(52)	1.35(3)	C(48)	C(49)	1.40(3)	
C(49)	C(50)	1.39(4)	C(50)	C(51)	1.37(4)	
C(51)	C(52)	1.38(4)				

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(<i>b</i>)							
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
I(1)	In(1)	I(3)	127.5(1)	I(1)	In(1)	I(2)	121.7(1)
I(1)	In(1)	P(1)	89.3(1)	P(1)	C(1)	C(14)	120(2)
I(1)	In(1)	P(2)	89.9(2)	P(1)	C(2)	C(3)	122(2)
I(2)	In(1)	I(3)	110.80(8)	P(1)	C(2)	C(7)	123(2)
I(2)	In(1)	P(1)	88.9(2)	C(3)	C(2)	C(7)	115(3)
I(2)	In(1)	P(2)	95.3(2)	C(2)	C(3)	C(4)	125(3)
I(3)	In(1)	P(1)	89.5(2)	C(3)	C(4)	C(5)	117(3)
I(3)	In(1)	P(2)	87.5(2)	C(4)	C(5)	C(6)	121(3)
P(1)	In(1)	P(2)	175.5(2)	C(5)	C(6)	C(7)	124(3)
In(1)	P(1)	C(1)	107.7(7)	C(2)	C(7)	C(6)	119(3)
In(1)	P(1)	C(2)	115.5(8)	P(1)	C(8)	C(9)	120(2)
In(1)	P(1)	C(8)	116.3(8)	P(1)	C(8)	C(13)	121(2)
C(1)	P(1)	C(2)	106(1)	C(9)	C(8)	C(13)	118(2)
C(1)	P(1)	C(8)	108(1)	C(8)	C(9)	C(10)	121(2)
C(2)	P(1)	C(8)	103(1)	C(9)	C(10)	C(11)	122(3)
In(1)	P(2)	C(14)	111.1(7)	C(10)	C(11)	C(12)	116(3)
In(1)	P(2)	C(15)	114.9(8)	C(11)	C(12)	C(13)	123(2)
In(1)	P(2)	C(21)	113.2(8)	C(8)	C(13)	C(12)	119(2)
C(14)	P(2)	C(15)	106(1)	P(2)	C(14)	C(1)	115(2)
C(14)	P(2)	C(21)	108(1)	P(2)	C(15)	C(16)	122(2)
C(15)	P(2)	C(21)	104(1)	P(2)	C(15)	C(20)	119(2)
C(16)	C(17)	C(18)	117(3)	C(16)	C(15)	C(20)	118(2)
C(17)	C(18)	C(19)	123(3)	C(15)	C(16)	C(17)	123(3)
C(18)	C(19)	C(20)	122(2)	C(15)	C(20)	C(19)	116(2)
P(2)	C(21)	C(22)	122(2)	P(2)	C(21)	C(26)	120(2)
C(22)	C(21)	C(26)	118(3)	C(21)	C(22)	C(23)	124(3)
C(22)	C(23)	C(24)	115(3)	C(23)	C(24)	C(25)	125(3)
C(24)	C(25)	C(26)	118(2)	C(21)	C(26)	C(25)	120(3)
C(28)	C(27)	C(32)	118(2)	C(48)	C(47)	C(52)	119(3)
C(27)	C(28)	C(29)	118(3)	C(47)	C(48)	C(49)	120(3)
C(28)	C(29)	C(30)	124(3)	C(48)	C(49)	C(50)	117(3)
C(29)	C(30)	C(31)	119(3)	C(49)	C(50)	C(51)	124(3)
C(30)	C(31)	C(32)	122(3)	C(50)	C(51)	C(52)	118(3)
C(27)	C(32)	C(31)	118(3)	C(47)	C(52)	C(51)	123(3)
P(3)	C(33)	C(34)	115(2)	C(33)	C(38)	C(37)	124(2)
P(3)	C(33)	C(38)	125(2)	C(36)	C(37)	C(38)	115(3)
C(34)	C(33)	C(38)	120(2)	C(35)	C(36)	C(37)	128(3)
C(33)	C(34)	C(35)	115(2)	C(34)	C(35)	C(36)	118(3)
P(3)	C(27)	C(28)	121(2)	P(4)	C(47)	C(48)	122(2)
P(3)	C(27)	C(32)	120(2)	P(4)	C(47)	C(52)	119(2)
C(27)	P(3)	C(33)	100(1)	C(40)	P(4)	C(41)	103(1)
C(33)	P(3)	C(39)	102(1)	C(40)	P(4)	C(47)	101(1)
C(27)	P(3)	C(39)	102(1)	C(41)	P(4)	C(47)	99(1)
P(3)	C(39)	C(40)	118(2)	P(4)	C(40)	C(39)	116(2)
P(4)	C(41)	C(42)	126(2)	P(4)	C(41)	C(46)	124(2)
C(42)	C(41)	C(46)	120(2)	C(41)	C(42)	C(43)	123(3)
C(42)	C(43)	C(44)	123(3)	C(43)	C(44)	C(45)	116(3)
C(44)	C(45)	C(46)	124(3)	C(41)	C(46)	C(45)	116(3)

Results and discussion

Crystallographic studies

The structure of InI_3 ·PPh₃, 1 (Fig. 1), shows that the stereochemistry at both indium and phosphorus is close to tet-

rahedral. The indium(III)-iodine bond distance (2.677(1) Å) is in keeping with the values in the literature for other four-coordinate derivatives, for which the range is 2.68 ± 0.04 Å (9). More particularly, the results reported for InI₃·PHPh₂ (r(In-I) (avg.) = 2.673(5) Å, r(In-P) (avg.) = 2.599(9) Å), and for **Fig. 1.** The molecular structure of InI₃·PPh₃, showing the numbering system; ORTEP diagram, with 30% probability ellipsoids.



 InI_3 ·PHBu^t₂ (r(In-I) (avg.) = 2.674(5) Å, r(In-P) = 2.586(6) Å)(10) are in good agreement with the values in Table 3.

The substance 2 is unusual, in that the lattice contains equal proportions of $InI_3 \cdot PPh_3$ and $InI_3(PPh_3)_2$. There are some important differences between the results for the $InI_3 \cdot PPh_3$ moiety (Table 5) and those for the pure compound given in Table 3. The In–I bond distance of 2.691(2) Å is significantly longer than in 1, as is In–P (2.616(9) compared with 2.603(7) Å). There are also interesting changes in the bond angles; I-In-I, which is 115.11(3)° in the isolated molecule in 1 changes to 113.92(5)° in the mixed lattice, while the corresponding values for In-P-C are 111.8(5)° and 110.18(1)°, so that the molecule is slightly flattened at both pseudo-tetrahedral sites in this mixed lattice, relative to the pure substance.

The 1:2 complex is directly comparable with the compound $InI_3(PMePh_2)_2$, for which r(In-I) = 2.736(4), 2.76(2) Å, and r(In-P) (avg.) = 2.716(4) Å (11). Both show a significant lengthening of the In-I bond relative to the values for the various 1:1 adducts, in keeping with the increased coordination number at indium (cf. ref. 9). Surprisingly, the two In-P bonds are of quite different lengths (2.86(1) and 2.99(1) Å), and these values are both much larger than the average of 2.65 Å derived from work on $InI_3(PMePh_2)_2$, $InBr_3(PMe_2Ph)_2$ (11), $InCI_3(PMe_3)_2$ (12), and $InCI_3(PPh_3)_2$ (13). We return to these results below.

The structure of compound **3** reveals the presence of an infinite chain in which planar InI_3 units are linked by bridging dppe,bidentate donors. The presence of isolated dppe molecules allows a comparison between the coordinated and the free state. Apart from a slight contraction of the P—C₆H₅ bonds, there are in fact no significant differences; the total P–P distance is essentially constant at ~5.2 Å in the two molecules. It is also interesting to compare the structure of $[InI_3(dppe)]_{\infty}$ with that of $(InI_3)_3(dppe)_2$ (12), which represents a sub-unit of the infinite chain structure. The stereochemistry at indium and phosphorus is almost identical in both cases, and the average bond distances in $(InI_3)_3(dppe)_2$ (r(In-I) = 2.731(15) Å, r(In-P) = 2.809(10) Å and $r(P-C_6H_5) = 1.83(1)$ Å are very close to those in Table 7.

The values for In—P bond length in these adducts call for some comment. We first note that the P-C bond distances in all the present structures give an average value of 1.84 Å, which is close to the sum of the covalent radii (0.77 + 1.10 =1.87 Å), in keeping with the expected formation of single bonds. The covalent radius of indium in tetrahedral InX_4^{-} species (X = Cl, Br, I) can be calculated from the known average In—X bond lengths (2.350(2), 2.479(2), 2.71(1) for X = Cl, Br, and I, respectively (14)) as 1.36(2) Å, in which case r(In-P) in a tetrahedral environment should be ca. 2.46 Å, which is significantly smaller than the values found in the present work for InI_3 ·PPh₃ in **1** and **2** (2.603(7), 2.616(9) Å) (Tables 3 and 5). For the five-coordinate species, r(In-P)(avg.) = 2.92(5) in 2 and 2.76(1) in 3, again substantially greater than that calculated. An alternative approach uses the conventional single bond covalent radii for these elements (15), from which r(In-I) = 1.50 + 1.33 = 2.83 Å, and r(In-P) = 1.50 + 1.09 = 2.59 Å. These values therefore substantially underestimate r(In-I) in both four- and five- coordinate species, while the calculated r(In-P) is slightly lower than the experimental value in InI_3 ·PPh₃, and significantly so in the other adducts. The large bond distance in the five-coordinate molecules implies the presence of very weak In-P interactions in these species in the crystalline state, which has important implications for the solution studies reported below.

NMR studies on InI₃(PPh₃)₂

The ³¹P resonance of a solution of $InI_3(PPh_3)_2$ in CDCl₃ at 293 K is a broad singlet, half width approximately 33 Hz, -16.85 ppm from the reference solution of 85% $H_3PO_4 = 0$; the comparable values for PPh₃ under the same conditions are $\delta = -5.44$ ppm and $\omega_{1/2} = 7.5$ Hz. Both the chemical shift (Fig. 4A) and the line width (Fig. 4B) of a solution of the 1:2 complex change with temperature until, at 213 K, the half width is ca. 100 Hz, and the chemical shift is -15.5 ppm. Below this temperature, the precipitation of crystalline material, identified as the 1:1 complex InI₃·PPh₃, was observed, and the slight maximum observed in Fig. 4A at 223 K may have been caused by the presence of small quantities of solid in the solution phase at this temperature.

The significant line width, the increase of this with decreasing temperature, the precipitation of $InI_3 \cdot PPh_3$, and the change in the average chemical shift towards the value for free PPh₃, are all in keeping with the existence in solution of the equilibria

- $[1] \qquad InI_3(PPh_3)_2 \ \leftrightarrows \ InI_3 \cdot PPh_3 + PPh_3$
- [2] $InI_3 \cdot PPh \Leftrightarrow InI_3 + PPh_3$

The change in the line width with decreasing temperature indicates that the rapid exchange observed at room temperature is being slowed, but clearly we were not able to achieve conditions under which the signals of the individual species could be observed.

The effect of adding PPh₃ to a solution of $InI_3(PPh_3)_2$ in CDCl₃ (0.1 M, room temp.) is illustrated in Fig. 5. For reasons

Fig. 2. The structure of 2 showing the numbering system for (A) InI_3 PPh₃ and (B) InI_3 (PPh₃); ORTEP diagram, with 30% probability ellipsoids.



that will be discussed below, this diagram shows both the average ³¹P chemical shift (5A) and the width at half-height (5B) as a function of the mole ratio of Ph₃P to the 1:1 complex InI₃·PPh₃ and both parameters move monotonically as a function of this ratio. The limiting chemical shift (-5.4 ppm) is identical to that for free PPh₃. The changes in $T_{1/2}$ show that the exchange processes in solution persist over the range studied, while the sharpening at high ligand: complex ratios indicates that the overall exchange is enhanced under these conditions.

When iodide ion, in the form of either n-Pr₄NI or n-Bu₄NI, is added to a solution of $InI_3(PPh_3)_2$ in CDCl₃, two important

phenomena are observed. The ³¹P chemical shift (Fig. 6A) changes linearly as I⁻ is added, to a point of inflexion at which the quantities of iodide and complex are equal. The ³¹P resonance at this point, and subsequently, is at -5.2 ppm, indicating the presence of free PPh₃ in the solution. The line width also changes during the addition of iodide, with the results shown in Fig. 6B. The point of inflexion again occurs when equimolar quantities of I⁻ and $InI_3(PPh_3)_2$ are present. The line width beyond that point ($\omega_{1/2} = 23$ Hz) is similar to that for free PPh₃ under the same conditions. Studies of the ¹¹⁵In resonance of these solutions showed

that no signal could be detected with a solution of $InI_3(PPh_3)_2$

Fig. 3. The structure of 3 showing the numbering system for (A) InI₃(dppe) and (B) dppe; ORTEP diagram, with 30% probability ellipsoids.



in CDCl₃, which is in keeping with earlier observations by many workers that this resonance is only detectable in species of high symmetry because of the high nuclear spin (I = 9/2). As I⁻ was added, however, a signal was detected at -980 ppm relative to InCl₄⁻ = 0 (see ref. (14), indicating the formation of InI₄⁻ in the solution. The intensity of this signal increased with further addition of R₄NI, and again reached a maximum when the concentration of InI₃(PPh₃)₂ and R₄NI were equal. Further addition of R₄NI caused the precipitation of R₄N[InI₄], identified by the characteristic Raman spectrum (139 s, 186 w cm⁻¹; cf. lit. values $v_1 = 139$, $v_3 = 186$ cm⁻¹ (16)), and in the case of *n*-Pr₄N[InI₄] by indium analysis (calcd. In 14.2%; found: In 14.0). These results all show that the process [3] takes place,

Fig. 4. Effect of temperature on ³¹P NMR spectrum of a solution of $InI_3(PPh_3)_2$, 0.1 M in $CDCl_3$; (A) change in chemical shift, (B) change in line width at half-height.



 $[3] \qquad InI_3(PPh_3)_2 + I^- \rightarrow InI_4^- + 2 PPh_3$

apparently quantitatively, under the conditions used.

The 1:1 complex InI₃·PPh₃ is insufficiently soluble in CDCl₃ for ³¹P investigations, but results were obtained with solutions in acetone. The 1:1 adduct in this solvent shows a sharp resonance at room temperature at -28.8 ppm, $\omega_{1/2} =$ 16.5 Hz. This is significantly sharper than the 1:2 species $(\omega_{1/2} = 105 \text{ Hz})$, and we conclude that the dissociation and ligand exchange are absent in this solution, so that eq. [2] lies to the left. The effect of adding PPh₃ to this solution is shown in Fig. 7. As with the 1:2 adduct, there are changes in both δ and $\omega_{1/2}$. The chemical shift of a mixture containing equimolar quantities of InI₃·PPh₃ and PPh₃ is -23.5 ppm, to be compared with the value for a solution of the 1:2 complex in $CDCl_3$ of -16.85 ppm. Given the effect of solvent on the equilibria involved, there is little to be gained by discussing this difference; the more important point is that addition of PPh₃ to InI_3 ·PPh₃ shifts the resonance towards that of the 1:2 complex. The increasing half width (Fig. 7B) with addition of ligand is evidence of ligand exchange, in keeping with eq. [1].

Dissociative equilibria involving $InI_3(PPh_3)_2$

The present results, and those from the earlier investigations (2), show clearly that eqs. [1], [2], and [3] describe partially

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Fig. 5. Effect of adding PPh₃ to a solution of $InI_3(PPh_3)_2$ (0.1 M in CDCl₃) at room temperature; (*A*) change in ³¹P chemical shift, and (*B*) change in line width.



Fig. 6. Effect of adding *n*-Bu₄NI to a solution of $InI_3(PPh_3)_2$ (0.1 M in CDCl₃) at room temperature; (A) change in ³¹P chemical shift, (B) change in line width.



the solution chemistry of $InI_3(PPh_3)_2$. For this system, the possible equilibria can be summarized as

 $[4] \qquad InX_{3}L_{n-1} + L \iff InX_{3}L_{n} \iff InX_{2}L_{n} + X^{-1}$

We note first that the dissociation into ionic species is established by the small but significant electrical conductivity in nitromethane and nitrobenzene (2). Such dissociation is germane to the present discussion only to the extent that free or associated charged species can be assumed to be present in the solvents used in the NMR investigations.

The preparative scale work on the InI_3/PPh_3 system showed that the reaction between these substances in ethyl acetate gives the 1:2 complex, which on recrystallization from the same solvent yields an equimolar solid lattice of 1:2 and 1:1 adducts that is also in keeping with the existence of this same equilibrium in ethyl acetate. Recrystallization of a solution of the 1:2 complex from cyclohexane gives only the 1:1 adduct. These effects, which have been discussed elsewhere (1), are a general feature of the adducts of indium trihalides and related compounds, and serve to emphasize the difficulty of identifying the "most stable" species in a series of possible adducts and (or) coordination numbers.

A quantitative analysis of the various results is hindered by the different solvents which were necessarily used in the various aspects of the work, and by the different concentration ranges involved ($\sim 10^{-3}$ M for conductivity measurements, $<10^{-2}$ for molecular weight determination, $>10^{-1}$ M for NMR studies, and >1 M in the preparative work). We take as a starting point the molecular weight determinations reported earlier (2) for two different sets of conditions. In chloroform at room temperature, the observed value is 614, and in benzene at the freezing point (5.5°C), $M_{obs} = 526$. If the only significant equilibrium is that of eq. [1], then

[5]
$$M_{\text{obs}} = \frac{(1-x)M_2 + M_1 + xL}{1+x}$$

where M_2 , M_1 , and M_L are the molecular weights of $InI_3(PPh_3)_2$, $InI_3 \cdot PPh_3$ and PPh₃ respectively, and x is the degree of dissociation of $InI_3(PPh_3)_2$. A value of $M_{obs} = 526$ corresponds to $x \rightarrow 1$ ($M_2 = 1020$, $M_1 = 758$, $M_L = 262$ to the nearest integer), and the result for chloroform is rather similar, so that the conclusion is that, at such dilutions, $InI_3(PPh_3)_2$ undergoes essentially complete dissociation to the 1:1 complex and free triphenylphosphine. This interesting result correlates nicely with the weak In—P bonding in the 1:2 complex (see above).

The ³¹P NMR results show that the various phosphoruscontaining species are undergoing rapid exchange under all **Fig. 7.** Effect of adding PPh₃ to a solution of InI_3 ·PPh₃ (0.1 M) in acetone at room temperature; (A) change in ³¹P chemical shift, (B) change in line width.



$$[6] \qquad \delta_{\rm obs} = \sum_{i} p_i \delta_i$$

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where p_i is the fractional population of the ³¹P spins present as the *i*th species with characteristic chemical shift δ_i , and one should therefore be able to calculate p_i or δ_i , depending on the assumptions made. If we assume that this solution is completely dissociated into InI₃PPh₃ and PPh₃, following the results just discussed, then from

$$[7] \qquad \delta_{\text{obs}} = p_2 \delta_2 + p_1 \delta_1 + p_L \delta_L$$

where the subscripts refer to the 1:2 and 1:1 complexes and the free ligand, we have $p_2 = 0$, and $p_1 = p_L = 0.5$, so that

[8]
$$\delta_{obs} = 0.5\delta_1 + 0.5 (-5.44) = -16.85 \text{ ppm}$$

from which $\delta_1 = -28.2$ ppm in CDCl₃. The value in acetone is -29.0 ppm (see above), and the agreement is satisfying

(assuming no large solvent effect), so that the ³¹P NMR results are in keeping with the molecular weight determinations in that both imply complete dissociation via eq. [1].

The addition of Ph₃P to a solution of InI₃(PPh₃)₂ can then be treated as increasing the concentration of PPh₃ in a solution initially containing equimolar quantities of InI₃·PPh₃ and PPh₃. For this reason, Fig. 5 deals with the results in terms of the mole ratio of these two components. A quantitative analysis of the chemical shift results in Fig. 5 appears impossible in the absence of a value for δ_2 , but the curve cannot be reproduced by assuming that PPh₃ is being added to InI₃·PPh₃ without formation of the 1:2 complex. The more acceptable model assumes the formation of the 1:2 complex by the reverse of eq. [1], which then leads to the conclusion that δ_2 must be close to δ_L , and, given the weak long-range nature of this In–P interaction in the solid state, this seems reasonable. It was not possible to further analyze the NMR results to derive the equilibrium constant for eq. [1].

The addition of R_4NI to a solution of $InI_3(PPh_3)_2$ causes δ_{obs} to move in a linear fashion, reaching a constant value when the quantity of I⁻ added is equal to the initial quantity of $InI_3(PPh_3)_2$ (Fig. 6). Given the complete dissociation of the latter at $[I^-]_{ad} = 0$, we can write

$$[9] \qquad InI_{3}L + L + I^{-} \rightarrow InI_{4}^{-} + 2L$$

for the limit at $[I^-]_{ad} = [InI_3L_2]_0$. For intermediate conditions, where the quantity of added $I^- = x$, for complete conversion, one has

[10]
$$\delta_{obs} = (1 - x)\delta_1 + (1 + x)\delta_L$$

which leads to a linear plot, as is observed in Fig. 6. This quantitative formation of InI_4^- is in keeping with the known behaviour of indium(III)-iodide systems, in which this tetrahedral anion is observed as an extremely stable species (1), and in the present situation much favored over the InI_3 ·PPh₃ adduct.

NMR studies of InI₃(dppe)

In view of the differing crystalline forms of this substance, it is important to note that all NMR studies discussed below refer to solutions of the compound InI_3 (dppe), as initially prepared (see Experimental). The ³¹P spectrum of a 0.1 M solution of this compound in CDCI₃ at room temperature is a sharp singlet, with $\delta = -15.9$ ppm and $\omega_{1/2} = 5$ Hz. The corresponding shift for dppe in the same solvent is -13.0 ppm, and the small change caused by coordination is in keeping with the structural similarities between free and bound ligand in the solid state (see above). The effect of lowering the temperature is illustrated in Fig. 8; the signal broadens gradually, with a sharp change at 223 K corresponding to the appearance of solid material, while the chemical shift changes by about 2 ppm over the same range. The studies of triphenylphosphine adducts of InI₃ discussed above clearly demonstrate that the four-coordinate species is thermodynamically more stable than the five-coordinate derivative, and the spectrum of $InI_3(dppe)$ can be interpreted in this light. A non-fluxional four-coordinate mononuclear complex would show two ³¹P resonances, as would a five-coordinate species with apical and equatorial phosphorus atoms; the observation of a single sharp resonance at room temperature and the relatively small tem-



Fig. 8. Effect of temperature on ³¹P NMR spectrum of a solution of $InI_3(dppe)$ (0.1 M in CDCl₃); (A) change in chemical shift, (*B*) change in line width.



perature effect in the spectra of InI_3 (dppe) itself are taken as evidence of the presence of the rapidly interconverting species (Scheme 1).

Ring-opening processes of this type have been shown to be a feature of the solution chemistry of other indium(III) compounds, and reflect the changes in coordination numbers associated with different ligand environments (17–19). The chemical shift observed is then the appropriately weighted average of the individual shifts of IA and IB and there will be two values for P_b and P_t in IA. The broadening of the signal with decreasing temperature (Fig. 8B) indicates the expected slowing of the exchange process, but it was not possible to identify these as separate resonances in the temperature range available to us. The addition of dppe (Fig. 9) produces a small change in δ , and the curve approaches asymptotically a value







of ca. -14.5 ppm. In the absence of a bonding interaction leading to higher complexes between InI₃(dppe) and free ligand, one would expect the linear relationship seen at low dppe concentrations in Fig. 9. There is an obvious deviation from this as the quantity of dppe is increased, but it is clear that an extrapolation to the chemical shift for free dppe would require the addition of large excess of this ligand. The addition of dppe (Fig. 9) also causes line broadening, and a shift in δ_{obs} that is almost linear with the dppe: complex ratio and corresponds to an averaging of δ_L and δ_C , the chemical shifts of the free ligand and the complex at low [dppe]. But at high ligand: complex mole ratios, δ_{obs} falls away from this linearity, which may be due to the formation in solution of species in which InI₃ is coordinated by two dppe ligands. In view of the preparative and crystallographic results, which show that InI₃(dppe), $(InI_3)_3(dppe)_2$, and $[InI_3(dppe)]_{\infty}$ are readily interconverted, and that indium is five-coordinate in at least two of these systems, such a complex would likely involve two monodentate ligands present in small but not insignificant proportions (Scheme 2). The average ³¹P chemical shift in such a species would presumably lie between the values for dppe (-13.0)and $InI_3(dppe)$ (-15.9 ppm).

The addition of strong σ -donor ligands, such as dimethyl sulphoxide, dimethylformamide, pyridine, or γ -picoline, to a solution of InI₃(dppe) in CDCl₃ leads to the quantitative release of free dppe, as shown by the ³¹P chemical shift changes. As in the InI₃-PPh₃ system, addition of iodide ion, as *n*-Bu₄NI, also results in the release of dppe and the formation of InI₄⁻, by the ¹¹⁵In resonance at -980 ppm. There is a quantitative difference from the InI₃/PPh₃ case, in that the dependence of δ on the complex: iodide mole ratio is not linear (Fig. 10). Extrapolation of the initial and final linear portions of this

Fig. 10. Effect of adding *n*-Bu₄NI to a solution of $InI_3(dppe)$ (0.5 M in CDCl₃) at room temperature; change in ³¹P chemical shift.



graph gives a point of inflexion at a mole ratio of I⁻: complex = 0.5, which can be interpreted in the following way. Firstly, we note that direct nucleophilic attack by I⁻ on a five-coordinate InI₃(dppe) (structure **IB**) would involve the formation of a six-coordinate InI₄P₂ intermediate, which seems most unlikely in the context of the known coordination chemistry of indium(III). An interaction between I⁻ and four-coordinate InI₃(dppe) (i.e., structure **IA**) might appear more favorable, but this would not give the reaction stoichiometry observed, and it may well be that steric blocking by dppe at the indium(III) centre would prevent this reaction pathway. We therefore propose that the first step is the weak dissociation of the complex.

[11] $InI_3(dppe) \Leftrightarrow InI_3 + dppe$

It is known that in non-coordinating solvents, the dimerization

$$[12] \qquad 2 \operatorname{InI}_3 \to \operatorname{In}_2 I_6$$

lies completely to the right. Two spectroscopic studies (20, 21) have shown that adduct formation by Ga_2X_6 (X = Cl, Br) involves as a first step the coordination of the donor at one of the metal atoms of the dimer, and that dissociation of the latter (i.e., the reverse of eq. [12]) is not a prerequisite. For the present system, one then has

$$[13] \qquad In_2I_6 + I^- \rightarrow InI_3 + InI_4^-$$

as the final step, so that the overall stoichiometry is

[14] 2 InI₃(dppe) +I⁻
$$\rightarrow$$
 InI₄⁻ + 2 dppe + 1/2 In₂I₆

in keeping with the results shown in Fig. 10. The differences in the behaviour of $InI_3(PPh_3)$ and $InI_3(dppe)$ in this respect are therefore a consequence of the different initial interactions, which are themselves a function of the coordination chemistry of indium(III).

General conclusions

The preparative studies on $InI_3 - PPh_3$ adducts demonstrate that here, as in other related systems, the influences of both solvent and ligand on apparently simple equilibria are complex, and not readily predictable with our present knowledge. The detailed information obtained from the NMR investigations for both PPh₃ and dppe derivatives emphasizes the difficulty of interpreting such matters in a quantitative manner. The most important general conclusion is that the interactions of such seemingly simple molecules are much more complicated than is apparent from a superficial examination, and that further studies of related systems would be profitable.

Acknowledgments

The present NMR work on $InI_3 - PPh_3$ systems is an extension of earlier studies carried out at Simon Fraser University; we wish to thank Mr. Victor Verigin for carrying out these experiments. Dr. S.J. Loeb (University of Windsor) is thanked for his help in the crystallographic studies. The research was supported in part by Research Grants (to D.G.T.) from the Natural Sciences and Engineering Research Council of Canada.

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