

# Synthesis, mass spectrometry and NMR spectroscopy studies of the $(\text{CH}_3)_2\text{In}(\text{C}_2\text{H}_5)$ system: X-ray crystal structure of a diphosphine-bridged complex

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## Abstract

The synthesis of homoleptic and heteroleptic alkylindium derivatives (generally as diethyl ether adducts) was carried out in high yields from  $\text{InI}_3$ . The nuclear magnetic resonance and mass spectra of the compounds  $\text{Me}_n\text{InEt}_{3-n}$  ( $n = 0, 1, 2$ , or  $3$ ) and of their trideuteromethyl analogues showed that both heteroleptic  $\text{Me}_2\text{InEt}$  and  $\text{MeInEt}_2$  exist as single compounds, although disproportionation to  $\text{InMe}_3$  and  $\text{InEt}_3$  has been observed at temperatures slightly higher than room temperature. The crystal structure of unusual diphosphine-bridged adduct,  $[(\text{InMe}_3)\text{diphos}(\text{Me}_2\text{InEt})] \cdot [(\text{InMe}_3)\text{diphos}(\text{InMe}_3)]$ , (diphos =  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ ) is reported.

**Keywords:** Indium; Alkyls; X-ray structure; Phosphine complexes; Preparations

## 1. Introduction

Ethylindium(III)  $\text{Me}_2\text{InEt}$  has been suggested as an alternative precursor to both  $\text{InMe}_3$  and  $\text{InEt}_3$  for the epitaxial deposition of In-based semiconducting thin films via metal organic chemical vapour deposition (MOCVD) [1]. The need for an alternative precursor stems from the fact that  $\text{InMe}_3$ , a solid at room temperature, does not allow a constant evaporation rate, with consequent serious problems in the reproducibility of the composition of ternary and quaternary alloys such as  $\text{In}_x\text{Ga}_{1-x}\text{As}$  and  $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ . Although  $\text{InEt}_3$  is a liquid at room temperature, it has a low vapour pressure and it is often necessary to heat the  $\text{InEt}_3$  bubbler and transport lines in order to achieve an appreciable growth rate of In-based thin films. This results in decomposition of the precursors and contamination of the final product. The use of  $\text{Me}_2\text{InEt}$ , which at room temperature is a liquid with a fairly high vapour pressure, should eliminate these difficulties. However, the thermal stability and even the existence of  $\text{Me}_2\text{InEt}$

have been questioned on the basis of proton NMR [2] and Raman spectroscopies [3], as well as mass spectrometry [4].

In an effort to clarify this situation, we have synthesized and investigated by mass spectrometry and NMR spectroscopy the homoleptic  $\text{InMe}_3 \cdot x\text{Et}_2\text{O}$  (**1**) and  $\text{InEt}_3$  (**2**), as well as the heteroleptic  $\text{Me}_2\text{InEt} \cdot x\text{Et}_2\text{O}$  (**3**) and  $\text{MeInEt}_2 \cdot x\text{Et}_2\text{O}$  (**4**), which are still relatively unstudied. To explore in detail the behaviour of these compounds, we also synthesized and studied their trideuteromethyl congeners, i.e.  $\text{In}(\text{CD}_3)_3 \cdot x\text{Et}_2\text{O}$  (**1a**),  $(\text{CD}_3)_2\text{In}(\text{C}_2\text{H}_5) \cdot x\text{Et}_2\text{O}$  (**3a**), and  $(\text{CD}_3)\text{In}(\text{C}_2\text{H}_5)_2 \cdot x\text{Et}_2\text{O}$  (**4a**). An adduct in which the diphosphine  $(\text{C}_6\text{H}_5)_2\text{P}-\text{CH}_2-\text{CH}_2-\text{P}(\text{C}_6\text{H}_5)_2$  (diphos) acts as a bridging ligand between the  $\text{InMe}_3$  and  $\text{Me}_2\text{InEt}$  moieties has been structurally characterized by single-crystal X-ray analysis.

## 2. Results and discussion

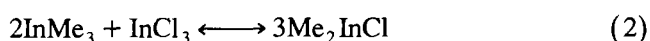
The synthesis of the alkylindium derivatives was carried out from  $\text{InI}_3$  instead of the previously reported  $\text{InCl}_3$  [5]. The reaction of  $\text{InI}_3$  with  $\text{LiMe}$  or  $\text{EtMgCl}$

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Table 1(a)  
<sup>1</sup>H chemical shifts (ppm)

	CH <sub>3</sub>	CH <sub>3</sub> (Et)	CH <sub>2</sub> (Et)	CH <sub>3</sub> (Et <sub>2</sub> O)	CH <sub>2</sub> (Et <sub>2</sub> O)
In(CH <sub>3</sub> ) <sub>3</sub> · xEt <sub>2</sub> O	−0.14 (s)	–	–	0.88 (t)	3.16 (q)
In(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	–	1.40 (t,3H)	0.50 (q,2H)	–	–
In(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>3</sub> ) · xEt <sub>2</sub> O	−0.18 (s)	1.46 (t)	0.56 (q)	0.85 (t)	3.17 (q)
In(CH <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> · xEt <sub>2</sub> O	−0.23 (s)	1.41 (t)	0.50 (q)	0.85 (t)	3.15 (q)
In(CD <sub>3</sub> ) <sub>3</sub> · xEt <sub>2</sub> O	–	–	–	0.81 (t)	3.15 (q)
In(CD <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>3</sub> ) · xEt <sub>2</sub> O	–	1.44 (t)	0.61 (q)	0.82 (t)	3.15 (q)
In(CD <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> · xEt <sub>2</sub> O	–	1.42 (t)	0.53 (q)	0.83 (t)	3.15 (q)

was found to proceed at a very high rate even in hexane solution, quantitatively producing MeInI<sub>2</sub> or Me<sub>2</sub>InI, which are intermediates for the subsequent synthesis of the heteroleptic MeInEt<sub>2</sub> and Me<sub>2</sub>InEt. The latter compounds were obtained as pure, halide-free colourless liquids. In contrast, the reaction with InCl<sub>3</sub> produces the intermediate Me<sub>2</sub>InCl only slowly (1–2 days) and in lower yields. It has been suggested that the reaction between InCl<sub>3</sub> and LiMe (1 : 2 molar ratio) proceeds in a stepwise manner, with step (2) far slower than step (1) [5]



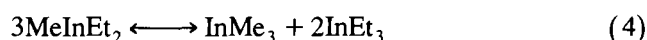
### 2.1. NMR spectra

<sup>1</sup>H and <sup>13</sup>C NMR spectra of all the compounds, reported in Tables 1a and 1b, were recorded at room temperature in anhydrous C<sub>6</sub>D<sub>6</sub>, using C<sub>6</sub>D<sub>5</sub>H as internal standard; chemical shifts were calculated respect to SiMe<sub>4</sub>.

The following sets of signals can be identified in the spectra: (a) The singlets at −0.14 ppm (for **1**), −0.18 ppm (for **3**) and −0.23 ppm (for **4**) arise from the CH<sub>3</sub> groups bonded to indium [2]. (b) The quartets in the range 0.50–0.61 and the triplets in the range 1.40–1.46 ppm in compounds **2**, **3**, **3a**, **4** and **4a** [2] are characteristic of the indium-bonded ethyl groups. (c) The quartets in the range 3.15–3.19 ppm and the triplets in the range 0.8–0.9 ppm are assigned to the ethyl groups of the coordinated ether molecules for all compounds except

**2**. These signals are slightly shifted towards lower field relative to those of free Et<sub>2</sub>O because of coordination.

The patterns and intensities of the above signals are sufficient to identify InMe<sub>3</sub> · Et<sub>2</sub>O [6,7] and InEt<sub>3</sub> [7]. However for **3**, **3a**, **4** and **4a** an unambiguous identification requires additional data because a rapid exchange of the alkyl groups in solution has been observed by Bradley et al. [2].



Furthermore, the proton NMR signals of CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> alone do not differentiate clearly between Me<sub>2</sub>InEt and MeInEt<sub>2</sub> as individual compounds, and 2 : 1 and 1 : 2 mixtures of InMe<sub>3</sub> and InEt<sub>3</sub>. The <sup>13</sup>C NMR spectra are somewhat more discriminating and show that **3** and **4** can not be mixtures of InMe<sub>3</sub> and InEt<sub>3</sub>, because signals of **1** and **2** are absent. In addition, the <sup>13</sup>C NMR spectra of the deuterated compounds **1a**, **3a**, **4a** show the signals expected for the assigned formulae, while the resonances of **3a** and **4a** are quite different from those of **2** and **1a**, which should be the final products expected from equilibria (3) and (4).

The <sup>1</sup>H NMR spectra show that all complexes coordinate approximately one molecule of Et<sub>2</sub>O (the coefficient *x* in the formulae ranges from 0.8 to 1.2), and this may be partially removed by distillation, as shown in Table 2. Only compound **2** was obtained in solvent-free form, suggesting that the acceptor power of the In atom in InEt<sub>3</sub> is lower than in the methylindium compounds owing to the greater electron-releasing effect of ethyl groups compared with the methyl groups. The experi-

Table 1(b)  
<sup>13</sup>C chemical shifts (ppm)

	<sup>13</sup> CR <sub>3</sub> R = H or D	<sup>13</sup> CH <sub>3</sub> (Et)	<sup>13</sup> CH <sub>2</sub> (Et)	<sup>13</sup> CH <sub>3</sub> (Et <sub>2</sub> O)	<sup>13</sup> CH <sub>2</sub> (Et <sub>2</sub> O)
In(CH <sub>3</sub> ) <sub>3</sub> · xEt <sub>2</sub> O	−8.00 (q)	–	–	14.80 (q)	65.74 (t)
In(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	–	11.39 (q)	10.39 (t)	–	–
In(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>3</sub> ) · xEt <sub>2</sub> O	−4.11 (q)	13.60 (q)	10.50 (t)	14.40 (q)	65.50 (t)
In(CH <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> · xEt <sub>2</sub> O	−4.02 (q)	11.85 (q)	8.76 (t)	15.30 (q)	65.82 (t)
In(CD <sub>3</sub> ) <sub>3</sub> · xEt <sub>2</sub> O	−4.39 (sept)	–	–	14.40 (q)	65.59 (t)
In(CD <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>3</sub> ) · xEt <sub>2</sub> O	−4.61 (sept)	12.49 (q)	10.77 (t)	14.48 (q)	65.63 (t)
In(CD <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> · xEt <sub>2</sub> O	−4.90 (sept)	12.48 (q)	11.56 (t)	14.51 (q)	66.08 (t)

Table 2  
Amounts of Et<sub>2</sub>O coordinated to Me<sub>n</sub>InEt<sub>3-n</sub> (n = 1, 2, or 3)

	x before distillation	x after distillation
In(CH <sub>3</sub> ) <sub>3</sub> · xEt <sub>2</sub> O	1.1	0.6
In(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>3</sub> ) · xEt <sub>2</sub> O	1	0.6
In(CH <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> · xEt <sub>2</sub> O	0.8	0.2
In(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	–	–
In(CD <sub>3</sub> ) <sub>3</sub> · xEt <sub>2</sub> O	–	–
In(CD <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>3</sub> ) · xEt <sub>2</sub> O	1.2	0.3
In(CD <sub>3</sub> )(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> · xEt <sub>2</sub> O	1.2	0.3

mental conditions of the distillation can also alter the composition of the heteroleptic compounds. For example, when **3** is distilled at 30°C, the intensities of the <sup>1</sup>H NMR signals of the product condensed at –10°C correspond to the expected stoichiometry of Me<sub>2</sub>InEt. However, when the distillation temperature is raised to 50°C, the <sup>1</sup>H NMR spectrum of the distillate (again collected at –10°C) shows an enrichment of the components containing ethyl groups. Such behaviour may be rationalized by the assumption that at 50°C the equilibria (3) and (4) shift to the right, and consequently the product appears enriched in the more volatile InMe<sub>3</sub> component. This assumption also explains the progressive increase of the ethyl/methyl ratio observed the <sup>1</sup>H NMR spectrum of the residue when Me<sub>2</sub>InEt and MeInEt<sub>2</sub> are subjected to a dynamic vacuum for prolonged periods at room temperature.

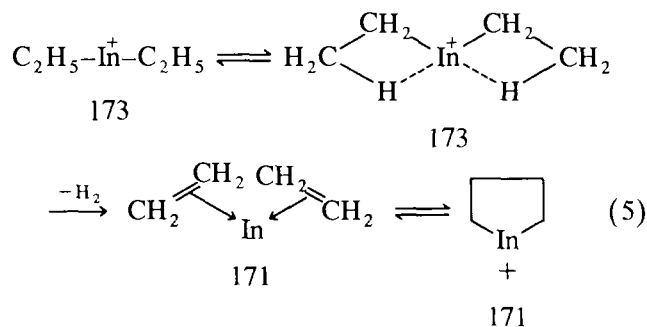
## 2.2. Mass spectra

The results of the mass spectra based on metastable ion studies (MIKE spectrometry and constant B<sup>2</sup>/E linked scans [8,9]) are reported in Table 3. No solvated [InR<sub>3</sub> · OEt]<sup>+</sup> ions are observed in any of the spectra, confirming the lability of the In–O bonds. The species [Me<sub>3-n</sub>InEt<sub>n</sub>]<sup>+</sup> (n = 0–3) can be considered as the parent ions for all systems. These species actually represent the ions of highest mass in the spectra of compounds **1**, **2**, **4**, **4a**, whilst in the case of **1a**, **3** and **3a** the corresponding ions are of very low abundance (at or

below 0.001%). Their presence can be well demonstrated by parent ion spectroscopy constant (B<sup>2</sup>/E linked scans [9] performed on [M–CH<sub>3</sub>]<sup>+</sup> for **3** and on [M–CD<sub>3</sub>]<sup>+</sup> for **1a** and **3a**). No peak of a dimeric species could be detected, either in the usual EI spectra or in the precursor ion spectra. The compounds appear to be monomeric in gas phase. The fragmentation patterns of the various species, which will be described in detail elsewhere, have several interesting aspects beside the common and obvious cleavage of the In–C bonds.

(a) The formation of carbene species (e.g. [CD<sub>3</sub>In=CD<sub>2</sub>]<sup>+</sup>; m/z = 149 in **3a** spectrum) through α-elimination in methyl derivatives or cleavage of a C–C bond in ethyl derivatives (e.g. Et<sub>2</sub>In=CH<sub>2</sub>, m/z 187 in **2**).

(b) β-elimination for ethyl-containing species leading to the formation of π-bonded ethylene complexes. A typical example is observed for **2** for which the decomposition of the ion Et<sub>2</sub>In<sup>+</sup> (m/z = 173) to the ion m/z = 171 ((C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>In<sup>+</sup>) is schematized as follows:



with the plausible formation of indacyclopentane ion.

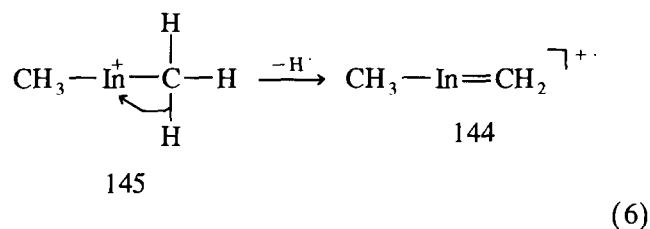
No evidence of hydride species was ever obtained, reflecting the well known instability of the In–H bond.

The mass spectra on the heteroleptic **3** and **4** species show no ions of the type [InMe<sub>3</sub>]<sup>+</sup> and [InEt<sub>3</sub>]<sup>+</sup> and that of the type Et<sub>2</sub>In<sup>+</sup> are not observed in the spectrum of **3**, nor of the type Me<sub>2</sub>In<sup>+</sup> in the spectrum of **4**. Thus, these heteroleptic compounds are characterized

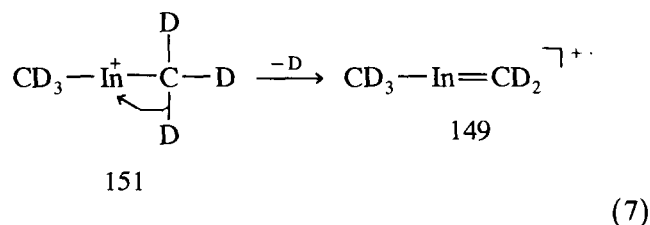
Table 3  
Mass spectra of compounds 1–4

Compound	m/z (% relative abundance in EI spectra)
<b>1</b>	[InMe <sub>3</sub> ] <sup>+</sup> 160 (1.5); Me <sub>2</sub> In <sup>+</sup> 145 (100); [InMe] <sup>+</sup> 130(8); [InCH] <sup>+</sup> 128 (2); In <sup>+</sup> 115 (32).
<b>1a</b>	[InCD <sub>3</sub> ] <sup>+</sup> 169 (0.3); (CD <sub>3</sub> ) <sub>2</sub> In <sup>+</sup> 151 (100); [In(CD <sub>3</sub> )CD <sub>2</sub> ] <sup>+</sup> 149 (0.1); [InCD <sub>3</sub> ] <sup>+</sup> 133 (11); [InCD] <sup>+</sup> 129 (0.2); In <sup>+</sup> 115 (76).
<b>2</b>	[InEt <sub>3</sub> ] <sup>+</sup> 202 (0.5); Et <sub>2</sub> In <sup>+</sup> C <sub>2</sub> H <sub>4</sub> 201 (0.3); Et <sub>2</sub> In <sup>+</sup> CH <sub>2</sub> 187, (0.1); Et <sub>2</sub> In <sup>+</sup> 173 (100); (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> In <sup>+</sup> 171 (3); EtIn <sup>+</sup> CH <sub>3</sub> 159 (6); [EtInCH <sub>2</sub> ] <sup>+</sup> 158 (1); [InC <sub>2</sub> H <sub>5</sub> ] <sup>+</sup> 144 (59); [InMe] <sup>+</sup> 130 (0.5); In <sup>+</sup> 115 (45).
<b>3</b>	[Me <sub>2</sub> InEt] <sup>+</sup> 174 (0.3); Me <sub>2</sub> In <sup>+</sup> C <sub>2</sub> H <sub>4</sub> 173 (12.6); MeEtIn <sup>+</sup> 159 (34); Me <sub>2</sub> In <sup>+</sup> 145 (38); [MeInCH <sub>2</sub> ] <sup>+</sup> or [InEt] <sup>+</sup> 144 (6); [InMe] <sup>+</sup> 130 (8); In <sup>+</sup> 115 (100).
<b>3a</b>	[(CD <sub>3</sub> ) <sub>2</sub> InEt] <sup>+</sup> 180 (0.1); CD <sub>3</sub> In <sup>+</sup> Et 162 (94); [(CD <sub>3</sub> ) <sub>2</sub> In] <sup>+</sup> 151 (100); [CD <sub>3</sub> InCD <sub>2</sub> ] <sup>+</sup> 149 (5); [InEt] <sup>+</sup> 144 (14); [CD <sub>3</sub> In] <sup>+</sup> 133 (20); In <sup>+</sup> 115 (100).
<b>4</b>	[MeInEt <sub>2</sub> ] <sup>+</sup> 188 (0.5); MeIn <sup>+</sup> C <sub>2</sub> H <sub>4</sub> 187 (0.3); Et <sub>2</sub> In <sup>+</sup> 173 (64); MeIn <sup>+</sup> Et 159 (60); [InEt] <sup>+</sup> 144 (18); [InMe] <sup>+</sup> 130 (5); In <sup>+</sup> 115 (100).
<b>4a</b>	[CD <sub>3</sub> InEt <sub>2</sub> ] <sup>+</sup> 191 (0.3); CD <sub>3</sub> In <sup>+</sup> EtC <sub>2</sub> H <sub>4</sub> 190 (0.2); Et <sub>2</sub> In <sup>+</sup> 173 (64); CD <sub>3</sub> In <sup>+</sup> Et 162 (100); [InEt] <sup>+</sup> 144 (24); [CD <sub>3</sub> In] <sup>+</sup> 133 (14); In <sup>+</sup> 115 (100).

by a specific behaviour and they appear to be pure, genuine individual species under mass spectrometric conditions. Comparison of the fragmentation patterns of the non-deuterated compounds with those of the corresponding deuterated ones confirms the above. For instance, the  $m/z$  144 ion is present in the spectra of all ethyl species **2**, **3**, **3a**, **4** and **4a**, consistent with the  $[\text{InEt}]^+$  formation arising through the loss of  $\text{C}_2\text{H}_5$  from  $\text{Et}_2\text{In}^+$  (**2**, **4**, **4a**), or of  $\text{CH}_3$  from  $\text{MeEtIn}^+$  (**3**), or of  $\text{CD}_3$  from  $\text{CD}_3\text{EtIn}^+$  (**3a**). In contrast, constant  $B^2/E$  and MIKE experiments have shown an additional pathway, only for **3**, which gives rise to an isobaric species of  $m/z$  144 to which a different formulation must be ascribed.



This hypothesis is supported by the parallel behaviour of the deuterated **3a**.



Overall, the mass spectrometric decomposition processes show the existence of both  $\alpha$ - or  $\beta$ -elimination pathways, which are considered the mechanisms by which the C contained in organometallic precursors may be incorporated ( $\alpha$ -elimination) or eliminated ( $\beta$ -elimination) from the growing layers [10]. Finally, it may be noted that the dissociation of In–H bond formed in connection with  $\beta$ -elimination processes is extremely easy, a phenomenon related to the low stability of In hydrides.

### 2.3. Structure of $\{[(\text{InMe}_3)(\text{Me}_2\text{InEt}) \cdot \text{diphos}] \cdot [(\text{InMe}_3)_2 \cdot \text{diphos}]\}$

Complexes of  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2$  with  $\text{Me}_2\text{InEt}$  have been described [2], but their structural characterization is still lacking. Here, the first structural evidence of the species  $\text{Me}_2\text{InEt}$  is reported.

The compound consists of two different molecules:  $[(\text{InMe}_3)_2 \cdot \text{diphos}]$  (**1a**) and  $[(\text{InMe}_3)(\text{Me}_2\text{InEt}) \cdot \text{diphos}]$  (**1b**) (Figs. 1(a) and 1(b)) present in a 1:1 molar ratio in the crystal. Each molecule is binuclear, with two indium(III) ions in a distorted tetrahedral environment linked across a centre of symmetry by a bridging diphosphine. Molecule **1b** is characterized by a

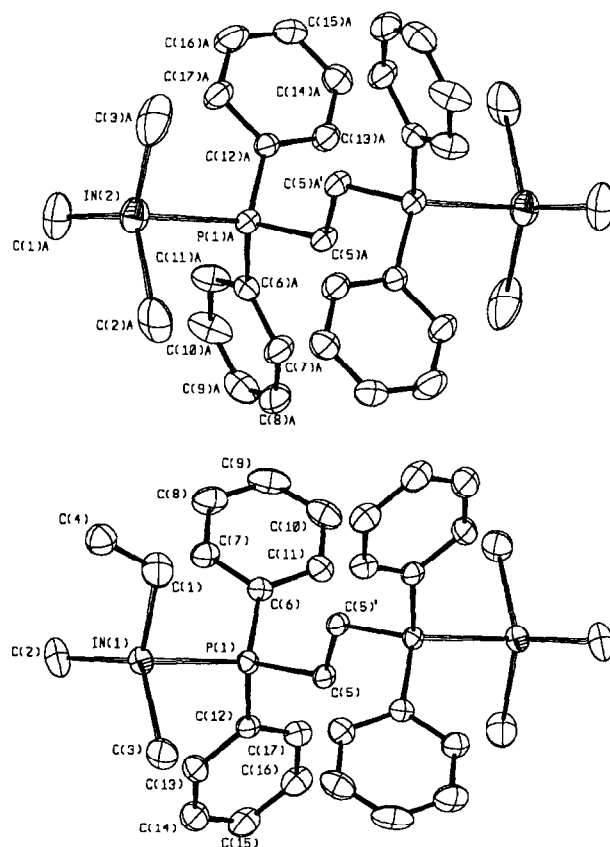


Fig. 1. General views: (**1a**)  $[(\text{InMe}_3)_2\text{diphos}(\text{InMe}_3)]$ ; (**1b**)  $[(\text{InMe}_3)\text{diphos}(\text{InMe}_2\text{Et})]$ .

statistical distribution (50%) of the C(4) carbon atoms of the ethyl group about the two otherwise centrosymmetric alkylindium moieties. Both **1a** and **1b** have a rather high thermal motion for the carbon atoms bonded to indium, preventing an accurate determination of the metal bond distances. However, the In–C bond distances (in the range 2.16–2.23 Å), are comparable with those of the ‘single species’  $[(\text{InMe}_3)_2 \cdot \text{diphos}]$  [7]. The values of the In–P distances are the same (2.76 Å) in both structures, equal to the value in the disordered  $[(\text{InMe}_3)(\text{EtInMe}_2) \cdot \text{diphos}]$  (**1b**) molecule.

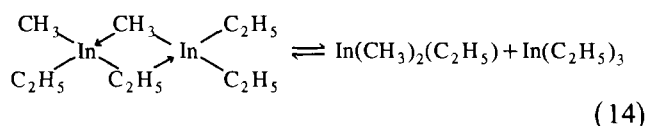
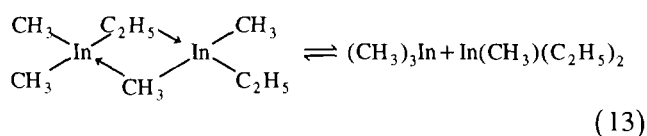
A comparison of the crystal structure of  $[(\text{InMe}_3)(\text{Me}_2\text{InEt}) \cdot \text{diphos}] \cdot [(\text{InMe}_3)_2 \cdot \text{diphos}]$  with that of  $[(\text{InMe}_3)_2 \cdot \text{diphos}]$  [7] shows that the unit cell of the former has a volume (1765.8 Å<sup>3</sup>) greater by 78.6 Å<sup>3</sup> than twice the volume of the latter. This increase in volume obviously results from the presence of the statistically distributed ‘extra’ carbon atom in **1b**.

### 2.4. Consideration in the behaviour of the alkylindium compounds

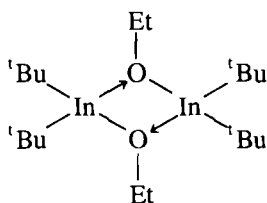
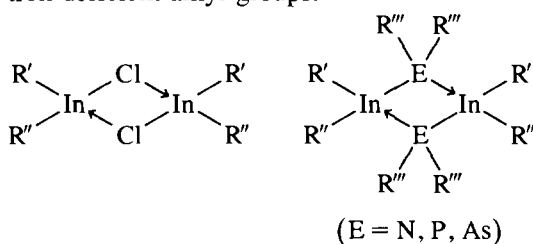
The existence of  $\text{Me}_2\text{InEt}$  is confirmed by the X-ray structure of its diphosphine adduct. However, the formation and stability of  $\text{Me}_2\text{InEt}$  clearly depend on physical and chemical conditions, such as temperature and the presence of Lewis bases, which can favour decomposi-

tion according to equilibria (3) and (4). The  $\text{MeInEt}_2$  species may be considered to be one of the products of (3), but our experiments suggest that it undergoes a ligand redistribution equilibrium such as (4), also, it is a transient species leading to the final stable products,  $\text{InMe}_3$  and  $\text{InEt}_3$ . This indicates that in the ethyl- and methyl-indium series the more symmetrical or homoleptic compounds are more stable than the unsymmetrically substituted or heteroleptic analogues.

The ligand redistribution equilibria in solution (3) and (4) probably involve the preliminary formation of alkyl-bridged electron-deficient species in which the lability of the  $\text{In}-\text{C}-\text{In}$  bonds favours the more stable homoleptic products.



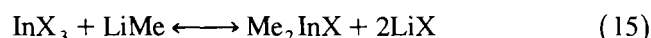
Stable heteroleptic alkylindium compounds have been recently obtained by Beachley et al. [11a]. These compounds, contained additional ligands (such as halide [11] and Group 5 elements such as N, P, As or O [12,13]), and therefore they are capable of forming bridged species much more stable than those of electron-deficient alkyl groups.



### 3. Conclusion

The results reported in this paper clarify the existence of  $\text{Me}_2\text{InEt}$  and its applicability to MOVPE. The mass,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{Me}_2\text{InEt}$  are different from those of the other compounds involved in the equilibria (3) and (4), and the structural characterization of the adduct  $[\text{InMe}_3(\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{InMe}_2\text{Et}]$  demonstrates its existence as an individual compound. However, the results also confirm that its

stability depends upon the temperature and/or the formation of Lewis base complexes which can shift the equilibria (3) and (4) towards the more stable  $\text{InMe}_3$  and  $\text{InEt}_3$  species. Accordingly, great care must be taken in the synthesis of pure  $\text{Me}_2\text{InEt}$  to avoid the reactions (15) and (16), since these require sublimation or distillation operations at ambient or higher temperatures. An alternative could be to use prepurified  $\text{InMe}_3$  and  $\text{InEt}_3$  as reactants under conditions (low temperature and long time) favouring the reverse of equilibria (3) and (4). Finally,  $\text{InI}_3$  is a better reactant than  $\text{InCl}_3$  for the synthesis of organoindium compounds.



## 4. Experimental

### 4.1. Materials and procedures

Indium(III) iodide (Johnson Matthey), methyl lithium (1.6 M solution in diethyl ether, Aldrich), ethylmagnesium chloride (2 M solution in  $\text{Et}_2\text{O}$ , Aldrich), trideuteroethyl lithium (0.5 M solution in  $\text{Et}_2\text{O}$ , Aldrich), and bis(diphenylphosphino)ethane (Aldrich) were used without further purification. The diethyl ether and hexane were distilled under dinitrogen from potassium/benzophenone.

All operations were carried out in glove boxes under purified dinitrogen. Proton and carbon NMR spectra were recorded on a Bruker AC 200 spectrometer in anhydrous  $\text{C}_6\text{D}_6$  solution using  $\text{C}_6\text{D}_5\text{H}$  as internal standard. Chemical shifts are quoted with respect to  $\text{SiMe}_4$ . Mass spectra were obtained on a VG ZAB 2F instrument operating in electron ionization (EI) conditions (70 eV, 200 mA, ion source temperature  $120^\circ\text{C}$ ). Metastable ion transitions were detected by mass analysed ion kinetic energy spectrometry (MIKES) [8]. Parent ion spectroscopy was achieved by constant  $B^2/E$  linked scans [9].

### 4.2. Iododimethylindium(III)

Methyl lithium (1.5 ml of 1.6 M solution in  $\text{Et}_2\text{O}$ , 2.4 mmol) was added to indium(III) iodide [14] (0.6 g, 1.2 mmol) in  $\text{Et}_2\text{O}$  (about 30 ml). A colourless solution was obtained after a few minutes. The ether was removed under vacuum and the residue was extracted with hexane. The hexane was evaporated to dryness to yield  $\text{Me}_2\text{InI}$  quantitatively as a colourless microcrystalline powder free from solvating  $\text{Et}_2\text{O}$  [15]. Anal. Found: C, 8.73; H, 2.19; I, 46.82.  $\text{C}_2\text{H}_6\text{In}$  (271.79). Calc.: C, 8.83; H, 2.22; I, 46.69%. MS  $m/z$ : 272 ( $\text{M}^+$ ), 257 ( $\text{M}^+ - \text{CH}_3$ ), 242 ( $\text{M}^+ - 2\text{CH}_3$ ), 145 ( $\text{Me}_2\text{In}^+$ ), 127 ( $\text{I}^+$ ), 115 ( $\text{In}^+$ ) and  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.58 (s,  $\text{InCH}_3$ ).

### 4.3. Diodomethylindium(III)

The compound was synthesized as described for  $\text{Me}_2\text{InI}$  using a 1:1  $\text{InI}_3$ : $\text{LiMe}$  molar ratio but more rapidly than previously described [16]. It was isolated as the  $\text{Et}_2\text{O}$  adduct in quantitative yield. Anal. Found: C, 12.92; H, 2.75; I, 55.56.  $\text{C}_5\text{H}_{13}\text{I}_2\text{InO}$  (457.76). Calc.: C, 13.12; H, 2.86; I, 55.44%.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.71 (s, 3H,  $\text{InCH}_3$ ), 0.93(t, 6H,  $(\text{CH}_3\text{CH}_2)_2\text{O}$ ), 3.24 (q, 4H,  $(\text{CH}_3\text{CH}_2)_2\text{O}$ ).

### 4.4. Dimethylethylindium (III) (3)

Ethylmagnesium chloride (0.6 ml of 2 M solution in  $\text{Et}_2\text{O}$  1.2 mmol) was added to 0.32 g of  $\text{Me}_2\text{InI}$  in  $\text{Et}_2\text{O}$  (about 30 ml) and the mixture was stirred for 10–15 min. The ether was removed under vacuum and the residue was distilled at  $25^\circ\text{C}$  and  $10^{-1}$  Torr, to give a colourless liquid that did not contain halides. MS ( $m/z$ ): 173 ( $\text{M}^+ - \text{H}$ ), 159 ( $\text{M}^+ \pm \text{Me}$ ), 145 ( $\text{M}^+ - \text{Et}$ ), 144 ( $\text{M}^+ - 2\text{Me}$ ), 130 ( $\text{InMe}^+$ ), 115 ( $\text{In}^+$ ).

Table 4

Atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(\text{InMe}_3)_2\text{diphos}(\text{InMe}_2\text{Et})] \cdot [(\text{InMe}_3)_2\text{diphos}(\text{InMe}_3)]$

Atom	x	y	z	$U_{\text{eq}}$
In(1)	-0.05733(4)	0.22830(3)	0.27148(4)	70.2(2)
P(1)	0.0403(1)	0.41448(9)	0.3080(1)	51.5(4)
C(1)	-0.2327(7)	0.2753(6)	0.3230(9)	110(3)
C(2)	-0.0402(7)	0.1544(5)	0.0729(6)	96(3)
C(3)	0.0621(7)	0.1808(6)	0.3992(7)	106(3)
C(4)	-0.321(1)	0.200(1)	0.265(2)	100(4)
C(5)	0.0570(4)	0.4903(4)	0.4708(4)	57(2)
C(6)	-0.0338(4)	0.4956(4)	0.2289(4)	58(2)
C(7)	-0.0924(5)	0.4496(5)	0.1170(5)	76(2)
C(8)	-0.1467(7)	0.5082(8)	0.0485(7)	110(4)
C(9)	-0.1403(7)	0.6107(8)	0.0899(9)	123(5)
C(10)	-0.0831(7)	0.6570(6)	0.2011(9)	105(3)
C(11)	-0.0298(5)	0.6011(5)	0.2717(6)	77(2)
C(12)	0.1852(4)	0.4093(4)	0.2608(4)	59(2)
C(13)	0.2358(5)	0.3160(5)	0.2089(6)	79(2)
C(14)	0.3463(6)	0.3120(7)	0.1704(7)	105(3)
C(15)	0.4041(6)	0.3999(7)	0.1835(7)	101(3)
C(16)	0.3558(5)	0.4918(6)	0.2353(6)	91(3)
C(17)	0.2469(5)	0.4962(5)	0.2733(5)	74(2)
In(2)	0.66630(4)	0.14835(4)	0.80829(5)	95.0(2)
P(1)A	0.4736(1)	0.1418(1)	0.6518(1)	59.5(5)
C(1)A	0.6224(9)	0.2794(8)	0.9571(8)	133(4)
C(2)A	0.7894(7)	0.1732(9)	0.6824(8)	126(5)
C(3)A	0.662(1)	-0.0047(8)	0.833(1)	139(7)
C(5)A	0.4893(5)	0.0539(4)	0.4985(5)	66(2)
C(6)A	0.4335(4)	0.2607(4)	0.6235(5)	65(2)
C(7)A	0.4607(8)	0.2832(5)	0.5203(6)	98(3)
C(8)A	0.4295(9)	0.3757(6)	0.5043(8)	121(4)
C(9)A	0.3720(7)	0.4447(6)	0.588(1)	111(4)
C(10)A	0.3446(6)	0.4237(6)	0.689(1)	118(4)
C(11)A	0.3768(6)	0.3328(5)	0.7078(7)	95(3)
C(12)A	0.3420(5)	0.1035(4)	0.6981(5)	60(2)
C(13)A	0.2442(5)	0.0809(5)	0.6200(6)	80(2)
C(14)A	0.1445(6)	0.0553(6)	0.6599(7)	92(3)
C(15)A	0.1405(6)	0.0533(5)	0.7753(7)	95(3)
C(16)A	0.2344(8)	0.0777(7)	0.8552(7)	118(4)
C(17)A	0.3358(6)	0.1029(6)	0.8176(6)	100(3)

Table 5

Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for  $[(\text{InMe}_3)_2\text{diphos}(\text{InMe}_2\text{Et})] \cdot [(\text{InMe}_3)_2\text{diphos}(\text{InMe}_3)]$

Molecule 1a		Molecule 1b	
In(2)–P(1)A	2.748(2)	In(1)–P(1)	2.752(2)
In(2)–C(1)A	2.161(9)	In(1)–C(1)	2.213(8)
In(2)–C(2)A	2.229(5)	In(1)–C(2)	2.214(7)
In(2)–C(3)A	2.225(9)	In(1)–C(3)	2.173(9)
P(1)A–C(5)A	1.827(5)	P(1)–C(5)	1.836(4)
P(1)A–C(6)A	1.815(6)	P(1)–C(6)	1.809(6)
P(1)A–C(12)A	1.817(6)	P(1)–C(12)	1.819(5)
P(1)A–In(2)–C(3)A	100.9(3)	P(1)–In(1)–C(3)	96.3(2)
P(1)A–In(2)–C(2)A	96.0(2)	P(1)–In(1)–C(2)	101.8(2)
P(1)A–In(2)–C(1)A	98.5(3)	P(1)–In(1)–C(1)	100.3(2)
C(2)A–In(2)–C(3)A	117.6(4)	C(1)–In(1)–C(2)	115.7(3)
C(1)A–In(2)–C(3)A	119.3(4)	C(1)–In(1)–C(3)	119.5(3)
C(1)A–In(2)–C(2)A	116.6(3)	C(2)–In(1)–C(3)	116.8(3)

### 4.5. Compound 1, 1a and 2

These were synthesized from the reaction of  $\text{InI}_3$  with  $\text{LiMe}$ ,  $\text{EtMgCl}$ , and  $\text{LiMe-d}_3$  respectively, in the appropriate molar ratios in diethyl ether followed by distillation or extraction with hexane.

### 4.6. Compounds 3a and 4–4a

These were synthesized by a similar method, using  $\text{Me}_2\text{InI}$  ( $\text{Me}_2\text{InI-d}_3$ ) and  $\text{MeInI}_2 \cdot \text{Et}_2\text{O}$  ( $\text{MeInI}_2\text{-d}_3 \cdot \text{Et}_2\text{O}$ ) respectively. NMR spectra are reported in Tables 1(a) and 1(b) and mass spectra are summarized in Table 3.

### 4.7. $[(\text{InMe}_3)_2\text{diphos}(\text{Me}_2\text{InEt})] \cdot [(\text{InMe}_3)_2\text{diphos}(\text{InMe}_3)]$

Bis-diphenylphosphinoethane (0.8 g, 2 mmol) was dissolved in the minimum volume of toluene and added to a solution of  $\text{Me}_2\text{InEt}$  (0.69 g, 4 mmol) in hexane. A pale yellow solution and a light tan precipitate were obtained, and the mixture was filtered and the hexane solution gave crop of white crystals after cooling at  $-30^\circ\text{C}$  for 2 days.

### 4.8. Crystal data for $[(\text{InMe}_3)_2\text{diphos}(\text{Me}_2\text{InEt})] \cdot [(\text{InMe}_3)_2\text{diphos}(\text{InMe}_3)]$

$M_r = 1450.6$ , triclinic space group  $P\bar{1}$ ,  $a = 11.728(4)$ ,  $b = 13.857(4)$ ,  $c = 11.453(3)$   $\text{\AA}$ ,  $\alpha = 107.79(4)$ ,  $\beta = 94.88(4)$ ,  $\gamma = 88.32(4)^\circ$ ;  $V = 1766(1)$   $\text{\AA}^3$ ,  $Z = 1$ ,  $D_x = 1.364$   $\text{g cm}^{-3}$ ,  $\lambda = (\text{Mo K}\alpha) = 0.71069$   $\text{\AA}$ ,  $\mu(\text{Mo K}\alpha) = 1.41$   $\text{mm}^{-1}$ ,  $F(000) = 732$ ,  $T = 295$   $\text{K}$ . An air-sensitive prismatic (white) crystal of dimensions  $0.40 \times 0.36 \times 0.48$   $\text{mm}^3$  was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 (Febo System) diffractometer with graphite-monochromated ( $\text{Mo K}\alpha$  radiation  $\lambda = 0.71069$   $\text{\AA}$ ).

The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying the orientation angles  $\chi$  and  $\Phi$  over a range of  $120^\circ$ , with  $6 \leq \theta \leq 9^\circ$ . For the determination of precise lattice parameters, 40 strong reflections with  $10 \leq \theta \leq 13^\circ$  were considered. Integrated intensities for 8078 reflections ( $h = \pm 14$ ;  $k = \pm 16$ ,  $l = 0 \rightarrow 13$  were measured in the interval  $\theta = 3\text{--}27^\circ$ ), using  $\theta/2\theta$  scans. Two standard reflections,  $-1, 4, 2$ ;  $1, 0, 4$  were collected every 180 reflections. There were no significant fluctuations of intensity other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption (transmission factors 0.96–1.00), as described by North et al. [17]. No correction was made for extinction.

The structure was solved by heavy atoms methods [18]. Refinement was carried out by full-matrix least squares; the function minimized was  $Sw(F_o^2 - F_c^2)^2$ , with weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 3.19P]$ , where  $P = \max(F_o^2 + 2F_c^2)/3$ . All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the C(4) carbon atom, which has an occupancy factor of 0.5 and was refined isotropically. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters ( $U_{\text{equiv}}$  of the parent carbon atom). Conventional  $R = 0.052$ , based on  $F$  values of 6055 reflections having  $F_o^2 \geq 3\sigma(F_o^2)$  and  $S = 1.24$ , ( $wR$  on  $F^2 = 0.139$ ). The final difference map showed a general background within  $-1.12$  to  $0.88 \text{ e \AA}^{-3}$ . Scattering factors were taken from Ref. [19]. Structure refinement and final geometrical calculations were carried out with SHELXL-93 [20] and PARST [21] programs; drawings were produced using ORTEP II [22]. Final atomic coordinates are given in Table 4; selected bond lengths and angles are given in Table 5. Anisotropic thermal parameters, hydrogen atoms coordinates, the remaining molecular dimensions and tables of calculated and observed structure factors are available as supplementary material from the authors. Full lists of structural parameters have been deposited at the Cambridge Crystallographic Data Centre.

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