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ADDUCTS OF $InCl_3$ WITH LEWIS BASES: CRYSTAL AND MOLECULAR STRUCTURE OF $[(InCl_3)_2(DME)_3]$

G. CARTA, F. BENETOLLO,* S. SITRAN, G. ROSSETTO, F. BRAGA
and P. ZANELLA

Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati CNR Area
della Ricerca, Corso Stati Uniti 4-35127 Padova, Italy

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Abstract—A number of adducts of $InCl_3$ with selected Lewis bases have been synthesized and characterized. The complex of $InCl_3$ with 1,2-dimethoxyethane ($DME = CH_3OCH_2CH_2OCH_3$) is characterized by two centrosymmetrically related $InCl_3 \cdot DME \cdot 0.5DME$ units, where the indium is six-coordinated to three chlorine atoms, two oxygen atoms of one chelating DME unit and one oxygen atom of the bridging DME ligand in a *fac*-octahedral arrangement. The suitability and limits of using $InCl_3 \cdot 3/2DME$ for the synthesis of $InMe_3$ ($Me = CH_3$) are discussed.

$InCl_3$ is the common starting material for the syntheses of $InMe_3$ and $InEt_3$, which in turn are the usual precursors for the deposition of InP via MOCVD (Metal Organic Chemical Vapour Deposition).[1] In order to obtain a good quality product, these precursors must be used in a very pure form, and the purity depends both on the original $InCl_3$ and on the synthetic reaction, which is carried out in diethyl ether (Et_2O) as follows:

$$InCl_3 + 3LiMe \longrightarrow InMe_3 + 3LiCl.$$

Since both $InCl_3$ and $InMe_3$ are Lewis acids, the donor character of the solvent and the presence of added Lewis bases may be expected to play an important role in the syntheses of $InMe_3$ and related precursors for MOCVD. Accordingly, we have investigated the reaction of $InCl_3$ with 1,2-dimethoxyethane (DME), with 18-crown-6 in diethyl ether (Et_2O) and with 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene, and have isolated and characterized a series of $InCl_3$ adducts with these ligands. The structure of the DME adduct, $[(InCl_3)_2(DME)_3]$, was established by single crystal X-ray analysis and will be compared with the structures reported for other adduct trihalides.

EXPERIMENTAL

Synthesis of the complexes

The starting materials ($InCl_3$, LiMe, DABCO, 18-crown-6 and solvents) were commercially available products and were used as received. Solvents were purified by distillation over potassium benzophenone. All procedures (synthesis and handling of samples) were carried out inside nitrogen-filled dry boxes with O_2 and H_2O controlled atmospheres. IR spectra, in the 4000–600 cm^{-1} range, were recorded on a Mattson, Galazy Series FTIR 3000 spectrophotometer using neat liquids or Nujol mulls sandwiched between KBr discs in an air-tight holder sealed on an O-ring. ^1H NMR spectra were recorded on a Bruker AC 200 instrument, using anhydrous C_6D_6 as solvent (C_6D_5H as internal standard, chemical shifts calculated with respect to tetramethylsilane). Mass spectra were recorded on a V.G. organic Ltd ZAB 2F spectrometer (El = 70 eV, probe temperature 70°C).

$(InCl_3)_2 \cdot (DME)_3$. $InCl_3$ (2.21 g, 10 mmol) was stirred for 24 h in 40 cm^3 of DME. The mixture was filtered and the solution was concentrated to a small volume under reduced pressure. Addition of n-hexane gave a colourless microcrystalline precipitate which was filtered, washed and dried *in vacuo*. Crystals suitable for X-ray diffraction were obtained by

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* Author to whom correspondence should be addressed.

slow diffusion of n-hexane into a saturated DME solution of the complex. Found : Cl, 29.7 ; Calc, for $C_{12}H_{30}D_6Cl_6In_2$: Cl, 29.8% (C and H could not be determined owing to air decomposition of the complex). IR absorptions (cm^{-1}) : 851.5 (s), 894.9 (s), 1038.6 (s), 1081 (w). Mass spectrum : *m*/*z* 502, 455, 431, 410, 407, 370, 355, 335, 335, 312, 310, 300, 277, 265, 246, 230, 220 (10.3%, $InCl_3^+$), 185 (100%, $InCl_2^+$), 150 (36%, $InCl^+$), 115 (83.4%, In^+).

$(InCl_3)_2 \cdot$(18-crown-6). 18-Crown-6 (520 mg, 2 mmol) was added slowly with stirring to a suspension of $InCl_3$ (442 mg, 2 mmol) in 30 cm^3 toluene heated at 50°C. The mixture was then refluxed for 2 h; the resulting insoluble colourless solid was filtered, washed with toluene and dried *in vacuo*. Found C, 20.2 ; H, 4.6 ; Cl, 28.7 Calc. for $C_{12}H_{24}O_6Cl_6In_2$: C, 20.4 ; H, 3.4 ; Cl, 30.1%.

$(InCl_3)_2 \cdot (DABCO)_{1.5}$. DABCO (672 mg, 6 mmol) was added with stirring to a suspension of $InCl_3$ (663 mg, 3 mmol) in diethyl ether. A solid formed immediately ; stirring was continued for 24 h and the resulting colourless solid was filtered, washed with Et_2O and dried *in vacuo*. Found C, 17.4; H, 3.1; N, 6.2. Calc. for $C_9H_{18}N_3Cl_6In_2$: C 17.7; H, 3.2; N, 6.9%.

$InMe_3 \cdot DME$. LiMe in Et_2O (6 mmol, 4 cm^3 of a 1.5 M solution) was added with stirring to 443 mg (2 mmol) of $InCl_3$ dissolved in 30 cm^3 of DME. The mixture was stirred for 24 h, after which the solvent was evaporated, the residue dissolved in toluene and filtered to remove the LiCl that had formed. The solution was refluxed for 1 h and an additional amount of LiCl separated out ; it was filtered off and the solution was evaporated under reduced pressure. The colourless low-melting solid residue (Cl^- test was negative) was identified as pure $InMe_3 \cdot DME$ by its ^1H NMR spectrum in C_6D_6. IR absorptions (cm^{-1}) : 868.3 (s), 1020.2 (s), 1053 (bw), 1066.5 (bw), 1114.8 (bw), 1192.9 (s), 1244.9 (s). ^1H NMR spectrum : δ (ppm) −0.14 [9H, s, $In(CH_3)_3$], 2.54 [4H, s, $CH_3O(CH_2CH_2)OCH_3$], 2.74 [6H, s, $CH_3O(CH_2CH_2)OCH_3$]. Mass spectrum: *m*/*z* 205 ($InMe_3 \cdot 1/2DME^+$), 160 (5.5%, $InMe_3^+$), 145 (100%, $InMe_2^+$), 130 (53.5%, $InMe^+$), 115 (68.3%, In^+), 90 (45.2%, DME^+).

$InMe_3 \cdot DME$ was reacted with $(C_6H_5)2P$—CH_2CH_2—$P(C_6H_5)_2$ in DME solution ; the white precipitate that formed was filtered and washed with DME. Sublimation of the product at 100°C (10.2 Torr) gave a low-melting colourless solid having a ^1H NMR spectrum identical to that of $InMe_3 \cdot DME$.

Thermogravimetric measurements

Experiments were carried out with a Netzsch STA 429 instrument under the following conditions : dynamic atmosphere N_2; flux 250 cm^3 min^{-1} ; increment of temperature 5°C min^{-1} ; Al_2O_3 crucibles with free surface 0.26 cm^2 pre-heated to 1200°C and cooled under an N_2 atmosphere ; reference neutral Al_2O_3 ; sampling was carried out inside the dry boxes under an N_2 atmosphere. Before analysis the samples were flushed with an inert gas inside the oven for nearly 6 h, to eliminate completely air from the support materials.

X-ray measurements and structure determination of $(InCl_3)_2 \cdot (DME)_3$

Crystal data. $[(InCl_3)_2(C_4H_{10}O_2)_3]$, $M_r = 712.73$, monoclinic, space group $P2_{1/n}$, $a = 8.440(2)$, $b = 11.579(2)$, $c = 13.457(2)$ Å, $\beta = 103.50(3)°$; $V = 1278.8(4)$ Å^3, $Z = 2$, $D_x = 1.85$ Mg m^{-3}, $\lambda = (Mo\text{-}K_\alpha) = 0.71069$ Å, $\mu(Mo\text{-}K_\alpha) = 2.45$ mm^{-1}, $F(000) = 700$, $T = 293$ K.

An air-sensitive prismatic (white) crystal of dimensions 0.28 × 0.32 × 0.20 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 (Febo System) diffractometer with graphite-monochromated ($Mo\text{-}K_\alpha$) radiation ($\lambda = 0.71069$ Å). The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying each of the orientation angles χ and Φ over a range of 120°, with $7 \leqslant \theta \leqslant 9°$. For the determination of precise lattice parameters, 25 strong reflections with $10 \leqslant \theta \leqslant 14°$ were considered. Integrated intensities for *hkl* reflections ($h = \pm 11$; $k = 0\text{–}14$, $l = 0\text{–}17$ were measured in the interval $\theta = 2\text{–}28°$), using $\theta\text{–}2\theta$ scans. These standard reflections, 0, 3, 4, −1, 4, 3 and 1, 4, 1 were collected every 180 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz and polarization effects and for absorption as described by North *et al.*[2] No correction was made for extinction.

The structure was solved by heavy atoms methods.[3] Refinement was by full-matrix least-squares minimising the function $\Sigma w(F_o^2 - F_c^2)^2$ with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 2.16P]$, where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and were assigned fixed, isotropic thermal parameters ($1.2U_{\text{equiv.}}$ of the parent carbon atom). For a total of 127 parameters, $R'_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.062$, $S = 1.181$ and conventional $R = 0.0227$ based on the F values of 1909 reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$. Scattering factors were taken from Ref. 4. Structure refinement and final calculations were carried out with SHELXL-93[5] and Parst[6] programs; the drawing was produced using ORTEP II.[7]

Lists of structure factors, atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre. Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, U.K.

RESULTS AND DISCUSSION

The reaction of $InCl_3$ with three Lewis bases, DME, 18-crown-6 and DABCO, has been investigated and the stoichiometry of the resulting complexes has been established on the basis of elemental and TG analysis, as well as physical measurements (IR, ^1H NMR and mass spectra). The complex with DME gave crystals suitable for structural analysis; accordingly the following discussion will focus chiefly on this.

The thermal behaviour of $(InCl_3)_2 \cdot (DME)_3$ was studied in the range 30–600°C under nitrogen (Fig. 1). No variation of weight was observed below 75°C; between 75 and 125°C a total weight loss of 12% took place (with an endothermal peak at 116°C), corresponding to the release of one mole of DME. In a separate experiment, a sample of $(InCl_3)_2 \cdot (DME)_3$ was heated at 116°C for 10 min: analysis of Cl^- content of the resulting compound confirmed the composition $InCl_3 \cdot DME$. This was stable up to 175°C; at this temperature it began to lose weight, with an endothermal peak typical of melting. In the range 175–320°C, a weight loss corresponding to 28.95% was observed, corresponding to the loss of the remaining DME ligand. Subsequent heating caused progressive sublimation of $InCl_3$ (endotherm at 430°C), which was complete at 600°C.

On the basis of the thermogravimetric results, the thermolysis of $(InCl_3)_2 \cdot (DME)_3$ can be represented by the two steps:

$$(InCl_3)_2 \cdot (DME)_3 \longrightarrow 2InCl_3 \cdot DME + DME \quad (1)$$

$$InCl_3 \cdot DME \longrightarrow InCl_3 + DME. \quad (2)$$

This degradation sequence is confirmed by the mass spectrum, which shows the following features.

(a) A series of high-mass, low-intensity peaks (*m/z* 502, 455, 431, 410, 407, 370, 335, 312, 310) which show the cleavage not only of chlorine atoms but also of organic fragments from the binuclear $(InCl_3)_2 \cdot (DME)_3$ complex.

(b) A series of low-mass, high-intensity peaks correspond to the stepwise dissociation of chlorine atoms (*m/z* 220, $InCl_3^+$; 185, InC_2^+; 150, $InCl^+$ and 115, In^+). The presence of the peaks at *m/z* 310 (very low intensity) and 220, corresponding to $[InCl_3 \cdot DME]^+$ and $InCl_3^+$, respectively, is consistent with the occurrence of reactions (1) and (2).

The single crystal X-ray analysis of the $InCl_3 \cdot DME$ complex confirmed the $(InCl_3)_2 \cdot (DME)_3$ formulation. An ORTEP view of the mol-

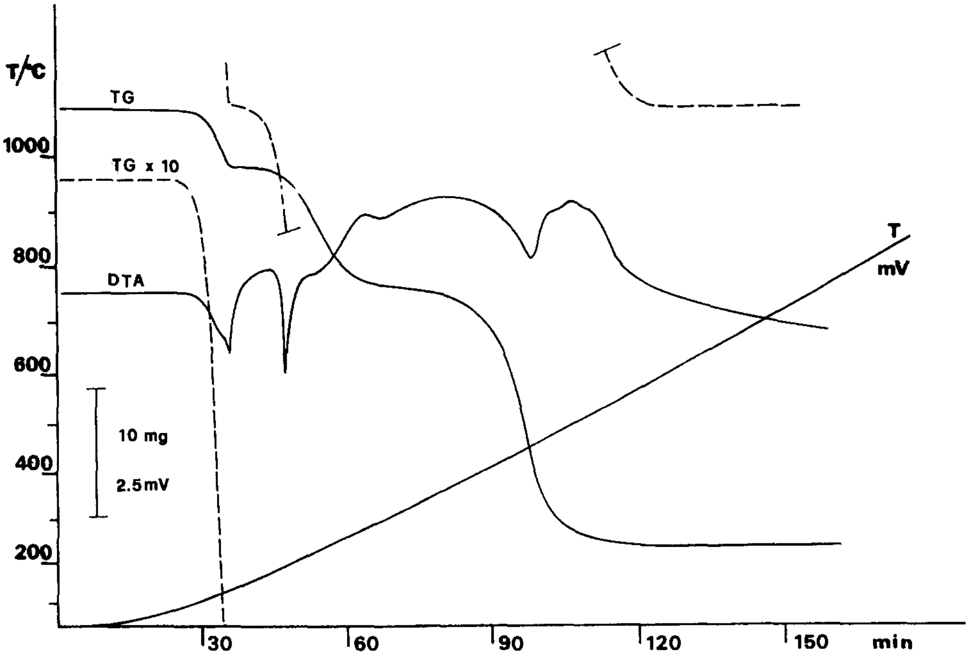

Fig. 1. Thermal behaviour of $(InCl_3)_2 \cdot (DME)_3$.

ecule is shown in Fig. 2 and selected bond lengths and angles are reported in Table 1. The molecule is binuclear, with two identical [$InCl_3(DME)$] moieties bridged by the —OCH_2CH_2O— chain of a third DME ligand. In each moiety the six-coordinated In^{III} is linked to three chlorine atoms, two oxygen atoms of a bidentate chelating DME and one oxygen of the bridging DME. The overall geometry corresponds to a distorted octahedron. The best mean plane calculated

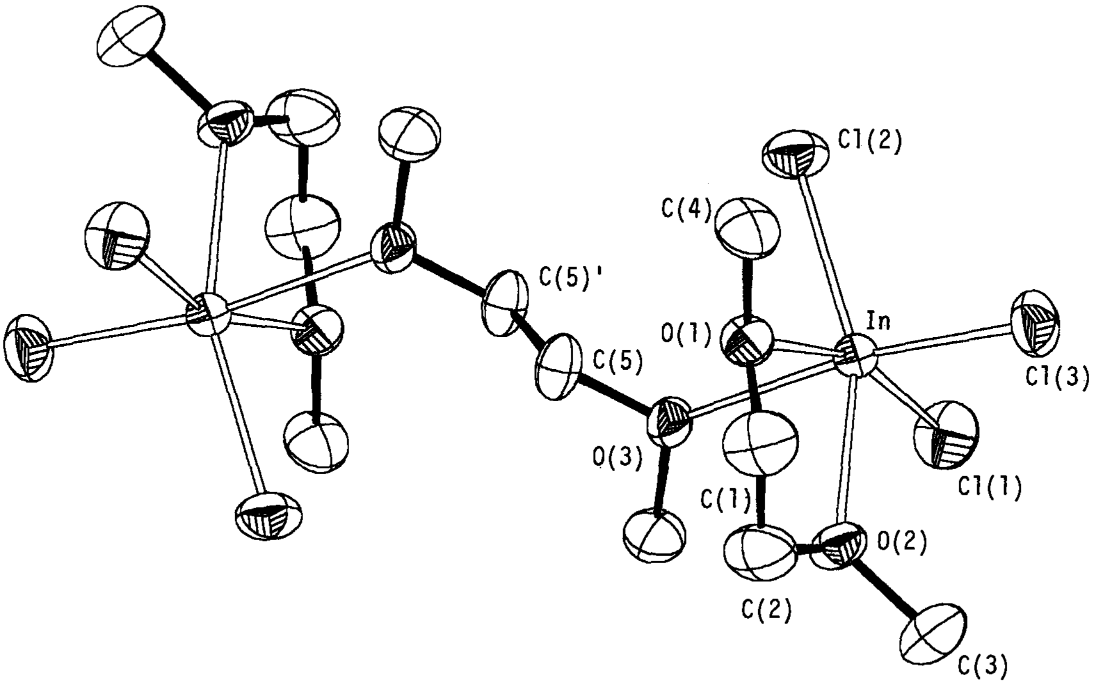

Fig. 2. ORTEP perspective view with the atom numbering scheme for $(InCl_3)_2 \cdot (DME)_3$ (ellipsoids are at 50% probability level).

Table 1. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $(InCl_3)_2 \cdot (DME)_3$

In—Cl(1)	2.392(1)	In—Cl(2)	2.391(2)
In—Cl(3)	2.404(1)	In—O(2)	2.289(3)
In—O(1)	2.304(3)	In—O(3)	2.326(3)
O(1)—C(1)	1.425(7)	O(1)—C(4)	1.442(6)
O(2)—C(2)	1.430(7)	O(2)—C(3)	1.425(8)
C(1)—C(2)	1.423(9)	O(3)—C(5)	1.444(6)
O(3)—C(6)	1.448(6)	C(5)—C(5)′	1.500(9)
O(1)—In—O(3)	80.2(1)	O(2)—In—O(3)	76.2(1)
O(2)—In—O(1)	71.7(1)	Cl(3)—In—O(3)	163.6(1)
Cl(3)—In—O(1)	87.5(1)	Cl(3)—In—O(2)	89.7(1)
Cl(2)—In—O(3)	88.0(1)	Cl(2)—In—O(1)	89.7(1)
Cl(2)—In—O(2)	157.2(1)	Cl(2)—In—Cl(3)	102.9(1)
Cl(1)—In—O(3)	89.3(1)	Cl(1)—In—O(1)	162.2(1)
Cl(1)—In—O(2)	92.0(1)	Cl(1)—In—Cl(3)	99.7(1)
Cl(1)—In—Cl(2)	104.4(1)	In—O(2)—C(3)	123.4(3)
In—O(2)—C(2)	114.1(3)	C(2)—O(2)—C(3)	115.4(4)
In—O(1)—C(4)	120.6(3)	In—O(1)—C(1)	113.0(3)
C(1)—O(1)—C(4)	111.7(4)	O(1)—C(1)—C(2)	110.2(5)
O(2)—C(2)—C(1)	112.0(5)	In—O(3)—C(6)	122.4(3)
In—O(3)—C(5)	123.4(2)	C(5)—O(3)—C(6)	113.6(4)
O(3)—C(5)—C(5)′	109.6(4)		

through the O(1), O(3), Cl(1) and Cl(3) atoms, which may be considered to constitute the equatorial plane of the octahedron, shows deviations from planarity [(O(1) −0.047(3) Å ; O(3) 0.045(4) Å ; Cl(1) −008(1) Å ; Cl(3) 0.009(2) Å] ; the indium atom is displaced by 0.2843(4) Å out of this plane towards the Cl(2) vertex. The Cl(2) and O(2) atoms represent the apical vertices of the octahedron ; the bond angle Cl(2)—In—O(2) [157.2(1) Å] deviates significantly from linearity, with the bending directed towards the O(3) atom of the bridging DME ligand. The In—Cl bond distances are all equal within the limit of their e.s.d.s, whereas the In—O distances of the chelating DME [In—O(1) = 2.304(3) Å and In—O(2) = 2.289(3) Å] are slightly shorter than the In—O distance of the bridging DME [In—O(3) = 2.326(3) Å]. The chelating DME ligands appear to be more congested than the bridging DME ligand, since the sum of the angles having O(1) and O(2) as the vertices (345.3 and 352.9°, respectively) are significantly less than the sum of the angles with O(3) as vertex (359.4°). Furthermore, the In—O(1) and In—O(2) bond lengths are shorter than the In—O(3) bond length (see Table 1).

The compound reported here is particularly interesting because the adducts of In^{III} halides with either mono- or bidentate ligands are usually pentacoordinated with a *trans*-trigonal bipyramidal geometry. Examples are $InCl_3(NMe_3)_2$,[8], $InCl_3(PPh_3)_2$ ($Ph = C_6H_5$),[9] $InCl_3(PMe_3)_2$ and $[(InI_3)_2(diphos)_3]$ (diphos = $PPh_2CH_2CH_2PPh_2$).[10] A similar geometry has also been described recently for the molecule $InCl_3 \cdot (THF)_2$ ($THF = C_4H_8O$, tetrahydrofuran), in which the chloride ions occupy equatorial positions while the oxygen atoms of the THF ligands are in the axial sites.[11]

Hexacoordinated $InCl_3$ complexes with mono- or bidentate ligands usually have a mononuclear octahedral structure. To our knowledge, the only other example of a hexacoordinated binuclear complex involving $InCl_3$ is $[(InCl_3)_2 \cdot (Me_3AsO)_3]$,[12] in which the oxygen atom of one arsine oxide ligand functions as a bridge between two In^{III} centres. A comparison with a series of $InCl_3 \cdot 3L$ complexes (where L = Me_3PO, MeOH, H_2O, $PhMe_2PO$, Me_2SO) shows that in $(InCl_3)_2 \cdot (DME)_3$, the In—Cl bonds are shorter [2.392(1)–2.404(1) Å vs 2.449–2.495 Å], while the In—O bonds are significantly longer [2.289(3)–2.326(3) Å vs 2.149–2.231 Å]. This suggests that in the DME complex steric factors influence the In—O bonds much more than the In—Cl bonds. The complex $(InCl_3)_2 \cdot (DME)_3$ is quite different from the complex formed by $GaCl_3$ and DME ("$GaCl_3 \cdot DME$") ; not only do the two compounds have different stoichiometries but the Ga^{III} species is ionic, $[GaCl_2 \cdot (DME)_2]^+[GaCl_4]^-$, with the metal tetracoordinated in the anion $GaCl_4^-$ (with an almost regular tetrahedral structure) and hexacoordinated in the cation $[GaCl_2 \cdot (DME_2)]^+$ [13] (with a strongly distorted octahedral structure).

Reaction of $InCl_3$ with LiMe (1 : 3 molar ratio), in DME solution, gave the chloride-free $InMe_3 \cdot DME$ complex ; this has a simple mass spectrum with a fragmentation typical of $InMe_3$ (m/z 160, $InMe_3^+$; m/z 145, $InMe_2^+$; m/z 130, $InMe^+$; m/z 115, In^+) with a very low peak at m/z 205 corresponding to $[InMe_3 \cdot 0.5DME]^+$. Thus, in this complex, the central In^{III} appears to be pentacoordinated. The difference in Lewis acid character between $InCl_3$ and $InMe_3$ is probably due to the higher electronic saturation of the indium atom as a consequence of the inductive effect of the methyl group. Attempts to react $InMe_3 \cdot DME$ with $Ph_2P—CH_2CH_2—PPh_2$, followed by sublimation in a manner similar to that employed for the purification of $InMe_3$[14] when prepared in Et_2O, isolated only unchanged $InMe_3 \cdot DME$. Thus, $InMe_3$ synthesized in DME is of limited utility in InP and related alloy MOVPE techniques, where the presence of an oxygen atom must be excluded.

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