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Diethylindium(III) derivatives: synthesis and characterization of diethylindium(III) dialkylamides and diethylindium(III) pyrrolide. X-Ray crystal structures of diethylindium(III) pyrrolide and diethylindium(III) bromide

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Abstract

The compounds Et_2InNR_2 (R = Me, Et, or $SiMe_3$) and $Et_2InPyrr$ (HPyrr = pyrrole) have been prepared by reaction of Et_2InCl with the corresponding lithium amide or pyrrolide in diethylether. Their ^1H NMR, IR and mass spectra are reported and discussed. The amides are dimers in the vapour phase. Diethylindium bromide is a layer polymer. The octahedral coordination geometry of indium is characterized by four distinct In–Br distances ranging from 2.777(2) to 3.848(2) Å. Diethylindium pyrrolide has a chain structure as shown by the relatively short intermolecular interactions between each indium atom and the double bonds of two adjacent different pyrrole units (3.063(5) and 2.950(5) Å, respectively). The indium coordination geometry is then trigonal bipyramidal, with the shortest bonds in the equatorial plane (In–C(5) 2.143(5) Å, In–C(7) 2.141(5) Å, In–N 2.166(4) Å).

Introduction

The relative dearth of organometallic indium compounds compared to those of other Group 13 elements and the importance of indium organometallic compounds in MOCVD (Metal Organic Chemical Vapour Deposition) of indium based semiconductor materials [1] prompted us systematically to synthesize and investigate different classes of indium compound, of potential interest for MOCVD. An ideal MOCVD precursor should be a volatile liquid, non-toxic, and dioxygen and moisture stable [2]. Previous work has shown that liquids rather than solids are often obtained in homo- and in hetero-leptic organoindium compounds by changing the alkyl groups from methyl to ethyl or bulkier groups [3]. Moreover, the use of bulky groups can, in principle, prevent dioxygen and water attack by shielding the indium atom. A proper combination of R and X in the heteroleptic $R_{3-n}InX_n$

series can improve the chemico-physical features required by MOCVD. It has been shown that compounds R_2InX, where X is an N ligand, form in most cases dimeric or even trimeric [4a] species [4]. In these molecules the indium atoms, electronically and coordinatively saturated by the bridging ligand, are prevented from further oligomerization, and rendered less volatile. Preliminary studies have shown the suitability of dialkylamidodialkylindium(III) derivatives as precursors for InP growth, excluding the simultaneous growth of InN [4d], which is too unstable under the MOCVD growth conditions. Several dimethylindium dialkylamides have been reported and structurally characterized [4]; here we report on the synthesis of Et_2InNMe_2 (**1**), Et_2InNEt_2 (**2**), $Et_2InN(SiMe_3)_2$ (**3**) and Et_2InPyrr (**4**). In agreement with the above considerations **2** and **3** are liquid whereas the dimethylindium analogues are solid. The full characterization of **1**–**4** is reported, together with the X-ray determination of the crystal structure of **4** and of Et_2InBr.

Experimental

All operations were carried out in purified dinitrogen-filled glove boxes. Commercial anhydrous $InCl_3$ (Heraeus), $HNMe_2$ (Alfa Products), $HN(SiMe_3)_2$ (Aldrich), solutions of LiBu in hexane (Aldrich), solutions of EtMgBr and EtMgCl (Aldrich), pyrrole (HPyrr) (Aldrich) were used without further purification. $HNEt_2$ (Baker) was distilled from molecular sieves prior to use; 2,4,6-triazole (HTriaz)(Aldrich) was sublimed at 45–50°C, 10^{-5} mmHg. All the solvents (Et_2O, THF, n-hexane, toluene) were distilled under dinitrogen from the potassium ketyl of benzophenone. $LiNEt_2$, $LiN(SiMe_3)_2$, $LiNMe_2$, LiPyrr, LiTriaz were prepared by reaction of LiBu with the corresponding amine at room temperature in n-hexane.

Proton NMR spectra were recorded on a Bruker AC 200 spectrometer in anhydrous C_6D_6. Chemical shifts are quoted with respect to Me_4Si using C_6D_5H as internal standard. Infrared spectra (4000–350 cm^{-1}) were recorded neat or as Nujol mulls on KBr plates in an air-tight holder sealed with an O-ring, with a Perkin–Elmer 580 B spectrophotometer. Mass spectra were obtained with a V.G. Organic Ltd. ZAB, 2F spectrometer (EI = 70 eV, T = 60–70°C). Ions containing In are referred to the ^{115}In isotope. Elemental analyses were performed by Dornis u. Kolbe Mikroanalitisches Laboratorium, Mülheim (Germany).

Synthesis of mixtures of Et_2InBr and Et_2InCl

$InCl_3$ (2 mmol, 442 mg) was suspended in Et_2O and 2 ml of a 2 M solution of EtMgBr in n-hexane (4 mmol) were slowly added. After 24 h stirring at room temperature, Et_2O was removed under vacuum and the residue extracted with n-hexane. White crystals of Et_2InBr were obtained from the saturated solution. Titration of the residue with $AgNO_3$ showed a Br/Cl ratio of 87:13. Other experiments were carried out in order to determine the dependence of the Br/Cl ratio on the reaction conditions. Reactions of $InCl_3$ and EtMgBr in Et_2O for 20–24 h gave Br/Cl ratios, after extraction from n-hexane, varying from 81:19 to 86:14. Increasing the reaction time (200 h) increased the ratio to between 90:10 and 92:8.

Synthesis of Et_2InCl

A typical preparation of Et_2InCl is as follows: $InCl_3$ (5 mmol, 1105 mg) was suspended in Et_2O and EtMgCl (5 ml of a 2 M solution in n-hexane, 10 mmol) was

Table 1

Experimental crystallographic data for Et_2InBr and $Et_2InPyrr$

	Et_2InBr	$Et_2InPyrr$
Formula	$C_4H_{10}BrIn$	$C_8H_{14}InN$
Molecular wt	252.85	239.03
Crystal colour	colourless	colourless
Crystal dimension (mm)	0.40×0.22×0.10	0.24×0.18×0.21
Crystal system	orthorhombic	monoclinic
Space group	$Cmc2_1$	$P2/a$
a (Å)	16.837(3)	13.536(3)
b (Å)	6.595(2)	6.699(2)
c (Å)	6.334(2)	10.417(3)
β (°)		90.23(3)
Z	4	4
U (Å^3)	703.3(3)	944.6(4)
D_c (g cm^{-3})	2.39	1.68
$F(000)$	472	472
2θ range (°)	2–52	2–56
Radiation (Å)	Mo-K_α(0.71069)	Mo-K_α(0.71069)
μ (cm^{-1})	85.80	22.47
Octants collected	h, k, l	$-h, k, l$
Standard reflections	220, 111, 020	220, −221
Scan method	$\theta/2\theta$	$\theta/2\theta$
No. reflections collected	855	2612
Scan speed (° min^{-1})	1.8	1.8
Scan width (°)	1.2	1.5
Background counts (s)	20	20
No. observed [$I \geq 3\sigma(I)$]	378	1389
No. parameters	34	98
Weighting scheme w	$[\sigma^2(F_o+0.000854(F_o)^2]^{-1}$	unit
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.023	0.028
$R = \Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.025	
Goodness-of-Fit	0.92	1.12

added dropwise at room temperature. After 20 h stirring, Et_2O was removed under vacuum, the residue was redissolved in n-hexane and Et_2InCl was extracted by refluxing the hexane for 2 h. n-Hexane was removed and the Et_2InCl employed for further reactions. Yield 80% with respect to $InCl_3$. In some cases Et_2InCl was not isolated, but used *in situ* after filtration of the Et_2O solution, assuming a quantitative yield with respect to $InCl_3$.

X-Ray structure determination of Et_2InBr

Crystals of Et_2InBr separated from a saturated solution of a mixture of Et_2InBr and Et_2InCl ($Et_2InBr/Et_2InCl > 8$) in n-hexane. The crystal data with other experimental details are summarized in Table 1. A colourless single crystal was used for data collection on a four circle Philips PW1100 diffractometer with graphite-monochromated Mo-K_α radiation. The intensity data were corrected for Lorentz-polarization effects and for absorption, by the method of North et al. [5]. The structure was solved using three-dimensional Patterson and Fourier techniques and refined with full-matrix least-squares. Hydrogen atoms were introduced

Table 2

Atomic coordinates ($\times 10^4$) for non-hydrogen atoms and U_{eq} values ($\times 10^3$) with esd's in parentheses

	x	y	z	U_{eq} (Å^2) ^{a}
Et$_2$InBr				
In	0	2640(1)	0	38.1(2)
Br	0	6825(2)	490(2)	39.8(3)
C(1)	1249(4)	1926(11)	393(16)	43(2)
C(2)	1795(6)	3156(17)	−927(20)	62(4)
Et$_2$InPyrr				
In	203.4(2)	2545.2(8)	1623.8(3)	50.4(1)
N	−79(3)	2534(7)	−424(4)	46(1)
C(1)	487(4)	3294(7)	−1383(5)	47(2)
C(2)	54(4)	2980(7)	−2544(5)	52(2)
C(3)	−826(4)	1949(7)	−2317(5)	52(2)
C(4)	−894(4)	1706(7)	−1024(5)	48(2)
C(5)	1737(3)	3185(8)	1935(5)	53(2)
C(6)	2046(5)	3253(10)	3338(6)	73(3)
C(7)	−1168(4)	1793(8)	2520(6)	55(2)
C(8)	−1169(5)	1777(11)	3961(6)	83(3)

^{a} U_{eq} = one-third of the trace of the orthogonalized U_{ij} tensor.

at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d(C–H) = 0.98 Å and U_{iso} = 0.08 Å^2). Atomic scattering factors were taken from ref. [6]. Data processing and computation were carried out using the SHELX 76 program package [7]. Geometrical calculations were made using the PARST program [8], and diagrams were produced using ORTEP [9]. Final fractional coordinates for non-hydrogen atoms with equivalent thermal parameters are reported in Table 2.

Synthesis of Et$_2$InNMe$_2$ (1)

Freshly prepared $LiNMe_2$ (4 mmol, 205 mg) was added to a stirred solution of Et_2InCl (4 mmol, 832 mg) in Et_2O. After 20 h stirring at room temperature, the colourless solution was filtered from a white precipitate. Et_2O was removed under vacuum and the residue was dissolved in n-hexane. A white precipitate (further LiCl) separated. n-Hexane was removed, giving a white, sticky product from which Et_2InNMe_2 was sublimed at 30°C, $P = 10^{-2}$ mmHg. Yield with respect to Et_2InCl: 65–70%. Anal. Found: C, 33.1; H, 7.3; N, 6.4; In, 53.1. $C_6H_{16}InN$ calc.: C, 33.2; H, 7.4; N, 6.4; In, 53.0%. NMR: δ (H) (200 MHz, C_6D_6): 2.47 (6H, s, NCH_3), 1.45 (6H, t, $InCH_2$$CH_3$), 0.80 (4H, q, In$CH_2$$CH_3$). IR (Nujol mull, KBr disks): 1580br, 1220m, 1130s, 1045m, 1000m, 960w, 910s, 625s, 480s, 440s. MS m/z (70 eV, 70°C): 434 (< 1%, M_2), 405 (100, M_2 − Et), 362 (10, M_2 − Et − NMe_2), 348 (8, M_2 − 3Et), 304 (5, M_2 − 3Et − NMe_2), 275 (11, M_2 − 4Et − NMe_2), 217 (18, M), 188 (12, M − Et), 173 (16, Et_2In), 158 (18, $InNMe_2$), 115 (31, In).

Synthesis of Et$_2$InNEt$_2$ (2)

Freshly prepared $LiNEt_2$ (4 mmol, 320 mg) was added to a stirred solution of Et_2InCl (4 mmol, 832 mg) in Et_2O. The solution was stirred at room temperature for 18 h, filtered from the LiCl, and Et_2O was removed *in vacuo* leaving a sticky pale yellow product. This residue was dissolved in n-hexane giving rise to further white precipitate and a pale yellow solution. The filtered solution was reduced in volume by removing n-hexane *in vacuo*. The residue was distilled (with partial decomposition) at 125°C and 0.5 mmHg, as previously reported [10], giving a pale yellow liquid which decomposes slowly leaving a greyish powder and a white sticky residue, not characterized (box atmosphere: O_2 less than 2 ppm, H_2O less than 1 ppm). The final yield referred to Et_2InCl is less than 50%. Anal. Found: C, 37.8; H, 8.1; N, 5.8; In, 48.2. $C_8H_{20}InN$ calc.: C, 39.2; H, 8.2; N, 5.7; In, 46.9%. NMR: δ (H) (200 MHz, C_6D_6): 2.87 (q, 4H, NCH_2CH_3), 1.49 (t, 6H, $InCH_2CH_3$), 0.82 (t, 6H, NCH_2CH_3), 0.76 (q, 4H, $InCH_2CH_3$). IR (neat, KBr): 1600br, 1460s, 1420m, 1375s, 1360m, 1345m, 1285m, 1230m, 1170m, 1140s, 1105m, 1040m, 1000s, 960m, 930w, 900w, 850m, 790s, 625s, 560s, 470s, 450sh. MS m/z (70 eV, 60°C): 461 (100%, $M_2 - Et$), 418 (6, $M_2 - NEt_2$), 403 (7, $M_2 - NEt_2 - Me$), 390 (47, $M_2 - NEt_2 - Et + H$), 361 (3, $M_2 - NEt_2 - 2Et$), 245 (3, M), 217 (3, $M - Et$), 186 (2, $M - 2Et$), 173 (3, $In + NCH_2$), 115 (4, In).

Synthesis of $Et_2InN(SiMe_3)_2$ (3)

A solution of Et_2InCl (5 mmol, 1040 mg) in Et_2O was cooled to -10°C. $LiN(SiMe_3)_2$ (5 mmol, 835 mg) was added and the solution stirred at that temperature for about 1.5 h. Et_2O was removed and n-hexane added. A pale yellow solution and a beige precipitate were obtained. The mixture was allowed to warm up to room temperature, then was filtered, n-hexane removed, and the pale yellow residue distilled at 110°C and 4.5 mmHg giving $Et_2InN(SiMe_3)_2$. Compound **3** is extremely air-sensitive and smokes on exposure to the atmosphere, but it is stable for months in an inert atmosphere. Yield with respect to Et_2InCl: 60–65%. Anal. Found: C, 35.8; H, 8.5; N, 4.1; Si, 16.9; In, 34.6. $C_{10}H_{28}InNSi_2$ calc.: C, 36.0; H, 8.4; N, 4.2; Si, 16.8; In, 34.5%. NMR: δ(H) (200 MHz, C_6D_6): 0.16 (18H, s, $SiCH_3$) 0.88 (4H, q, $InCH_2CH_3$) 1.35 (6H, t, $InCH_2CH_3$). IR (neat, KBr plates) 1460m, 1420m, 1380m, 1250bs, 1160m, 1090w, 1020–960bs, 930sh, 850bs, 780s, 750s, 660s, 610s, 490m, 455m, 350s. Mass spectra: unfortunately technical problems, mainly the extremely fast decomposition of **3** under our experimental conditions, prevented us from an accurate evaluation of the relative abundances of the peaks. Only the most significant m/z values and their assignments are reported here. MS m/z (70 eV, 30°C): 434 ($M_2 - NSiMe_3 - 2Et - Me$), 333 (M), 319 ($M - Me$), 304 ($M - Et$), 290 ($M - Et - CH_2$), 275 ($M - 2Et$), 260 ($M - 2Et - Me$), 245 ($M - 2Et - 2Me$), 173 (Et_2In), 161 [$HN(SiMe_3)_2$], 146 [$HN(SiMe_3)(SiMe_2)$], 115 (In), 100 [$N(SiMe_2)$], 73 $SiMe_2$.

Synthesis of $Et_2InPyrr$ (4)

Et_2InCl (5 mmol, 1040 mg) was dissolved in Et_2O and LiPyrr (5 mmol, 365 mg) was added at room temperature. After 4 h stirring, a white precipitate was filtered off, Et_2O removed and the pale yellow residue dissolved in n-hexane. A small quantity of white precipitate formed and was filtered off. By cooling the n-hexane solution at -10°C, white crystals of $Et_2InPyrr$ were obtained. Compound **4** is stable in inert atmosphere. It melts at about 70°C without any visible decomposition. Yield with respect to Et_2InCl: 70%. Anal. Found: C, 40.2; H, 5.8; N, 5.9; In, 48.0. $C_8H_{14}InN$ calc.: C, 40.3; H, 5.9; N, 5.9; In, 47.9%. NMR: δ (H) (200 MHz, C_6D_6): 6.8 (2H, s, α-*CH*), 6.3 (2H, s, β-*CH*), 1.31 (6H, t, $InCH_2CH_3$), 0.7 (4H, q, InCH_2CH_3). Ir (Nujol mull, KBr disks): 1470s, 1460s, 1420m, 1380s, 1370s, 1300m, 1230m, 1150s, 1090s, 1040s, 1030s, 1000m, 950w, 930m, 910s, 860s, 825m, 750s, 640s, 500s. MS m/z (70 eV, 70°C): 449 ($<1\%$, M_2-Et), 391 (5, M_2-3Et), 354 (2, M_2-2Et-Pyrr), 297 (7, M_2-4Et $-$ Pyrr), 239 (8, M), 181 (12, InPyrr), 173 (50, Et_2In), 144 (7.5, EtIn), 115 (100, In), 67 (12, HPyrr).

X-Ray structure determination of ***4***

Crystals of **4** were obtained from n-hexane solution cooled at −10°C. A colourless single crystal was used for analysis; data collection and treatment were carried out as described for the compound Et_2InBr. Crystal data are in Table 1; final fractional coordinates are in Table 2.

Reaction between Et_2InCl and LiTriaz

Et_2InCl (4 mmol, 832 mg) was dissolved in Et_2O and LiTriaz (4 mmol, 300 mg) was added at room temperature. The solution was checked by ^1H NMR after 2, 24, and about 100 h, but only the signals attributable to Et_2InCl were present. The same experiment was tried in toluene. In this case the reaction mixture was heated under reflux for 1 h, but the ^1H NMR of the solution did not change.

Results and discussion

Attempts to prepare Et_2InCl using $InCl_3$ and EtMgBr gave rise to mixtures of Et_2InCl and Et_2InBr whose ratio varied with the reaction time. The presence of Et_2InBr is probably due to the following sequence of reactions.

$$InCl_3 + 2\ EtMgBr \rightarrow Et_2InCl + MgBrCl$$

$$2\ MgBrCl \rightarrow MgBr_2 + MgCl_2$$

$$2\ Et_2InCl + MgBr_2 \rightarrow 2Et_2InBr + MgCl_2$$

The driving force of the process is the different solubilities of $MgBr_2$ and $MgCl_2$ in the reaction solvent. In fact $MgBr_2$ forms adducts such as $MgBr_2 \cdot 2Et_2O$ [11], which enhance its solubility compared to $MgCl_2$. The mixtures were titrated after extraction with n-hexane (2 h reflux) and presumably after a longer reaction time Et_2InCl would disappear.

Crystals of Et_2InBr separated from an n-hexane solution of a mixture Et_2InBr/Et_2InCl ($Et_2InBr/Et_2InCl > 8$). The crystal structure of Et_2InBr contains six-coordinate indium atoms, with the indium surrounded by two ethyl groups and a bromine atom, as well as being coordinated to the bromine atoms of three neighbouring molecules (Fig. 1). Selected bond lengths and angles are reported in Table 3. The structures of Me_2InBr [12] and Me_2InCl [13] have been determined. Surprisingly, the structure of Et_2InBr is more close to that of Me_2InCl than that of the bromine derivative. The structures are all polymeric with octahedral coordination. Me_2InBr is a two-dimensional symmetric polymer: its structure is formed by strictly planar layers of In–Br entities with an In–Br distance of 3.105 Å. Perpendicularly the methyl groups are colinear, but asymmetrically coordinated, at distances of 2.116(6) and 2.226(6) Å respectively. Me_2InCl has three distinct indium–chlorine distances: 2.673(7), 2.954(6), and 3.450(9) Å. The indium and the

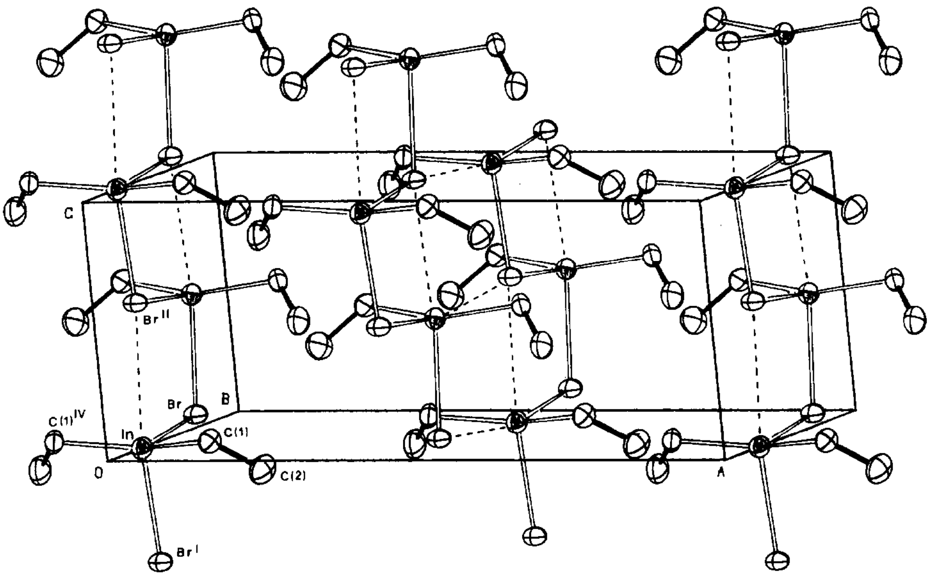


Fig. 1. Et$_2$InBr: unit cell content (dotted lines indicate In–Br distances > 3 Å).

chlorine atoms are on a mirror plane and on the opposite sides are the two methyl groups, with an In–C(1) bond distance of 2.179(7) Å and a C(1)–In–C(1)′ angle of 167.3°.

Table 3

Selected bond lengths (Å) and angles (°) with esd's in parentheses [a]

Et$_2$InBr			
In–Br	2.777(2)	In–Br^{I}	2.878(2)
In–Br^{II}	3.495(2)	In–Br^{III}	3.848(2)
In–C(1)	2.170(7)	C(1)–C(2)	1.48(1)
Br–In–C(1)	101.7(2)	In–C(1)–C(2)	114.6(6)
Br–In–Br^{I}	89.4(1)	C(1)–In–C(1)^{IV}	151.6(3)
Br–In–Br^{II}	77.8(3)	Br^{I}–In–Br^{II}	177.2(4)
Et$_2$InPyrr			
In–N	2.166(4)	In–C(5)	2.143(5)
In–C(7)	2.141(5)	N–C(1)	1.360(6)
N–C(4)	1.382(6)	C(1)–C(2)	1.358(8)
C(2)–C(3)	1.398(8)	C(3)–C(4)	1.360(8)
C(5)–C(6)	1.519(9)	C(7)–C(8)	1.500(9)
C(5)–In–C(7)	145.3(2)	N–In–C(7)	106.2(2)
N–In–C(5)	108.5(2)	In–N–C(4)	125.8(3)
In–N–C(1)	128.6(3)	C(1)–N–C(4)	105.6(4)
N–C(1)–C(2)	110.7(5)	C(1)–C(2)–C(3)	106.9(5)
C(2)–C(3)–C(4)	106.7(5)	N–C(4)–C(3)	110.0(4)
In–C(5)–C(6)	114.5(4)	In–C(7)–C(8)	116.2(4)

[a] ^{I} at $-x, -y+1, z-1/2$; ^{II} at $-x, -y+1, 1/2+z$; ^{III} at $x, -1+y, z$; ^{IV} at $-x, y, z$.

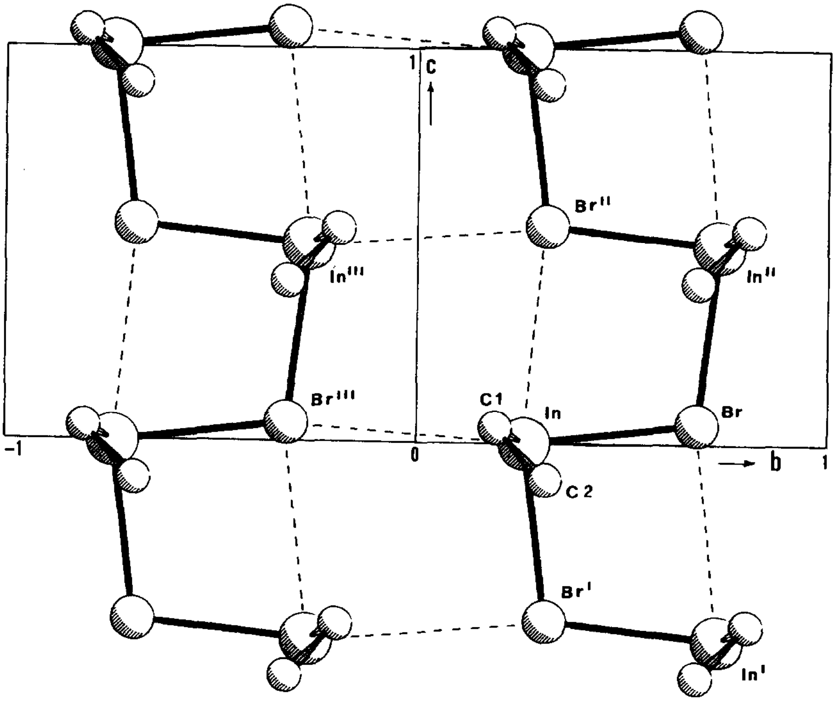


Fig. 2. A layer of In and Br atoms on the *b*, *c* plane.

In Et_2InBr, which is also a two-dimensional polymer (Fig. 2), there is a further reduction of molecular symmetry which is only *m* (C_s), whereas it is *mm* (C_{2v}) in Me_2InCl and 4*mm* (C_{4v}) in Me_2InBr. The layers containing indium and bromine atoms are still planar but in this case there are four distinct In–Br distances ranging from 2.777(2) to 3.848(2) Å, which follow the trend of indium–chlorine distances quoted above. The In–C bond distance of 2.170(7) Å is comparable to the In–C bond distance in the chlorine derivative, but in this case the C(1)–In–$C(1)^{IV}$ angle reduces to 151.6(3)°. The C(1)–C(2) bond distance and the In–C(1)–C(2) angle have the expected values of 1.48(1) Å, and 114.6(6)°. The average of the four In–Br distances is 3.238(2) Å, which is larger than 3.105 Å found in Me_2InBr, while the average of the two In–C bond distances of Me_2InBr 2.176(6) Å compares well with the value of 2.170(7) Å found in the present determination. The substitution of the methyl by the ethyl groups, seems to influence only the metal–halogen distances.

As does Me_2InCl, Et_2InCl, routinely prepared by $InCl_3$ and EtMgCl in order to avoid any Br^- contamination, easily reacts with different lithium amides giving the corresponding Et_2InNR_2.

$Et_2InCl + LiNR_2 \rightarrow Et_2InNR_2 + LiCl$

R = Me, Et, or $SiMe_3$

$Et_2InCl + LiPyrr \rightarrow Et_2InPyrr + LiCl$

The reactions were carried out at room temperature using Et_2O as solvent, except for the reaction with lithium hexamethyldisilazide. In that case, the reaction

Table 4

^{1}H chemical shifts (ppm) of the X group in Et_2InX and Me_2InX compounds

X	Me_2InX	Ref.	Et_2InX	Ref.
NMe_2	2.41	[4c]	2.47	This work; solvent: toluene-d_8
NEt_2	0.82	[4c]	0.82	This work
	2.87		2.87	
$N(SiMe_3)_2$	0.20	[4c]	0.16	This work; solvent: toluene-d_8
Pyrr	6.7	[14]	6.8	This work
	6.1		6.1	
Pyrazole	6.24	[14]	6.07	[14]
	7.43		7.26	

^{1}H chemical shifts (ppm) of the Et_2In moiety in Et_2InX

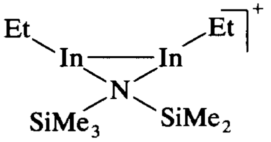
X	$InCH_2CH_3$ (CH$_2$ italic)	$InCH_2CH_3$ (CH$_3$ italic)	Ref.
Cl	0.90	1.39	This work
NMe_2	0.80	1.45	This work
NEt_2	0.76	1.49	This work
Pyrr	0.70	1.31	This work
Pyrazole	0.76	1.13	[14]; solvent: toluene-d_8
$N(SiMe_3)_2$	0.76	1.35	This work
Et	0.44	1.27	[16]

vessel was kept below 0°C, otherwise, on adding $LiN(SiMe_3)_2$ to Et_2InCl, considerable decomposition takes place. All the compounds resemble the analogous dimethyl indium derivatives, being dimers in the vapour phase, soluble in organic solvents, and air-sensitive. The main difference is that the diethyl derivatives are generally more volatile, so that **2** and **3** are liquid at room temperature, whereas the corresponding dimethyl derivatives melt at 80–90°C and 37–38°C, respectively, and **1** can be sublimed under very mild conditions. Interestingly, if X = pyrazole both the dimethyl and diethyl R_2InX derivatives are liquid [14], but if X = pyrrole they are both solid. Attempts to use more bulky substituents such as triazole, in order to increase the volatility, failed under our experimental conditions.

The ^{1}H NMR data of the new compounds and of other related compounds are summarized in Table 4. The chemical shifts of the X group in Et_2InX and Me_2InX are essentially the same and are generally downfield (except for the protons on the β-carbon of the diethylamide) with respect to the parent amines as already noted [15]. The ^{1}H chemical shifts of the Et_2In moiety change with X, though not dramatically. The $In\mathit{CH_2}CH_3$ resonance is shifted downfield on passing from Et (0.46 ppm) to the amides (0.70–0.80 ppm) to the Cl (0.90 ppm) suggesting that the withdrawing effect of N and Cl heteroatoms is the most effective perturbation on the α-proton chemical shift. It can be reasonably supposed that this scalar effect becomes less important for the $InCH_2\mathit{CH_3}$ resonance, for which dipolar, long-range interactions have to be taken into account. Due mainly to these interactions the ^{1}H shifts of $InCH_2\mathit{CH_3}$ in C_6D_6 vary between 1.49 ppm (NEt_2) and 1.31 ppm (Pyrr). Actually the range of chemical shifts is narrow and can be strongly affected by slight changes in the experimental conditions (solvent, temperature, field homogeneity).

The mass spectra of the compounds showed the presence of dimeric species in the vapour phase of **1**, **2** and **4**. The ions due to the dimer species were not detected in our experimental conditions, but for both the diethylamide and the dimethylamide derivatives the most intense peak is assignable to a fragment arising from the dimer by loss of an ethyl group. The mass spectrum of **4** also contains ion fragments derived from the dimer by subsequent loss of ethyl groups but the relative abundances of such peaks are very low compared to the most intense one due to $^{115}In^+$.

Compound **4** is monomeric in the solid state (*vide infra*) with unusual interactions between an indium atom and the double bonds of two pyrrole moieties, which create a polymeric chain. Perhaps discrete dimers are present in the vapour phase, but the ratio dimer/monomer is very low. As for the tetramethyl homologues, the dimers tend to lose preferentially the ethyl groups instead of the amido groups and retain the In_2N_2 core. The sylilamide derivative decomposes so fast that the spectrum was not easily obtained. In our standard conditions (70 eV) no peaks derived from the dimer were seen, except for a peak at *m/z* 434 assignable to a species such as:



If **3** has a dimeric structure we cannot prove it by the data to hand.

The infrared spectra contain bands tentatively assigned to C–N, In–N and In–C bonds, by comparison with reported data. Bands at 480 cm^{-1} for **1**, 470 for **2**, 490 for **3** and 500 for **4** can be assigned to the InC_2 asymmetric stretch [17]. A band at 445 cm^{-1} in Me_2InNEt_2 is assigned to vibration of the In_2N_2 core [4d]. In our case a band at 440 for **1** and a shoulder at 450 cm^{-1} for **2** may be related to an analogous vibration, indicating their dimeric nature. As far as **3** is concerned, the In_2N_2 vibration could give rise to the band at 350 cm^{-1} analogously to $In(N(SiMe_3)_2)_3$ for which it appears at 360 cm^{-1} [18]. Compound **4** shows no bands below 500 cm^{-1}, because in the solid state the saturation of indium is not achieved via nitrogen bridging atoms, but via interactions with the double bonds of the pyrrole (*vide infra*). Other characteristic bands occur in the 950–1050 cm^{-1} region and are related to NC_2 symmetric and asymmetric stretches. In the case of **3**, in addition to a strong band at 780 cm^{-1} assignable to ν_s $MNSi_2$ by comparison with $Me_2InN(SiMe_3)_2$ (791) [4c], several bands attributable to $SiMe_3$ vibration modes were observed, such as at 1250 cm^{-1} δ_s Me(Si), 810–880 ν_{as} Me(Si), 670 ν_{as} SiC_3.

The X-ray crystal structure of **4** is shown in Fig. 3. Compound **4** contains apparently tricoordinated indium molecules. The indium atom is only 0.0296(6) Å out of the plane of the two carbon atoms of the ethyl groups and of the pyrrole nitrogen, which are bonded to the metal at distances of 2.142_{av} Å for In–C and of 2.166(4) Å for In–N. Selected bond lengths and angles are reported in Table 3. The planar pyrrole ring is tilted with respect to the coordination plane by 16.1(2)°. The In–C bond distances are here significantly shorter than in Et_2InBr, and the In–N distance is among the shortest reported. A comparable value of 2.14 Å for the $In–N_{amide}$ distance has been found only in the monomeric $MeIn[MeN(CH)_4N]_2$ [19].

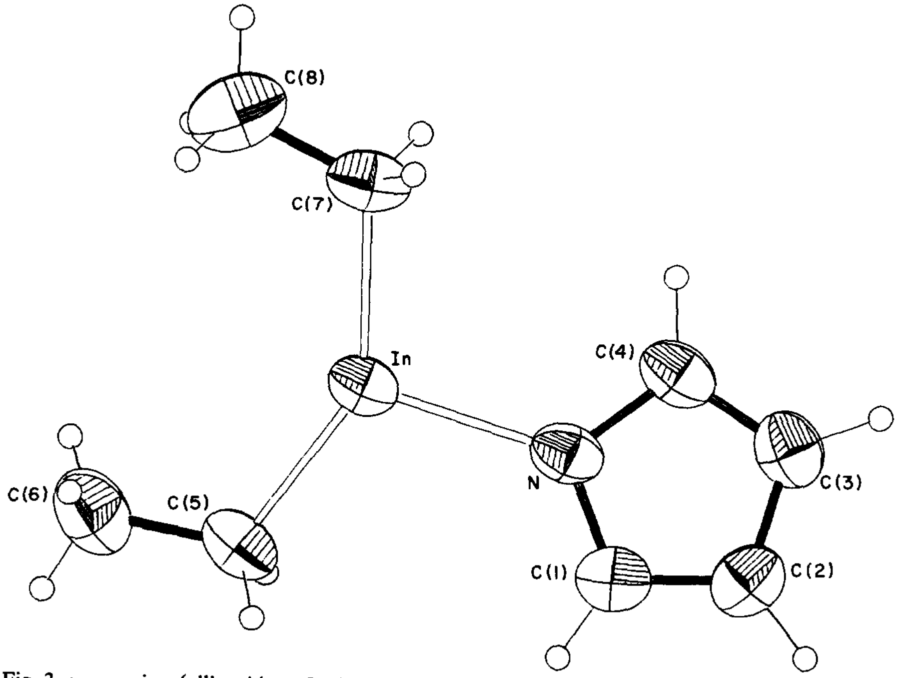


Fig. 3. ORTEP view (ellipsoids at 50% probability) of the $Et_2InPyrr$ unit.

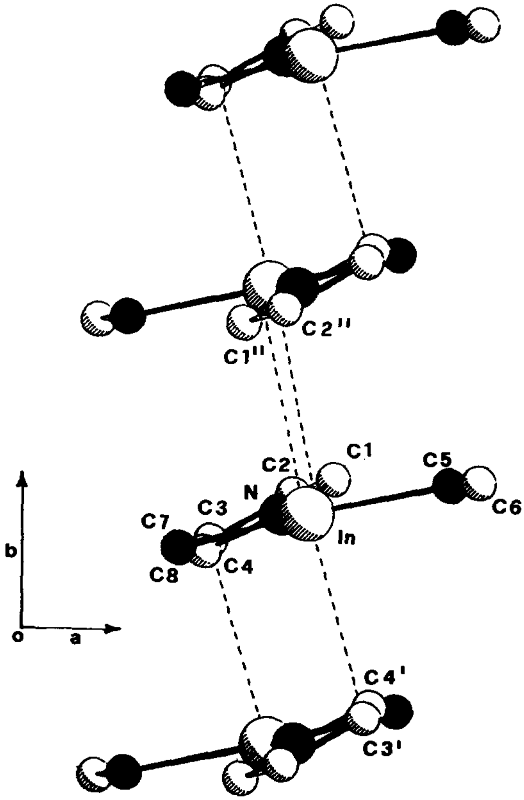


Fig. 4. Coordination and bondings for $Et_2InPyrr$ units (the atoms in black are those coordinated to the metal).

Table 5

Selected short intermolecular contacts in $Et_2InPyrr$ [a]

In · · · N′	3.628(5)	In · · · N″	3.529(5)
In · · · C(2)′	3.839(5)	In · · · C(1)″	2.950(5)
In · · · C(3)′	3.208(5)	In · · · C(2)″	3.167(5)
In · · · C(4)′	3.063(5)	In · · · C(3)″	3.851(5)

[a] Symmetry operation ′ at $-x$, $-y$, $-z$; ″ at $-x$, $1-y$, $-z$.

In principle, it would appear that here there is a coordinatively unsaturated indium compound. A close examination of the crystal packing shows relatively short contacts among molecules situated at the position $-x$, $-y$, $-z$ (labelled with ′) and $-x$, $1-y$, $-z$ (labelled with ″), which determine columns of a sandwich structure along the *b* crystallographic axis (see Fig. 4). In fact, each indium atom is between two adjacent pyrrole units. The In · · · C(4)′ and In · · · C(1)″ contacts of 3.063(5) and 2.950(5) Å, respectively, are somewhat shorter than the value of 3.11(4) Å reported for a "long bridge bond" in the tetrameric structure of Me_3In [20] (a recent more accurate structure determination of the same compound [21] gives a value of 3.083(12) Å). If we consider the four shortest In · · · C intermolecular contacts (Table 5), they involve on one side C(1)″–C(2)″ and on the other side C(3)′–C(4)′.

Thus, there is an interaction between indium and the two double bonds of the pyrrole ligand, that is oriented to maximize contacts with two indium atoms. The distances between the midpoints of the two pyrrole double bonds (M_1 for C(1)″–C(2)″ and M_2 for C(3)′–C(4)′) and indium are In–M_1 2.984(5) and In–M_2 3.062(5) Å. The angle M_1–In–M_2 is 171.2(2)°. The coordination geometry around indium is trigonal bipyramidal, the apices of the bipyramid being M_1 and M_2. This is very reminiscent of the structure of $Me_2In(\mu$-1-propynyl) [22] which has an In–M distance of 2.899 Å, where M is the midpoint of the triple bond of the propynyl moiety of adjacent molecules, and a M_1–In–M_2 angle of 173.27°, for which a trigonal bipyramidal geometry has been devised. The particular molecular packing and short contacts found in **4** could be the stabilizing factor for this apparently unsaturated compound.

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