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Dialkylindium derivatives of unsaturated nitrogen heterocycles—preparation, spectroscopic properties and the use in MOVPE *

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Abstract

A series of dialkylindium azolides of the type $R_2In(NR')$ (with R = Me and Et) have been synthesized by the reaction of InR_3 with various N-heterocycles (pyrrole, pyrazoles, imidazole and 1,2,4-triazole) or by treatment of R_2InCl with a lithiated azolide, Li(NR') in an inert solvent. The compounds have been characterized by NMR (^1H, ^{13}C) and vibrational (IR and Raman) spectroscopy, and their mass spectra are discussed. The pyrazole derivatives are dimeric in solution and in the gas phase, whereas, as indicated by the mass spectral data, the triazole compound is trimeric in the gas phase, and the imidazole derivative seems to be polymeric. The spectroscopic data suggest that the dimethylindium-pyrrole compound has an unusual structure, which is not comparable with those of the other organoindium azolides. Dimethylindiumpyrazole was used in metalorganic vapor phase epitaxy (MOVPE) experiments to grow InP layers.

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* MOVPE = metalorganic vapor phase epitaxy.

Introduction

In the last few years there has been an unexpected renaissance in studies of the chemistry of organoindium compounds many of the new products obtained being synthesized because of their possible use as indium-source materials in the metalorganic vapor phase epitaxy (MOVPE) of III/V semiconductors. Although the growth of In-containing III/V-compound epitaxial layers of excellent quality with Me_3In or Et_3In is now well developed [1], up to now none of the In-containing precursors could meet all of the essential requirements such as ease of handing, high volatility, and stability.

Some P-containing adducts such as Me_3InPEt_3 (TMI–TEP), which were studied in the early 1980s [2], and more recently novel amine adducts such as $Me_3InNH^iPr_2$ and intramolecular adducts such as $Me_2In(CH_2)_3N(CH_3)_2$ (DADI) have been used successfully for MOVPE [3].

Use of such compounds helps to overcome some of the problems encountered with the trialkyls (Me_3In is solid, whereas liquid precursors are preferred and both of the In-alkyls tend to undergo unwanted side reactions with the hydrides used in the MOVPE process), but they suffer from their rather low volatility. We therefore decided to investigate other organoindium compounds, mainly pyrazole derivatives. Besides their possible use in MOVPE, we were also interested in their spectroscopic and chemical properties, and so we made a wide range of In-containing N-heterocycles and characterized them by NMR-, vibrational- and mass-spectroscopy, and also by elemental analysis.

Experimental

All operations were carried out under dried nitrogen or argon. Solvents were purified by standard procedures. All the heterocyclic nitrogen compounds, H(NR′), were commercially available, and were used after distillation, sublimation, or recrystallization.

$InMe_3$ was prepared from $InCl_3$ and LiMe in a 1:4 ratio. The initially formed $Li[InMe_4]$ complex is treated with $InCl_3$ (1:1), and fractionation yields high purity $InMe_3$ in 75–80% yield [5]. Commercially available $InEt_3$ was used in the preparation of the diethylindium derivatives.

The vibrational spectra (IR and Raman) were recorded on a Perkin–Elmer 283 and a Coderg PH-0 instrument (excitation with the 6471 Å line of a krypton laser) and NMR spectra on Bruker WP 60, AC 200, and AC 250 spectrometers. The mass spectra were obtained with a high-resolution, double-focusing Varian MAT 711 instrument.

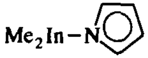
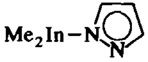
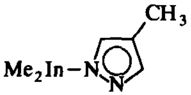
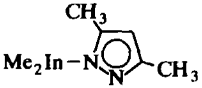
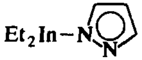
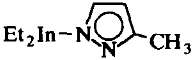
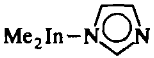
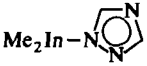
For the preparation of the organoindium derivatives I to V (Table 1) the two methods were used as follows:

Method A

To a vigorously stirred solution of InR_3 (or its etherate) in a few ml of ether, benzene, or toluene was slowly added the solution or suspension of an equimolar amount of the heterocyclic compound in the same solvent. In contrast to observations on simple, aliphatic amines [4], alkane formation begins to start at room temperature. When this alkane formation slows down, the solution is refluxed for

Table 1

Preparative, analytical, and physical data

Compound	R_3In/R_2InCl (g/(mmol))	H(NR')/Li(NR') (g/(mmol))	Method (solvent)	Yield (%)	Elemental analyses (Found (calc.) (%))					M.p. (°C)	B.p. (°C/torr (Pa))
					C	H	N	In	M		
 (I)	7.04 (44)	2.95 (44)	A (C_6H_6)	91	33.94 (34.16)	4.68 (4.78)	6.61 (6.64)	53.85 (54.42)	422 [a] (210.97)	118–120 (dec.)	70–74/0.1 (14) (subl.)
 (IIa)	9.91 (62) 1.71 (9.5)	4.22 (62) 0.74 (10)	A (C_6H_6) B (Et_2O)	81 60	28.01 28.10 (28.33)	4.31 4.23 (4.28)	13.00 13.10 (13.22)	54.00 53.97 (54.17)	424 ± 8 [b] – (211.96)	23–26	160/11 (1465)
 (IIc)	6.40 (40)	3.28 (40)	A (C_6H_6)	87	32.10 (31.89)	4.97 (4.91)	12.25 (12.40)	50.01 (50.81)	452 ± 10 [b] (225.99)	54–56	108–110/0.2 (27)
 (IId)	7.67 (48)	4.61 (48)	A (Et_2O)	92	34.90 (35.03)	5.44 (5.46)	11.85 (11.67)	47.70 (47.84)	485 ± 12 [b] (240.02)	77–79 [e]	50–55/10^{-4} (0.014) (subl.)
 (IIIa)	5.86 (29) 1.98 (9.5)	1.95 (28.7) 0.74 (10)	A (Et_2O) B (Et_2O)	90 55	34.91 34.66 (35.03)	5.47 5.40 (5.46)	11.32 10.88 (11.67)	47.28 46.96 (47.84)	451 [a,c] – (240.02)	liquid	125/4 (533)
 (IIIb)	6.67 (33)	2.80 (34)	A (Et_2O)	85	37.65 (37.82)	5.99 (5.95)	10.86 (11.03)	44.92 (45.20)	479 [a,c] (254.04)	liquid	130/4 (533)
 (IVa)	7.04 (44)	2.90 (43)	A (C_7H_8)	~ 100	28.53 (28.33)	4.35 (4.28)	13.09 (13.22)	54.10 (54.17)	– (211.96)	150–152	
 (V)	1.95 (12)	0.69 (10)	A (Et_2O)	75	22.80 (22.56)	3.69 (3.79)	20.44 (19.73)	52.30 (53.92)	624 [a,d] (212.95)	189–192 (dec.)	–

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[a] Mass spectrum. [b] In C_6H_6, cryoscopically. [c] $[M_2 - R]^+$ peak. [d] $[M_3 - R]^+$ peak. [e] 58–60 °C reported in [6].

another 2–3 h. Then either (a) the solvent is removed and the residue purified by distillation or sublimation (see Table 1), or (b) the less-soluble and non-volatile products are filtered off, washed twice with benzene or hexane, and dried under vacuum (compounds IV and V). Table 1 lists the most important physical constants, the quantities of starting materials and the elemental analyses for the products.

Method B

A suspension of Li(NR′), (prepared from H(NR′) and Li^nBu) in ether is slowly added to a suspension of the stoichiometric quantity of R_2InCl in ether. The mixture is stirred for ca. 6 h at room temperature, the solvent then removed under vacuum, and the residue dissolved in n-hexane. The insoluble LiCl is then filtered off. However, complete removal of the formed chloride is often difficult because of its fineness, and so this method is less satisfactory. After removal of the solvent, the subsequent procedure is as described for method A. Details are again given in Table 1.

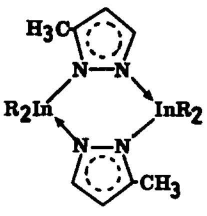
The compounds listed in Table 1 are mostly new, and are either colourless oily liquids (IIa, IIIa, IIIb) or white solids. Their sensitivity to moisture or oxygen in the air is remarkably low and falls with increasing number of nitrogen atoms in the ring and with further substitution by CH_3-groups. The azolide I is thus the least stable compound, and is even light sensitive; exposure to daylight and especially to the light from a krypton laser (used for the Raman spectra) leads to rapid formation of metallic indium, as also takes place at temperatures a little above the melting point. Compounds I–III are all soluble in common, aprotic solvents.

Spectroscopic investigations

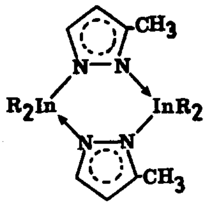
The mass spectra of the compounds IIa, IIIa and IIIb (see Table 2) show an identical extensive fragmentation pattern: next to the $[^{115}In]^+$ peak appears the main peak in the spectra, which corresponds to the dimer-ion $[M_2 - R]^+$. The $[M_2]^+$ ion itself is not seen. The triazole derivative V is trimeric under the specified experimental conditions; below $m/z = 411$ ($[M_2 - R]^+$) its fragmentation pattern is mainly like that for compounds II and III, and so a similar structure is suggested for the dimeric species of all these compounds.

Compound I also gives ions from dimers in the mass spectrum, but in this case the base peak is for the ion $[InR_2]^+$, the $[M_2 - R]^+$ and $[^{115}In]^+$ ions have lower intensities. The molecular ion $[M_2]^+$ is also seen. It cannot be decided on the basis of the MS data to what extent the single nitrogen atom of the pyrrole ring may serve as a connecting link without disturbance of the aromatic π-system.

The ^1H and (so far as solubility allowed their recording) the ^{13}C NMR spectra (see Table 3) are consistent with the assumed structures. Low temperature studies for IIb and IIIb down to −40 °C revealed no splitting of the R_2In signals. Thus, in contrast to the analogous Ga compound $[Me_2GaN_2C_3CH_3]_2$ [8,10], it probably exists not a mixture of the two isomers **A** and **B**, but only in the symmetrical from **A**:



A



B

(A, M = Ga, In) (B, M = Ga)

The In–(N–N)$_2$–In rings in the organoindium diazoles II and III are undoubtedly non-planar, as may be concluded by consideration of the structures of some analogous Ga compounds that have been studied by X-ray diffraction [9]. In likewise the (probably) tetrameric derivative IVb can be assumed to have a similar ring structure to that in the Ga-compound $[Et_2GaN_2C_3CH_3]_4$, although the nature and extent of the [M–(NCN)]$_4$-ring puckering may not be necessarily identical [7].

Although the bands of the heterocyclic ligands (NR′) dominate the vibrational spectra (IR and Raman) of the new compounds, observation of the main character-

Table 2

Mass spectral data for compounds I, IIa, IIIa, IIIb and V (70 eV, source temperature 25–35 °C, relative intensities in %)

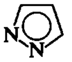
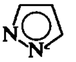
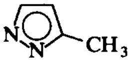
Compound fragment ion	m/z (Int)				
	I	IIa	IIIa	IIIb	V (100 °C)
$[M_3-R]^+$	–	–	–	–	624 (1.5)
$[M_2]^+$	422 (9.3)	–	–	–	426 (0.5)
$[M_2-R]^+$	407 (29.5)	409 (89)	451 (100)	479 (100)	411 (100)
$[M_2-2R]^+$	392 (1.7)	–	422 (14)	–	396 (12)
$[M_2-3R]^+$	–	379 (9)	393 (27)	421 (32)	381 (4)
$[M_2-(NR')]^+$	356 (34.1)	–	–	–	358 (2.5)
$[M_2-R-(NR')]^+$	–	342 (86)	384 (3)	398 (12)	343 (14)
$[M_2-2R-(NR')]^+$	326 (14.1)	–	–	–	328 (3)
$[M_2-3R-(NR')]^+$	–	–	326 (7)	340 (13)	313 (1.5)
$[In_2(NR')]^+$	296 (3.9)	297 (5)	297 (17)	311 (17)	298 (9.5)
$[M]^+$	211 (9.3)	212 (2)	–	–	213 (1.5)
$[M-R]^+$	–	197 (32)	211 (78)	225 (14)	198 (17)
$[In(NR')]^+$	181 (3.1)	182 (15)	182 (6)	196 (7)	183 (8)
$[InR_2]^+$	145 (100)	145 (68)	173 (17)	173 (14)	145 (95)
$[InR]^+$	130 (5.2)	130 (10)	–	–	130 (55)
$[In]^+$	115 (53.3)	115 (100)	115 (65)	115 (51)	115 (67)
$[(NR')]^+$	–	67 (18)	67 (17)	81 (27)	68 (20)
$[(HNR')]^+$	67 (8.7)	–	–	–	–
(NR′) =					

Table 3

NMR spectral data (^1H and $^{13}C\{^1H\}$, δ in ppm relative to $SiMe_4$ at 30 °C) for the compounds I–V and related Ga derivatives

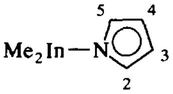
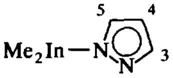
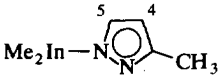
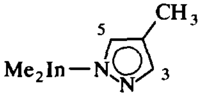
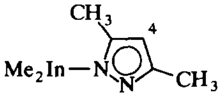
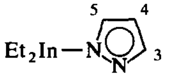
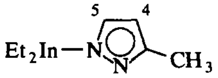
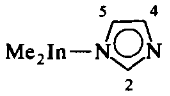
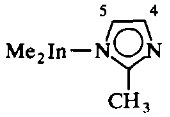
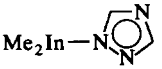
Compound	a: b:	^1H δ(RIn) ^{13}C [J in Hz]	$\delta(CH_3)$	δ(HC-ring) [J in Hz]	Solvent	Ref.
 (I)	a	−0.03(s)	–	6.30(br,$H^{3,4}$), 6.82(br,$H^{2,5}$)	C_6D_6	[a]
	b	−5.5	–	110.2($C^{3,4}$), 129.6($C^{2,5}$)	C_6D_6	[a]
Me_2Ga–...	a	−0.19(s)	–	6.19(m,$H^{3,4}$), 6.67(m,$H^{2,5}$)	C_6D_6	[16]
 (IIa)	a	0.19(s)	–	6.24(t,H^4), 7.43(d,$H^{3,5}$) [2] [2]	C_6D_6	[a]
	b	−7.0	–	105.1(C^4), 140.0($C^{3,5}$)	C_6D_6	[a]
Me_2Ga–...	a	0.03(s)	–	6.04(t,H^4), 7.39(d,$H^{3,5}$) [2.2] [2.2]	C_6D_6	[8]
	b	−6.6	13.0	the same as IIIb	C_6D_6	[a]
 (IIb)	a	−0.10(s)	2.37(s)	6.17(d,H^4), 7.55(d,H^5) [2.1] [2.1]	$CDCl_3$	[10]
Me_2Ga–...	a	−0.13(s)	2.37(s)	the same as IIb	$CDCl_3$	[8,10]
 (IIc)	a	0.20(s)	1.96(s)	7.20(s,$H^{3,5}$)	C_6D_6	[a]
	b	−7.08	8.46	115.1(C^4), 139.5($C^{3,5}$)	C_6D_6	[a]
 (IId)	a	0.04(s)	2.04(s)	5.70(s,H^4)	C_6D_6	[a]
	b	−5.35	13.21	106.1(C^4), 150.8($C^{3,5}$)	C_6D_6	[a]
Me_2Ga–...	a	−0.1(s)	2.4(s)	5.9(s,H^4)	CCl_4	[6,8]
 (IIIa)	a	0.85(q) [8.7] 1.19(t)	–	6.39(t,H^4), 7.64(d,$H^{3,5}$) [2] [2]	$CDCl_3$	[a]
	b	6.6, 11.7	–	104.7(C^4), 139.6($C^{3,5}$)	$CDCl_3$	[a]
Et_2Ga–...	a	0.63(q) 1.09(t)	–	6.13(t,H^4), 7.46(d,$H^{3,5}$)	C_6D_6	[11]
 (IIIb)	a	0.77(q) [8.7] 1.12(t)	2.36(s)	6.15(d,H^4), 7.52(d,H^5) [2] [2]	$CDCl_3$	[a]
	b	6.7, 11.5	12.9	104.6(C^4), 140.5(C^5), 149.3(C^3)	$CDCl_3$	[a]
 (IVa)	a	−0.10(s)	–	6.89(s,$H^{2,4,5}$)	CCl_4	[a]
Me_2Ga–...	a	−0.15(s)	–	6.87(s), 7.05(s)	CCl_4	[8]
 (IVb)	a	−0.01(s)	1.76(s)	6.69(s,$H^{4,5}$)	$CDCl_3$	[7]

Table 3 (continued)

Compound	a: b:	^1H δ(RIn) ^{13}C [J in Hz]	δ(CH_3)	δ(HC-ring) [J in Hz]	Solvent	Ref.
Me_2Ga–...	a	−0.25(s)	1.49(s)	6.81(s)	$CDCl_3$	[7]
 (V)	a	−0.15(s)	–	7.88, 7.91($H^{3,5}$) [2.5]	$(CD_3)_2SO$	[a]
Me_2Ga–...	a	−0.05(s)	–	8.0(s)	$CDCl_3$	[8]

[a] This work; s = singlet, d = doublet, t = triplet, br = broad.

istic vibrations of the R_2In groups usually presents no problem. The data (cm^{-1}) are as follows:

Compound no.	$\nu_{as}(InC_2)$	$\nu_s(InC_2)$	$\rho(CH_3In)$	$\delta_s(CH_3In)$
IIa, c; IVa, b; V	523 ± 3	490 ± 3	715 ± 5(br)	1170 ± 5 + ring-mode
IIIa, b	~ 495	~ 461	~ 633	

Both of the InC_2 vibrations of the compounds containing two or more associated molecules have remarkably constant frequencies for the various compounds. For these vibrations a nearly corresponding (distorted) tetrahedral coordination of the metal atoms is expected. It is also possible to estimate a bond angle of 135 ± 3° for the Me_2In derivatives on the basis of a relationship between $\Delta\nu = (\nu_{as} - \nu_s)$ InC_2 and the C–In–C valence angle [12] (for angles > 115°) or the simple equation: $(\Delta\nu + 102) \pm 3° = \sphericalangle$C–In–C.

In the case of the Me_2In-derivatives the association takes place, as in the homologous, X-ray analyzed Ga compounds [7,9], via (at least) two nitrogen atoms of the aromatic heterocycles. Since the π-system of these rings remains, it was to be expected that the H–N valence and deformation vibrations (e.g. for pyrazole, $HN_2C_3H_3$, at 3507 ν(NH), 1127 δ(NH) and 525 cm^{-1} γ(NH) [13]) would be missing, but not expected were the marked changes in the ring modes, especially for the various C–H vibrations. The compilation in Table 4 presents selected data from the spectra of the dialkylindium derivatives of pyrazoles (and substituted pyrazoles). It shows the ring vibrations with the highest frequencies, as well as some ring and C–H deformations. For comparison the corresponding vibrations for pyrazole are also shown. From this Table it can be seen that substitution of a ring H-atom by a methyl group causes a more drastic change in the frequencies than does replacement of a nitrogen-bonded H-atom by a R_2In group. A similar comparison can be made between the spectra of imidazole [15] and its derivatives IVa and IVb [16].

The In–N vibrations of the complex molecule frame $(In–N–N–)_n$ (n = 2–4) are not characteristic, so give no information about the ring structure. For the dimeric amino compounds of the type $(R_2In–NR'_2)_2$, frequencies around 450 ± 50 cm^{-1} are assigned to the In–N vibrations [4,17]. We think that this frequency band is substantially lower for the dialkylindium azolides II–V (by approximately 280 ± 50 cm^{-1}) and so can only be seen in the Raman spectrum because the IR spectrum is limited by the conditions of measurement. We assigned the following polarized

Table 4

Some IR and Raman spectral data for pyrazole and compounds IIa, IIc, IIIa and IIIb [a]

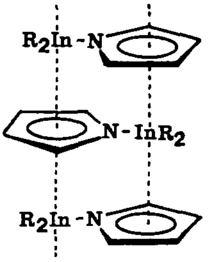
Compound	$HN_2C_3H_3$		IIa	IIc	IIIa	IIIb
	matrix [13]	solution [14]	liquid	liquid	liquid	liquid
ν(ring)	1530s/-	1543w/-	1522mw/vw,p	1565m/w,p	1513w/vw,p	1498ms/mw,p
	1449s/-	1450w/-	1495ms/vw,p	1455-/vw,p	1491ms/vw,p	1489ms/vw
	1393s/-	1397s/-	1412ms/vw,dp	?	1412ms/vw,dp	1422mw/w,dp
	1357m/-	1360s/-	1374s/mw,dp	1362ms/w,dp	1372s/m,dp	1373mw/vw,dp
δ(CH)	1256m/-	1265w/-	1269s/ms,p	1311s/mw,p	1268ms/ms,p	1321mw/ms,p
δ(ring)	909m/-	910m/-	921mw/mw,p	1018s/s,p	917w/m,p	916-/m,p
γ(CH)	748vs/-	760s/-	755vs/vvw	830vs,br/vvw	755vvs/vvw	767vs/vw,dp
γ(ring)	612w/-	613s/-	622s/vw,dp	622s/w,dp	619s/vw,dp	~ 625s/vw,dp

[a] Intensities for IR/Raman: vs = very strong, s = strong, m = middle, w = weak, vw = very weak, p = polarized, dp = depolarized, br = broad.

Raman frequencies of strong to medium intensity to a vibration with a high In–N valence bond contribution: 249 (IIa), 234 (IIIa), 228 (IIc) and 226 (IVa) cm^{-1}.

The pyrrole compound I does not fit into this otherwise general binding scheme: the InC_2 vibrations with the wavenumbers of 531 (ν_{as}) and 485 (ν_s) cm^{-1} fall outside the specified narrow limits; the frequency difference $\Delta\nu$ corresponds to an C–In–C angle of around 150 °. The light sensitivity, the comparatively low solubility in aprotic, organic solvents, and the low decomposition temperature are additional properties that distinguish compound I from the di- and tri-azoles II to V. As the vibrational spectra of I is very similar to those of pyrrole above 600 cm^{-1}, the association can not involve the single nitrogen atom of the pyrrole ring since this would destroy the π-system of the heterocycle.

In the ideal symmetric arrangement, single (nearly) planar molecules are linked by the π-system of the pyrrole ring. This structure with five-fold coordinated metal centres is almost similar to that of the propynyl species $[Me_2InC{\equiv}CCH_3]_n$ [18]:



Instead we favour a structure more or less like that of the analogous $[Me_2GaC_5H_5]_n$ [19] because of the analogy with the cyclopentadiene derivative $[Me_2InC_5H_5]_n$ [20], which is isoelectronic with $[Me_2InNC_4H_4]_n$ and also has comparable properties.

Whether discrete dimers or only fragments of a polymeric chain exist in the gaseous state or in solution cannot be decided by vibrational spectroscopy because of the low volatility and low solubility, respectively.

Table 5

Vibrational spectrum (IR and Raman) for $Me_2InNC_4H_4$ (I)

IR (Int) [a] (Nujol/KEL-F)	RE (Int) [b] (solid)	Assignment
3108vw,sh	–	
3085w	–	ν(CH-ring)
306vw,sh	–	
2967mw	–	
2913w	–	$\nu_{as}(CH_3)$
2913w	–	$\nu_s(CH_3)$
1481w	–	
1446mw	1450vw,br	ν(ring)
1400w	–	$\delta_{as}(CH_3)$
1368mw	1364w	
1295m	–	ν(ring)
1230m	–	
1168m	–	
1160m,sh	1161m	$\delta_s(CH_3) + \nu_s$(ring)
1152s	1151w	
1091s	1088w	
1080ms,sh	–	
1045m	–	δ(CH-ring, in plane)
1026vs,br	–	
909ms	908w	
878vw	–	δ(ring, in plane)
851s	–	
827m	825w,br	γ(CH-ring)
781ms	–	
732ms	–	
719vs,br	–	$\rho(CH_3)$
641s	–	
616s	–	γ(ring)
552vw	–	?
531m	530w,br	$\nu_{as}(InC_2)$
508m	503vw,br	ν(InN)
482ms	485vvs	$\nu_s(InC_2) + \gamma$(ring)
408w	–	
375w	–	ν(In-ring)

[a] Intensities see Table 4. [b] Raman spectrum recorded with a rotating sample holder [23]; because of the light sensitivity of the compound the spectrum is only of low quality.

In the assignment of the listed IR and Raman frequencies of I in Table 5 the spectra of $R_2MC_5H_5$ (R = Me, Et and M = Ga, In) [19,21] and the vibrational analysis of the starting material HNC_4H_4 [22] and of the lithiated compound $LiNC_4H_4$ [16] were used for comparison.

Epitaxial growth

In a study of the value of the investigated compounds in MOVPE, the most promising precursor IIa was condensed into a standard glass bubbler, which was then attached to a MOVPE apparatus designed for testing of novel precursors of unknown or low vapor pressure. It consists of a horizontal quartz reaction chamber with rectangular cross section heated by lamps, a gas manifold in vent-run configuration and conventional gas channels for H_2 and PH_3. The organometallic gas channel is designed so that all gas lines from the bubbler to the reactor can be heated to any chosen temperature between room temperature and ca. 130 °C. Thus even for precursors needing high bubbler temperatures (due to their low vapor pressure) precondensation in the gas lines or valves can be suppressed. Bubbler temperatures up to about 80 °C can be used. All growth parameters except for those for the In-bubbler were adjusted as in our standard InP growth (see, e.g., [3] and [24]): Growth temperature, 580 °C; PH_3 flow (10% in H_2), 30 sccm; Total H_2 flow, 2.8 slm; Reactor pressure, atmospheric. The Me_2In-pyrazole bubbler temperature was varied between 50 and 80 °C, and the bubbler flow was adjusted to 80 or 100 sccm.

At lower bubbler temperatures and moderate growth times the grown InP layers were too thin to be directly evaluated by our standard method. Thus, the thickness was measured by secondary ion mass spectroscopy (SIMS). At a bubbler temperature of 80 °C, a bubbler flow of 100 sccm, and growth times of up to 6 h, layers thick enough for direct evaluation could be grown with a growth rate of about 0.5 μm/h. By comparing the growth rates with those obtained with DADI as In-precursor in the same MOVPE reactor [3], we estimated a vapor pressure of 40 Pa at 80 °C for Me_2In-pyrazole. All layers showed mirror-like surfaces to the naked eye, but with some fine structure visible in an interference-contrast microscope. We could not detect any predeposits upstream of the susceptor, this behaviour being

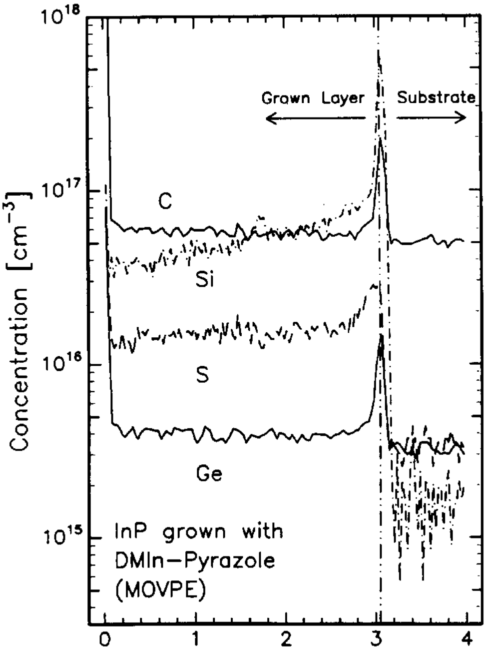


Fig. 1. Results of Secondary Ion Mass Spectroscopy (SIMS) of an InP-layer grown by MOVPE using Me_2In-pyrazole IIa as In precursor. The elements C, Si, S and Ge have been evaluated.

similar to that for DADI and the well-known $Me_3In\text{-}PEt_3$ adduct [2]. In particular, no side reactions of Me_2In-pyrazole with PH_3 could be detected. A preliminary electrical evaluation of these layers by Hall experiments in van der Pauw geometry showed a rather high concentration of *n*-type dopant impurities. (We evaluated carrier concentrations $n = 6$ and 4×10^{16} cm^{-3} and mobilities of $\mu = 3350$ and 5300 cm^2/Vs at room temperature and 77 K, respectively.) This is probably due to the limited purity of this first batch. Low-temperature photoluminescence experiments confirmed these results. Some increase in purification in the bubbler by bubbling hydrogen, previously observed for many compounds, was detectable in Hall and SIMS experiments. The latter showed that Si and S were the main impurities, with concentrations in the purest layers of 5×10^{16} and 1.5×10^{16}, respectively (see Fig. 1), in good agreement to the Hall experiments, while C and Ge were detected only near the detection limit (6×10^{16} and 4×10^{15} cm^{-3}, respectively).

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