Inorganica Chimica Acta, 170 (1990) 95–101

Synthesis and Reactivity of Dimethylindium Derivatives: Molecular and Electronic Structure of Bis(μ-diethylamido)-tetramethyldi-indium(III)*

G. ROSSETTO, D. AJÒ, N. BRIANESE, U. CASELLATO, F. OSSOLA, M. PORCHIA, A. VITTADINI, P. ZANELLA
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti, 35100 Padua (Italy)
and R. GRAZIANI
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, 35100 Padua (Italy)

(Received October 6, 1989)

Abstract

Me_2InCl reacts with $LiNEt_2$ in diethyl ether solution to give the easily sublimable compound $[Me_2InNEt_2]_2$ whose UV photoelectron spectra are reported and discussed in combination with its molecular and crystal structure, in particular as regards the In–N interactions within the dimeric molecule. Reactions of $[Me_2InNEt_2]_2$ with moderately acidic agents such as R_2PH lead to cleavage of the In–NEt_2 bond and formation of Me_2InPR_2 ($R = Et, C_6H_5$).

Introduction

Organometallic chemistry of group 13 elements (Ölander numbering) is attracting renewed interest due to the large utilization of these compounds (together with group 15 hydrides) as precursors in the preparation of epitaxial thin films of III–V semiconductors by MOVPE (metal-organic vapour phase epitaxy) or MOMBE (metal-organic molecular beam epitaxy) [1]. Investigations are aimed at elucidating the reaction mechanism which is still unclear and at solving several problems still existing in the MOVPE technique such as: carbon incorporation as unwanted dopant, parasitic prereactions, high toxicity of arsine and phosphine, hazards connected to the pyrophoric character and high sensitivity to moisture of metal alkyls. In this context intense efforts are devoted at present to the synthesis of organometallic compounds containing both group 13 and 15 elements in the same molecule and to test the possibility for their use as precursors; this characteristic could make the process of epitaxial growth easy [2].

We have undertaken a systematic investigation in this field and here we report a convenient method for the synthesis of $[Me_2InNEt_2]_2$, the determination of its molecular structure by X-ray diffraction and information about its electronic structure obtained by UV photoelectron (PE) spectroscopy. The combination of PE and mass spectroscopies has been recently proved useful in the investigation of group 15 ring systems and their thermal fragmentations products [3]. Moreover, its reactivity in the protolytic reaction with R_2PH that has led to the formation of the new organoindium derivative $[Me_2InP(C_6H_5)_2]_2$ is described.

Experimental

All operations were carried out in purified nitrogen filled glove boxes. Solvents were dried and purified by standard procedures [4]. Me_2InCl [5] and $LiNEt_2$ [6] were synthesized according to published procedures. Commercially available anhydrous $InCl_3$ (Ventron Alfa), solutions of LiMe in Et_2O and of $LiBu^n$ in hexane (Aldrich), and all the dialkylphosphines (Ventron Alfa) were employed without further purification. Proton NMR spectra were recorded on a Bruker AC 200 instrument; the solutions of the sample were prepared using anhydrous C_6D_6 (C_6D_5H as internal standard, chemical shifts calculated with respect to $SiMe_4$). Infrared spectra, in the range 4000–600 cm^{-1} were recorded on a Perkin-Elmer spectrophotometer 580 B using nujol mulls (between NaCl or KBr disks in an air-tight holder sealed with an O-ring). Mass spectra were recorded on a V.G. Organic Ltd. ZAB 2F spectrometer ($EI = 70$ eV; probe temperature 100 °C; in the assignments In refers to ^{115}In). Elemental analyses were carried out by Dornis u. Kolbe, Mikroanalytisches Laboratorium, Mülheim, F.R.G.

---

*A preliminary account was presented at the XIII International Conference on Organometallic Chemistry, September 4 - 9, 1988, Torino, Italy.

In addition we wish to inform readers that a paper [17], describing the molecular structure of the same compound and whose data agree with ours, has appeared when the manuscript of this article was already drawn up.

0020-1693/90/$3.50

Synthesis of [Me_2InNEt_2]$_2$

A total of 0.079 g (5 mmol) of $LiNEt_2$ was added with vigorous stirring to a suspension of 0.827 g (5 mmol) of freshly prepared Me_2InCl in 20 ml of Et_2O. The suspension was kept under vigorous stirring at room temperature for 24 h. After this time the mixture was filtered to separate the formed LiCl and the solvent was removed under vacuum. The resulting white glassy product was sublimed at 37 °C, $P = 5 \times 10^{-3}$ mmHg, giving a white crystalline solid, yield 75%.

Anal. Found: C, 33.38; H, 7.35; N, 6.35. Calc. for $C_6H_{16}NIn$: C, 33.21; H, 7.43; N, 6.45%.

Vapor Phase Pyrolysis of [Me_2InNEt_2]$_2$

The apparatus used consists of two coaxial quartz tubes with a gold foil put on the external bottom of the inner tube which was heated by an inside electrical resistance. $[Me_2InNEt_2]_2$ was placed on the bottom of the tube which was thermostated at 37 °C and connected to a vacuum pump. The gold foil was heated at 400 °C and after 30 min, the experiment was stopped and the apparatus was allowed to cool to room temperature. The obtained deposit on the gold foil was analyzed by SIMS and identified as very pure metallic indium. $m/z = 113$ ($I = 4\%$), and $m/z = 115$ ($I = 96\%$). No other species were detected.

Synthesis of [Me_2InPEt_2]$_3$

A total of 0.090 g (5 mmol) of Et_2PH was slowly added to a stirred solution of 1.085 g (5 mmol) of $[Me_2InNEt_2]_2$ in toluene (50 ml). The mixture was stirred, at room temperature for 24 h and then refluxed for 6 h. The solvent was removed under vacuum, and the resulting glassy product was dried *in vacuo* for 2 h.

Anal. Found: C, 31.5; H, 7.05; P, 12.84. Calc. for $C_6H_{16}PIn$: C, 30.80; H, 6.89; P, 13.24%.

Synthesis of [Me_2InPPh_2]$_2$

A total of 0.269 g (5 mmol) of Ph_2PH was added to a stirred solution of 1.085 g (5 mmol) of $[Me_2InNEt_2]_2$ in toluene (50 ml). The mixture was stirred at reflux for 6 h and then the stirring was continued, at room temperature, for a further 18 h. The suspension was filtered (a very small amount of grey powder identified as indium by SIMS was formed), the solvent was removed under vacuum and the resulting product was dried under vacuum for 2 h, obtaining a white powder.

Anal. Found: C, 51.22; H, 5.16; P, 10.55. Calc. for $C_{14}H_{16}PIn$: C, 50.94; H, 4.89; P, 9.38%.

X-ray Crystallography of [Me_2InNEt_2]$_2$

Crystals of $[Me_2InNEt_2]_2$ suitable for X-ray determination were obtained by slow sublimation at 37 °C, $P = 5 \times 10^{-3}$ mmHg. A crystal of max. dimensions 0.2 mm, sealed under nitrogen in a thin-walled glass capillary was used for the X-ray measurements. Data collection was made on a Philips diffractometer with Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal data: $C_{12}H_{32}N_2In_2$, formula weight 431.6, triclinic, $P\bar{1}$, $a = 8.373(5)$, $b = 8.485(5)$, $c = 7.557(5)$ Å, $\alpha = 118.24(3)$, $\beta = 76.00(3)$, $\gamma = 103.60(3)°$, $V = 454.4$ Å^3, $D_c = 1.58$ g cm^{-3} for $Z = 1$, $\mu = 24.9$ cm^{-1}.

Quantum Mechanical Calculations

The molecular geometry was taken from the X-ray crystal structure of the methylated derivative [7], since the difference between the latter structure and that described elsewhere in the present paper is not significant.

Hartree–Fock–Slater (HFS) Discrete Variational (DV-Xα) calculations [8] were performed on a VAX-11/750 (Digital Equipment Corporation) computer.

Numerical atomic orbitals (through 5d on In, 2p on C, N and 1s on H) obtained for the neutral atoms were used as basis functions. Due to the size of the investigated systems, orbitals 1s–4p (In) and 1s on both carbon and nitrogen were treated as a part of a frozen core in the molecular calculations, after being orthogonalized against the valence orbitals. In calculating the potential, the true charge density was replaced by a superimposition of multipolar densities in addition to atomic radial densities, with an expansion basis consisting of five localized radial functions multiplied by spherical harmonics with $l = 0$, 1, 2 attached to nuclear sites. The Gaspar–Kohn–Sham value was used for exchange-correlation scaling parameter [9]. The Mulliken scheme was used to compute atomic orbital populations and Slater's transition state (TS) formalism [10] was used to calculate the ionization energies (IEs).

Photoelectron Spectra

He(I) and He(II) excited PE spectra were recorded at 35 °C on a Perkin-Elmer PS-18 spectrometer modified by inclusion of a hollow-cathode discharge lamp giving high photon flux at the He(II) wavelengths (Helectrons Developments). The spectrometer was connected in line with a MINC 23 computer (DEC). Data acquisition was carried out by several sweeps over 500 distinct channels. Typical sweep time amounts to 5–10 min. The spectra were calibrated by reference to the peaks of inert gases admitted into the target chamber and to 1 s^{-1} He self ionization.

Results and Discussion

$R_2InNR'_2$ (R, R′ = alkyl group) compounds have been obtained by thermal decomposition of the adducts $R_3InNR'_3$ [7, 11, 12]. We have found that treatment of Me_2InCl with $LiNEt_2$ in Et_2O solution, at room temperature and in a 1:1 molar ratio produced $[Me_2InNEt_2]_2$ according to the reaction

$$Me_2InCl + LiNEt_2 \longrightarrow Me_2InNEt_2 + LiCl$$

that represents an alternative method for the formation of the In–N bond. $[Me_2InNEt_2]_2$ is an oily compound, at room temperature, and it can be obtained as a white crystalline solid by sublimation. It is very volatile and soluble in diethyl ether, tetrahydrofuran and both in aromatic and aliphatic hydrocarbons and undergoes easy protolytic cleavage of the In–N bond by R_2PH ($R = Et, C_6H_5$) according to the reaction

$$Me_2InNEt_2 + R_2PH \longrightarrow Me_2In\text{-}PR_2 + HNEt_2$$

that is a very useful synthetic route to pure compounds containing In–P bonds. The already described $[Me_2InPEt_2]_3$ was identified by its known IR spectrum [13] and elemental analyses; in addition its ^1H NMR and mass spectrum are reported and discussed here. On the other hand $[Me_2InP(C_6H_5)_2]_2$ represents a new organoindium derivative; it is a white substance, poorly soluble in benzene and does not sublime but decomposes at 100–120 °C, giving mainly tetraphenyldiphosphine together with other unidentified products as detected by mass spectrometry. This is the main reason why a study of this compound by PE spectroscopy has not so far been successful.

The infrared spectra of the two new organoindium compounds are reported in Table 1. $[Me_2InNEt_2]_2$ shows bands due to In–C and N–C bonds that have been assigned by comparison with the spectrum of the analogous $[Me_2InNMe_2]_2$ suggesting a dimeric nature of the compound [7]; other bands in the range 850–543 cm^{-1} are not assignable but are known to be present in other metallo–diethylamido complexes [14, 15]. On the other hand $[Me_2InP(C_6H_5)_2]_2$ shows a band at 1156 cm^{-1} assignable to the stretching CH_3–In [13] and other characteristic absorptions due to the phenyl groups bonded to a phosphorous atom [16].

TABLE 1. Infrared spectra

$[Me_2InNEt_2]_2$		$[Me_2InP(C_6H_5)_2]_2$	
Wavenumbers (cm^{-1})	Assignment	Wavenumbers (cm^{-1})	Assignment
1511w		1570w	δ C=C
1162w	δs CH_3–In	1305m	
1146s	ρ C–N	1156w	δs CH_3–In
1110w		1026m	P–C_6H_5
1043m	νas NC_2	730s	π C–H
1002m	νs NC_2	691m	
898w			
850w			
792m			
701m			
561m			
543w			
508m	νas InC^2		
478w	νs InC_2		

TABLE 2. ^1H NMR spectra

Compound	Chemical shifts (ppm)	Assignments
$[Me_2InNEt_2]_2$	0 (s, 6H)	CH_3–In
	2.93 (q, 4H)	$\mathrm{N-C}H_2\mathrm{-CH_3}$
	0.86 (t, 6H)	$\mathrm{N-CH_2-C}H_3$
$[Me_2InPEt_2]_3$	0.12 (s, 6H)	CH_3–In
	1.68 (q, 4H)	$\mathrm{P-C}H_2\mathrm{-CH_3}$
	1.09 (m, 6H)	$\mathrm{P-CH_2-C}H_3$
$[Me_2InP(C_6H_5)_2]_2$	0.26 (s, 6H)	CH_3–In
	7.03 (m, 3H)	C_6H_5 *m, p*
	7.50 (m, 2H)	C_6H_5 *o*

The ^1H NMR spectra in C_6D_6 are reported in Table 2. They agree with the proposed formulations and the signals can be easily assigned on the basis of their intensities and multiplicities.

The mass spectra of the compounds were obtained under electron impact (EI) conditions and the m/z values and the abundances of the most significant fragments are reported in Table 3. The ions present in the spectrum of $[Me_2InNEt_2]_2$ indicate its dimeric nature in the gas phase. The relative abundance of the parent ion $2M^+$, ($m/z = 434$) is very low ($I = 1$), it easily loses NEt_2 or CH_3 giving more stable fragments. In Scheme 1 we suggest the possible decomposition pathway with some probable structures of fragment ions. It is probable that the ion 419 m/z is, at first, formed with the structure (A) and subsequently it changes into structure (B) that better explains the formation of other abundant fragments present in the spectrum.

The mass spectrum of $[Me_2InPEt_2]_3$ does not contain the parent ion assignable to the trimeric species; however the trimeric nature can be inferred by the presence of the primary ion at $m/z = 687$ corresponding to a species arising from $[Me_2InPEt_2]_3$ by loss of a CH_3 group. Other numerous and important ion fragments result from the loss of Me, Et and PEt_2 groups. Moreover it is observed that the spectrum presents peaks assignable to $Et_4P_2^+$ and to its decomposition fragments; this can be probably due to the thermal decomposition of $[Me_2InPEt_2]_3$ species under the experimental conditions.

The same behaviour is strongly pointed out by $[Me_2InP(C_6H_5)_2]_2$. In fact its mass spectrum presents a peak, at very low relative abundance ($I = 1.3$), due to a protonated dimer indicating the dimeric nature of the compound in the gas phase, and other very

TABLE 3. Mass spectra

$[Me_2InNEt_2]_2$			$[Me_2InPEt_2]_3$			$[Me_2InP(C_6H_5)_2]_2$		
m/z	Relative abundance	Assignments	*m/z*	Relative abundance	Assignments	*m/z*	Relative abundance	Assignments
434	1	$In_2N_2Et_4Me_4^+$	687	5	$In_3P_3Et_6Me_5^+$	661	1.3	$In_2P_2Ph_4HMe_4^+$
419	48	$In_2N_2Et_4Me_3^+$	658	0.5	$In_3P_3Et_5Me_5^+$	475	1.8	$In_2PPh_2Me_4^+$
362	39	$In_2NEt_2Me_4^+$	612	2	$In_3P_3Et_6^+$	370	44	$P_2Ph_4^+$
275	7	$InN_2Et_2MeH^+$	526	7	$In_3P_3Et_2Me_2^+$	262	11	PPh_3^+
217	9	$InNEt_2Me_2^+$	468	2	$In_2P_2Et_4Me_4^+$	185	100	PPh_2^+
216	100	$InNEtCHCH_3Me_2^+$	453	30	$In_2P_2Et_4Me_3^+$	184	100	$PPhC_6H_4^+$
202	40	$InNEt_2Me^+$	451	21	$In_3P_2CEtMe^+$	183	100	$P(C_6H_4)_2^+$
187	9	$InNEt_2^+$	423	3	$In_2P_2Et_4Me^+$	145	100	$InMe_2^+$
186	16	$InNEtCHCH_3^+$	394	4	$In_2P_2Et_3Me^+$	139	13	P_2Ph^+
172	14	$InNEtCH_2^+$	379	26	$In_2PEt_2Me_4^+$	130	20	$InMe^+$
145	91	$InMe_2^+$	349	8	$In_2PEt_2Me_2^+$	115	100	In^+
143	5	$InMeCH^+$	318	5	$In_2Et_2Me_2^+$	109	82	$PPhH^+$
131	4	$InMeH^+$	305	2	In_2PEtMe^+	108	100	PPh^+
130	6	$InMe^+$	293	3	$InP_2Et_4^+$	107	100	$PC_6H_4^+$
115	88	In^+	234	2	$InPEt_2Me_2^+$			
			219	33	$InPEt_2Me^+$			
			204	7	$InPEt_2^+$			
			178	3	$Et_4P_2^+$			
			149	6	$Et_3P_2^+$			
			145	98	$InMe_2^+$			
			115	100	In^+			

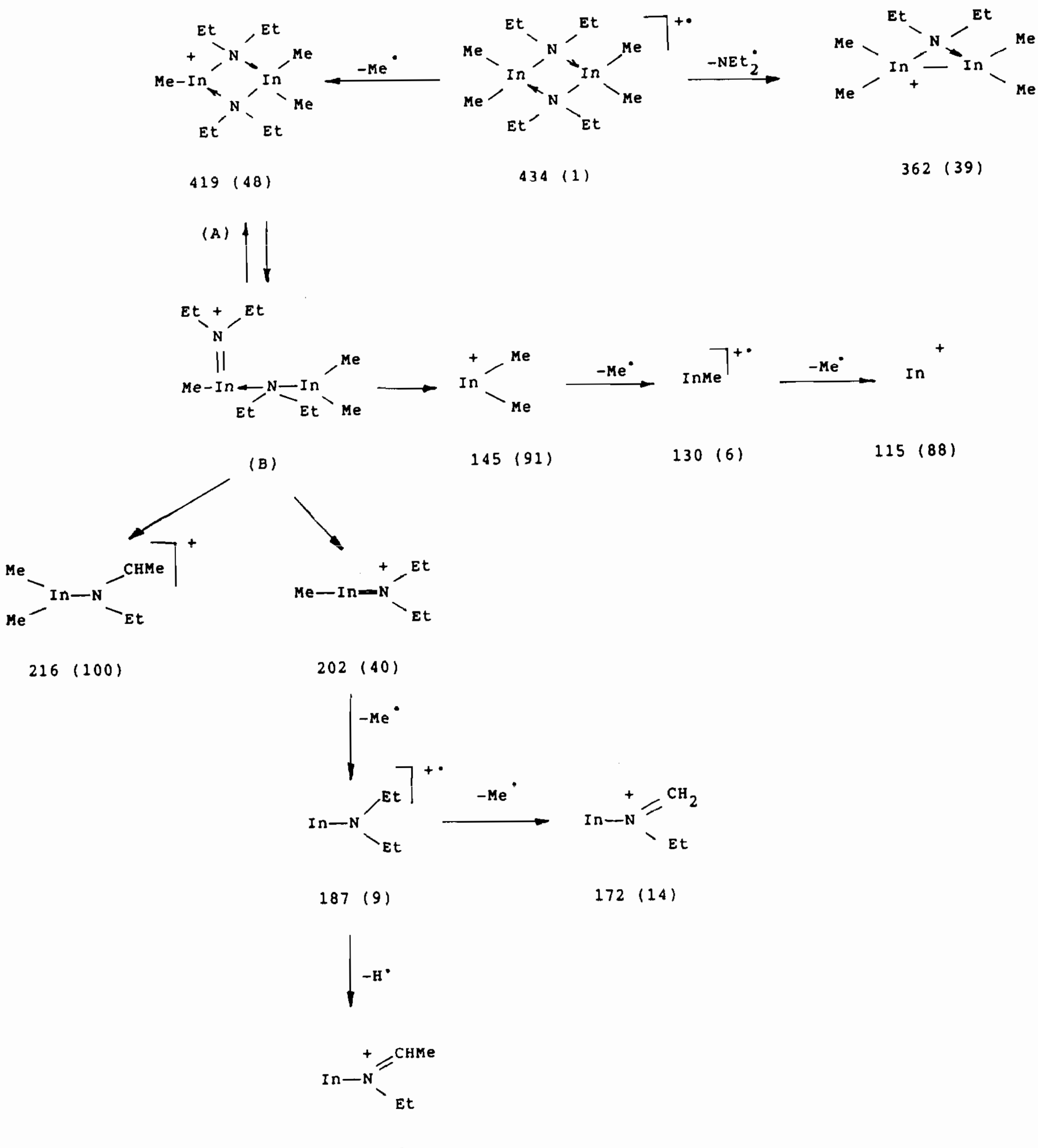
intense peaks assignable to $(C_6H_5)_4P_2$ and derivable from its fragmentation pathway. The high abundance of these peaks suggests that the compound undergoes a facile thermolysis giving tetraphenyldiphosphine.

The structural data of $[Me_2InNEt_2]_2$ agree with those recently published in ref. 17; the molecule is centrosymmetric (point symmetry C_i) and it may be described as a dimeric unit in which an almost square N_2In_2 cycle is held together by two bonds In–N of the same length, in which the sp^3 ibridization of both In and N atoms make indistinguishable the formally covalent and coordinative In–N bonds. The asymmetric unit of the triclinic cell comprises one half molecule. The N_2In_2 moiety is planar and the In...In contact distance [3.270 Å] is longer than the N...N one [3.044 Å], which obliges the N–In–N angles [85.9°] to be slightly smaller (and the In–N–In angles to be larger) than 90°. Nevertheless, the geometrical constraints of the tetra-atomic cycle, obliging the mentioned angles to be significantly smaller than 109°, causes an enlargement of the opposite C–N–C [113.2°] and especially of the C–In–C [125.3°] angles, introducing severe distortions in the tetrahedral arrangements around these atoms. As already observed in other indium compounds [7, 18], the In–C distances agree with the sum of the covalent radii, while In–N are slightly longer. However, the $(CH_3)_2In$ systems, in the present and other papers [7, 19], exhibit significantly shorter In–N distances with respect to analogous $(CH_3)_3In$ adducts [18c]. The structure as a whole strictly resembles that of other dialkylamido indium compounds such as $[Me_2NInMe_2]_2$ [7] and $\{Me_2In[\overline{N(CH_2)_2N(Me)CH_2\dot{C}H_2}]\}_2$ [19] with comparable values for bond distances and angles. Moreover, a significant difference can be noted for the In–N lengths in $[Me_2InN(CH_3)(C_6H_5)]_2$ [12]. In fact the In–(μ-NEt_2) distances of 2.233(5) and 2.234(5) Å are shorter than the In–(μ-$N(CH_3)(C_6H_5)$) distances of 2.280(2) and 2.284(2) Å. This can be explained on the basis of the resonance due to the aromatic ring that decreases the electron density of the nitrogen atom reducing the strength of the In–N bonds.

Electronic Structure

On the basis of the results of mass spectroscopy the dimeric form of $[Me_2InNEt_2]_2$ has been assumed in the interpretation of UV photoelectron spectra of Me_2InNEt_2. In order to reduce computational efforts, the ethyl groups have been replaced with methyl ones, and the molecular geometry has been idealized to D_{2h} symmetry. (See 'Experimental'.)

The $In_2R_4N_2R'_4$ system is isoelectronic with cyclobutane. apart from substitution of hydrogen atoms with alkyl groups. In the four-member cycle, σ MOs originating from n_σ and n_π MOs of methylenic fragments transform as $a_{1g} + b_{1g} + e_u$ (in the D_{4h} point group) or $a_g + b_{1g} + b_{2u} + b_{3u}$ (in D_{2h}),



Scheme 1.

and they correspond to MOs $8a_g$, $7b_{3u}$, $6b_{2u}$, $4b_{1g}$ (see Table 4). Apart from the ring system, the other low-energy MOs represent the In–C and C–H bonding interactions, since N–C bonding orbitals are considerably more stable.

The He(I) and He(II) PE excited spectra of $[Me_2InNEt_2]_2$ are shown in Fig. 1.

On the basis of transition-state ionization energy (*TSIE*) calculations, we expect six ionization events in the low *IE* part of the PE spectrum. Actually, in the 7–11 eV spectral region are present five well distinguishable bands (labeled A, B, C, D and E) [measured vertical *IE* values (eV): 7.87, 8.35, 8.66, 9.57 and 9.79], plus a not clearly discernible shoulder B′ on the low *IE* side of band B. Following the striking agreement between computed and experimental *IE* pattern, we can straightforwardly assign the low *IE* bands (see Table 4).

TABLE 4. Charge density analysis of $[Me_2InNMe_2]_2$ and spectral assignments

MO	ϵ	*TSIE*	Orbital composition (%)[a]						Overlap population		Character	Assignment
			2In			$4CH_3$	2N	$4CH_3'$	In–N	In–C		
			s	p	d							
$7b_{3u}$	−5.30	7.72		5	2	21	47	24	0.056	0.005	σ_{In-N}	A
$4b_{1g}$	−5.39	8.02		6	1		59	33	0.108	−0.002	σ_{In-N}	B′, B, C
$5b_{2g}$	−6.20	8.53		11	2	85		2	0	0.127	σ_{In-C}	
$7b_{1u}$	−6.28	8.61		14	1	82		3	−0.005	0.133	σ_{In-C}	
$6b_{2u}$	−6.88	9.70		3	2	1	64	30	0.053	−0.004	σ_{In-N}	D, E
$9a_g$	−7.09	9.34	10	12	2	53	16	6	0.008	0.100	σ_{In-C}	
$6b_{3u}$	−8.18		39		1	39	3	18	0.037	0.122	σ_{In-C}	
$6b_{1u}$	−9.10					33	5	62	0	0	$\sigma_{CH_3'}$	
$5b_{3g}$	−9.14					25	6	69	−0.001	−0.001	$\sigma_{CH_3'}$	
$4b_{2g}$	−9.35					95		5	0	−0.001	σ_{CH_3}	
$3a_u$	−9.43				1	87		12	0	−0.003	σ_{CH_3}	
$8a_g$	−9.46		23	1	1	24	22	29	0.075	0.030	σ_{In-N}	

Net atomic charges[a] (Mulliken populations): In, +1.13; C, −1.09; H, +0.23; N, −0.41; C′, −0.73; H′, +0.26. [a]The primes refer to methyl groups bonded to nitrogen atoms.

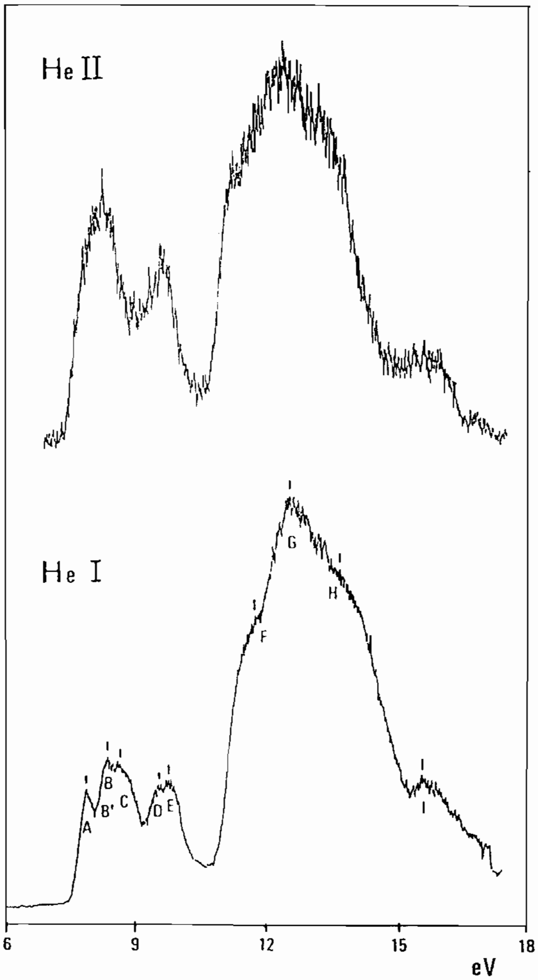


Fig. 1. He(I) and He(II) PE excited spectra of $[Me_2InNEt_2]_2$.

The He(II) spectrum is of little help in our assignment. In fact, In AOs are almost uniformly spread on the outer MOs.

Conclusions

$[Me_2InNEt_2]_2$ has been readily formed by replacing Cl of Me_2InCl by the NEt_2 group; its dimeric structure is due to the coordinative interaction of the N lone pair electron of a Me_2InNEt_2 unit with the vacant 5p orbitals of the In atom of another Me_2InNEt_2 unit. Results obtained by PE spectroscopy about the electronic structure are in tune with the assumption of the dimeric form even though the presence of the monomeric form cannot be ruled out. As regards the interactions within the $(In-N)_2$ cycle, the In–N OP are comparable to the In–C ones, and the HOMO is strongly involved in the In–N interaction. This could be of interest in reactivity studies and can explain the preferential fission of In–N bond by weak protic reagents such as HPR_2. $[Me_2InNEt_2]_2$ exhibits properties typical of precursors of the MOCVD technique such as a good volatility and pyrolytic decomposition to pure In metal. Several organometallic compounds containing M–N bonds (M = Al, Ga, In) have been recently reported to give good III–V materials [20]. In addition $[Me_2InNEt_2]_2$ is very insensitive to moisture compared to $(CH_3)_3In$. It could be used for the preparation of In based binary pnictides (InP, InAs, InSb) by reaction with P, As, and Sb containing reagents; under such conditions the thermally unstable possibly competitive InN is not formed. Suitable investigations and experiments with MOCVD reactor are planned. Whereas $R_2InPR'_2$ compounds, because of their low volatility, are not useful in this technique, they would seem to be interesting precursors for the MOMBE process that involves very low pressures [2b].

Acknowledgements

The authors are indebted to Mr F. Braga and Mr P. Silvestri for their technical assistance and to Mr B. Facchin for the SIMS spectra.

References

1 (a) R. J. M. Griffiths, *Chem. Ind.*, (1985) 247; (b) B. V. Zhuk, *Russ. Chem. Rev.*, *54* (1985) 770; (c) M. J. Ludowise, *J. Appl. Phys.*, *58* (1985) R31; (d) T. F. Kuech, *Mater. Sci. Rep.*, *2* (1987) 1.

2 (a) A. H. Cowley, B. L. Benac, J. G. Ekerdt, R. A. Jones, K. B. Kidd, J. Y. Lee and J. E. Miller, *J. Am. Chem. Soc.*, *110* (1988) 6248; (b) D. A. Andrews, G. J. Davies, D. C. Bradley, M. M. Faktor, D. M. Frigo and E. A. D. White, *Semicond. Sci. Technol.*, *3* (1988) 1053.

3 S. Elbel, H. Egsgaard and L. Carlsen, *J. Chem. Soc., Dalton Trans.*, (1988) 195.

4 D. D. Perrin, W. L. F. Armarego, D. R. Perrin, in *Purification of Laboratory Chemicals*, Pergamon, New York, 2nd edn., 1982.

5 H. C. Clark and A. L. Pickard, *J. Organomet. Chem.*, *8* (1967) 427.

6 R. G. Jones, G. Karmas, G. A. Martin Jr. and H. Gilman, *J. Am. Chem. Soc.*, *78* (1956) 4285.

7 K. Mertz, W. Schwarz, B. Eberwein, J. Weidlein, H. Hess and H. D. Hausen, *Z. Anorg. All. Chem.*, *429* (1977) 99.

8 (a). F. W. Averill and D. E. Ellis, *J. Chem. Phys.*, *59* (1973) 6412; (b) A. Rosen, D. E. Ellis, H. Adachi and F. W. Averill, *J. Chem. Phys.*, *65* (1976) 3629.

9 (a) R. Gaspar, *Acta Phys. Sci. Hung.*, *3* (1954) 263; (b) W. Kohn and L. J. Sham, *Phys. Rev.*, *A140* (1965) 1133.

10 J. C. Slater, in *Quantum Theory of Molecules and Solids. The Self-consistent Field for Molecules and Solids*, Vol. 4, McGraw-Hill, New York, 1974.

11 O. T. Beachley, G. E. Coates and G. Kohnstam, *J. Chem. Soc.*, (1965) 3248.

12 O. T. Beachley Jr., C. Bueno, M. R. Churchill, R. B. Hallock and R. G. Simmons, *Inorg. Chem.*, *20* (1981) 2423.

13 O. T. Beachley and G. E. Coates, *J. Chem. Soc.*, (1965) 3241.

14 G. E. Coates and R. N. Mukheriee, *J. Chem. Soc.*, (1964) 1295.

15 A..P. Gray, *Can. J. Chem.*, *41* (1963) 1511.

16 L. J. Bellamy, in *The Infrared Spectra of Complex Molecules*, Methuen, London, 2nd edn., 1986, p. 315.

17 K. A. Aitchison, J. D. J. Backer-Dirks, D. C. Bradley, M. M. Faktor, D. M. Frigo, M. B. Hursthouse, B. Hussain and R. L. Short, *J. Organomet. Chem.*, *366* (1989) 11.

18 (a) M. Veith, H. Lange, O. Recktenwald and W. Franck, *J. Organomet. Chem.*, *294* (1985) 273; (b) M. Veith and O. Recktenwald, *J. Organomet. Chem.*, *264* (1984) 19; (c) D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse and B. Hussein, *J. Organomet. Chem.*, *325* (1987) 55.

19 A. M. Arif, D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse and B. Hussain, *J. Chem. Soc., Dalton Trans.*, (1987) 2159.

20 A. Brauers, *Third European Workshop on Metalorganic Vapour Phase Epitaxy, Montpellier, June 5–7, 1989.*