SYNTHESIS AND CHARACTERIZATION OF DIETHYLPHOSPHINO Ga(III) AND In(III) COMPLEXES WITH COVALENT METAL-PHOSPHORUS BONDS

F. MAURY* and G. CONSTANT

Laboratoire de Cristallochimie, Réactivité et Protection des Matériaux, ERA 263, Ecole Nationale Supérieure de Chimie, 118 route de Narbonne, 31077 Toulouse Cedex, France

(Received 22 September 1983; accepted 1 November 1983)

Abstract—The covalent derivatives $[Et_2M-PEt_2]_3$ (M = Ga, In) have been prepared from Lewis acid-base complexes, $R_3M.PHEt_2$, by alkane elimination and characterized by elemental analyses, IR, ¹H and ³¹P NMR spectroscopy. Features of the mass spectra reveal a trimeric form and the strength of the $[M-P]_n$ ring. For the compound $[ClMeGa-PEt_2]_n$, spectral data are consistent with a weakening of the $[Ga-P]_n$ chain, in good agreement with the pyrolysis results.

Group III organometallic trialkyls, $MR_3(M = AI, Ga, In; R = Me, Et)$ and group V hydrides (AsH₃, PH₃) are generally used to elaborate III–V semiconductor materials by the organometallic Chemical Vapour Deposition process.¹ The formation of intermediates such as Lewis acid-base complexes and covalent compounds in the chemical mechanisms^{2,3} led us to use directly these species to simplify and sometimes to improve the process.^{4,5}

The goal of our investigations is to foresee whether organometallic compounds can be used as precursors in this process from their physicochemical properties. The principal adduct limitation, as source of III and V elements, seems to be the relative fragility of the donor-acceptor bonds.⁴ Consequently, molecules with covalent bonds between the III and V elements were interesting to test since covalent bond strength is generally more important than donor-acceptor bond strength.

The reaction of group III trialkyls with ligands containing acidic hydrogen yields adducts which readily eliminate alkanes to produce unsaturated covalent intermediates. Usually, cyclization occurs to give dimeric or trimeric more stable compounds.

$$R_{3}M + HXR'_{2} \rightarrow R_{3}M.XR'_{2}H \rightarrow RH^{\dagger}$$
$$+ [R_{2}M - XR'_{2}]_{n}$$

Such nitrogen-derivatives are very numerous and various⁶⁻⁹ whereas related dialkyl phosphino com-

pounds were essentially studied only by Coates *et* $al.^{10,11}$

In this paper we describe the preparation and the characterization of the cyclic compounds $[Et_2M-PEt_2]_3$ (M = Ga, In) and $[ClMeGa-PEt_2]_n$ and discuss the stability of the $[M-P]_n$ ring.

EXPERIMENTAL

Starting materials

All compounds were handled under purified nitrogen or argon atmosphere. Solvents were purified by conventional means.¹² Triethylgallium (b.p. 140°C/745 mm; lit. 143°C/760 mm) was prepared from the Ga₂Mg₃ alloy by a Grignard reaction.¹³ Triethylindium was obtained by reaction between InCl₃ and an excess of ethyllithium in diethyl ether and purified by distillation (b.p. 64°C/4 mm; lit. $53^{\circ}C/3$ mm). The chlorodimethylgallium (Ventron) and diethylphosphine (Stream Chemical, Inc.) were not purified prior to use. All complexes were prepared by following the same procedure.

Preparation of complexes

(1) $[Et_2Ga-PEt_2]_3$. A slight excess of HPEt; (52.6 mmoles) was slowly added to GaEt; (49.0 mmoles) and cooled to -20° C. The mixture was stirred 15 min at this temperature before being warmed. The temperature was increased and ethane was slowly evolved from 100°C. Heating was progressively increased and controlled in such a way that a regular ethane evolution was observed in the bubbler at the outlet of the apparatus. The volume of alkane was measured with a gas burette

^{*}Author to whom correspondence should be addressed.

Table	1.	Analytical	and	IR	data
-------	----	------------	-----	----	------

	Analys	is fou	nd (cal	cd.) (%) de	egree of	Sublimation	
Compound	С	Н	Ρ	Ga/In	Cl as	sociation	temperature	IR bands (cm ⁻¹)
[Et ₂ Ga - PEt ₂] ₃	43.6 (44.3)	9.3 (9.2)	13.6 (14.3)	32.9 (32.2)	-	3 ^a	100-110°C/0.05	mm 1418, 1243, 1184, 1040, 1029, 990, 973, 959, 930, 889, 754, 739, 646, 527, 498
[ClMeGa - PEt ₂] _n	27.6 (28.6)	5.7 (6.2)	13.9 (14.8)	30.7 (33.4)	16.6 (16.9)	2.6 ^b	150-160°C/0.05	mm 1420, 1250, 1195, 1040, 1030, 970, 945, 920, 890, 850, 815, 755, 660, 580, 560
[Et ₂ In - PEt ₂] ₃	38.2 (36.7)	8.0 (7.6)	12.6 (11.9)	40.8 (43.8)	-	3 ^a	visc. liq.	1418, 1242, 1160, 1040, 1025, 995, 970, 952, 919, 886, 754, 735, 620, 467, 450

a) obtained by mass spectrometry ; b) in benzene solution, by cryoscopic measurements.

connected to the apparatus and heating was maintained until the theoretical volume corresponding to quantitative reaction was obtained (required: 1098 cm^3). In these conditions, the reaction mixture was heated at $100-150^{\circ}$ C for 5 hr. After cooling to room temperature, the remaining white solid mass was dissolved in dry benzene, filtered to remove insoluble particles due to some decomposition, recrystallized and dried under vacuum.

(2) The reaction between HPEt₂ and GaMe₂Cl, led to methane elimination in the range $100-180^{\circ}$ C during 24 hr (volume evolved, found: 1180 cm^3 , required: 1228 cm^3). The white solid compound [ClMeGa-PEt₂]_n was obtained by recrystallization from methylene chloride.

(3) The formation of $[Et_2In-PEt_2]_3$ was easier since ethane was briskly evolved from 20°C. Heating for 2 hr was necessary and the maximum temperature reached at the end of the reaction was 100°C. Removal under vacuum of diethyl ether traces, coming from triethylindium, led to a viscous oil which was subjected to physical measurements (Table 1).

Spectra

IR spectra were recorded as Nujol mulls by using KBr plates in the range 4000–400 cm⁻¹ by means of a Perkin–Elmer model 457 spectrometer. Proton magnetic resonance spectra were recorded at 250 MHz on a Cameca spectrometer and ³¹P

Table	2. '	H	and	³¹ P	NMR	dataª

Compound	Metal		Phosphine		
	CH ₂	снз	CH ₂	СН3	
[Et ₂ Ga - PEt ₂] ₃	0.50 m (J(GaH)2)	1.15 t (8.0)	1.75 q (7.2)	1.13 m (J(PH)14)	- 71.5 s
[Et ₂ In - PEt ₂] ₃	0.63 q	1.29 t (7.8)	1.83 q (7.5)	1.22 m (J(PH)14.5)	- 74.3 s
[C1MeGa - PEt ₂] _n	-	0.54 s	2.44 m	1.64 m	- 68.2 m
* •		0.65 s	<u></u>		

Solvent CDCl₃ ;a) chemical shift (ppm, relative to TMS for ¹H and to H_3PO_4 for ³¹P spectra), multiplicity (s = singlet, t = triplet, q = quartet, m = multiplet), (coupling constant (Hz)).

NMR spectra were obtained at 36.44 MHz on a Brucker instrument. Mass spectra were recorded either on a VG micro mass 70–70 or 305 F mass spectrometer at a ionizing potential of 70 eV, a source temperature of 180–200°C and using direct insertion into the ion source.

RESULTS AND DISCUSSION

According to previous works,^{7,11} the alkane elimination was easier with indium than gallium as metal atom. Moreover, a chlorine atom in place of an alkyl group on the gallium atom seems to increase the difficulty of alkane elimination since the quantitative formation of $[CIMeGa-PEt_2]_n$ requires 24 hr at 100–180°C but only 5 hr at 100–150°C for $[Et_2Ga-PEt_2]_3$ derivative. Thermal decomposition in a sealed tube, at high pressure of reactants, leads frequently to polymer formation¹¹ whereas our procedure led to the isolation of crystalline compounds, as indicated by X-ray powder diffraction pattern of the two gallium derivatives.

IR spectra of these compounds were recorded (Table 1) and the quantitative elimination of al-

kane from adducts, $R_3M \leftarrow PHEt_2$, was verified by the absence of P-H stretching vibrations in the range 2350-2450 cm⁻¹. The characteristic bands of PEt₂, MEt₂ (M = Ga, In) and GaMeCl groups were identified on the basis of previous studies.^{6,11} Thus, two intense bands are found at 1040 and 1029 cm⁻¹ for P-CH₂ rocking vibrations and a sharp doublet at 754 and 739 cm^{-1} for the P–C stretching modes. Furthermore, the symmetrical and antisymmetrical metal-carbon stretching vibrations require more energy in the case of [ClMeGa-PEt₂], than for [Et₂Ga-PEt₂], 560 and 580 cm⁻¹ and 498 and 527 cm⁻¹, respectively. This probably correlates with the difference between the bond strengths of Ga-Me and Ga-Et and is in good agreement with the difficulty to eliminate the methyl groups without breaking of the Ga-P bond in the thermal decomposition experiments.³

NMR data of these compounds are reported in Table 2. The ³¹P NMR spectra of $[Et_2M-PEt_2]_3$ (M = Ga, In) are constituted by just one peak whereas a complicated multiplet is obtained in the same range for $[ClMeGa-PEt_2]_n$. The integrations in the ¹H NMR spectra conformed to the the-

	[Et ₂ Ga - PEt ₂] ₃	<u>.</u>		[Et ₂ In - PEt ₂] ₃			
m/e	rel. intensity	assignment	m/e	rel. intensity	assignment		
625, 623, 621, 619	2; 6; 9; 4	Ga3P3Et11+	757	5	In ₃ P ₃ Et ₁₁ +		
565, 563, 561, 559	1; 2; 3; 1	$Ga_3P_2Et_{10}^+$	555	4	In2P3Et8+		
467, 465, 463	2; 4; 3	Ga ₂ P ₃ Et ₈ ⁺	527	2	$In_2P_3Et_7H^+$		
407, 405, 403	17; 47; 35	Ga2P2Et7+	523	7	In2P2Et8+		
379, 377, 375	1; 3; 2	$Ga_2P_2Et_6H^+$	511	3	In ₂ P ₃ Et ₆ CH ₂ ⁺		
367, 365, 363	1; 3; 2	Ga2P2Et5CH6+	495, 493	47; 4	$In_2P_2Et_7^+$		
347, 345, 343	14; 31; 21	Ga2PEt6 ⁺	467	1	$In_2P_2Et_6H^+$		
337, 335, 333	1; 3; 2	$Ga_2P_2Et_4CH_5^+$	437	7	In ₂ P ₂ Et ₅ +		
319, 317, 315	1; 2; 2	Ga ₂ PEt ₅ H ⁺	435, 433	13; 1	$\text{In}_{2}\text{PEt}_{6}^{+}$		
289, 287, 285	2; 5; 4	Ga2PEt4+	409	1	$In_2P_2Et_4H^+$		
249, 247	5;7	$GaP_2Et_4^+$	405	1	$In_2PEt_5^+$		
221, 219	3;4	GaP ₂ Et ₃ H ⁺	377	11	$In_2^{PEt_4^+}$		
189, 187	23; 36	GaPEt ₃ +	319	9	$1n_2^{PEt_2^+}$		
160, 158	4;6	GaPEt ₂ +	233	12	InPEt3 ⁺		
129, 127	32; 51	GaEt2+	204	4	InPEt2 ⁺		
101, 99	6; 10	GaEtH ⁺	201	12	InEt ₃ + (-H)		
90	17	PEt ₂ H ⁺	173, 171	75; 3	InEt ₂ +		

Table 3. Mass spectra data

oretical ratios of the different types of proton on the basis of simple monomers. The coupling between gallium (I = 3/2) and hydrogen atoms bound to the alpha carbon appears in the spectra of $[Et_2Ga-PEt_2]_3$ (J(GaH) 2.0 Hz) whereas for the others a broadening of the quartet peaks, at about 0.6 ppm, is only observed. The peaks assigned to CH₂-M with $[Et_2In-PEt_2]_3$ are shifted downfield compared to those of $[Et_2Ga-PEt_2]_3$, which indicates that the size of the metal atom is more important than its electronegativity.¹⁴ Furthermore, the substitution of an alkyl group on gallium atom by a chlorine atom enhance, by inductive effect, the deshielding of CH₂-P.

The ¹H NMR spectra of $[Et_2M-PEt_2]_3$ are consistent with a trimer cyclic structure with, in solution rapid inversion at room temperature between two chair forms of a six-membered ring. On the contrary, for [ClMeGa-PEt_2]_n, the two peaks in the intensity ratio 1/2 assigned to CH₃-Ga and the complexity of the other signals can be interpreted from a mixture, in solution, of two compounds in the ratio 1/2. Cryoscopic molecular weight measurements in benzene solution of this compound give M = 556, 533 and a mean degree of association equal to 2.6 that corresponds exactly to a mixture of dimer and trimer in the ratio 1/2 according to the proton NMR results.

The mass spectroscopic data are summarized in Table 3. Those of $[Et_2M-PEt_2]_3$ (M = Ga, In) show that the primary ions are always fragments derived from trimeric molecules by loss of one Ethyl group followed by competitive loss of either MEt₃ or PEt groups. In both spectra the more important peaks are those of M⁺ and MEt₂⁺ followed by M₂P₂Et₇⁺, M₂PEt₆⁺, M₂PEt₄⁺ and MPEt₃⁺. The ionfragments obtained by M-Et and P-Et cleavage are numerous and their abundances suggest a relatively simple fragmentation pattern due to the stability of [M-P]_n ring.

The mass spectrum of $[ClMeGa-PEt_2]_n$ is more complicated and ions derived from trimeric molecule are not detected. Fragments arising from dimeric species are observed (Ga₂ Cl₂ P₂ Et₃ Me⁺ Ga₂ Cl₂ PEt₄⁺...) but also ions such as Ga Cl₂ P C₅ H₁₅⁺ due to ion-molecule side reactions, and several ions containing bromine and coming from impurities in GaMe₂Cl. A Negative Chemical Ionization mass spectrum with methane displays characteristic quintuplets at m/e = 623 and 491 assigned to [ClMeGa-PEt₂]₃-H and [Ga₃ Cl₃ P₂ Et₃ Me₂], respectively. Next to these trimeric species, this spectrum reveals ions containing bromine and Ga_x Cl_{x+1} entities which are very enhanced and numerous corroborating a recent work on this spectrometry.¹⁵

In conclusion, the trimeric covalent compounds $[Et_2M-PEt_2]_3$ (M = Ga, In) have a similar fragmentation pattern and the preferential process, which involves M-Et and P-Et bond cleavage, implies considerable stability of the [M-P], ring. The fragility of this chain seems to increase with the number of polar functions. Thus, with [ClMeGa-PEt₂], a weakening of the Ga-P σ bond strength is assumed to explain the complexity of the fragmentation. These results are in good agreement with the pyrolysis study of these organometallic molecules³ since no GaP coating was obtained from [ClMeGa-PEt_{2]}, probably because the Ga-P σ bonds are broken in the vapour phase, whereas the two other compounds led to III-V semiconductor layers.

Acknowledgements—We wish to thank the Centre de Spectrométrie de Masse (Lyon) and the Service de RMN á Haut Champ (UPS, Toulouse) for recording spectra.

REFERENCES

- H. M. Manasevit and W. I. Simpson, J. Electrochem. Soc. 1969, 116, 1725.
- R. Didchenko, J. E. Alix and R. H. Toeniskoetter, J. Inorg. Nucl. Chem. 1960, 14, 35.
- F. Maury and G. Constant, Proc. of IV European Conference on CVD (Edited by J. Bloem, G. Verspui and L. R. Wolff), p. 257, Eindhoven (1983).
- 4. A. Zaouk, E. Salvetat, J. Sakaya, F. Maury and G. Constant J. Cryst. Growth, 1981, 55, 135.
- 5. F. Maury and G. Constant, J. Cryst. Growth 1983, 62, 568.
- 6. O. T. Beachley, G. E. Coates and G. Kohnstam, J. Chem. Soc. 1965, 3248.
- A. Storr and B. S. Thomas, J. Chem. Soc. (A) 1971, 3850.
- J. Muller, K. Margiolis and K. Dehnicke, J. Organometal. Chem. 1972, 46, 219.
- 9. J. R. Jennings, I. Pattison, K. Wade and B. K. Wyatt, J. Chem. Soc. (A) 1967, 1608.
- G. E. Coates and J. Graham, J. Chem. Soc. 1963, 233.
- 11. O. T. Beachley and G. E. Coates, J. Chem. Soc. 1965, 3241.
- D. D. Perrin, W. L. F. Armarego and D. R. Perrin, In *Purification of Laboratory Chemicals*, 2nd Edn. Pergamon Press, Oxford (1980).
- L. M. Goloubinsdkaia, V. I. Bregadze, B. I. Kozirkin and B. G. Gribov, UDK 547-256-81 (1976).
- B. Sen and G. L. White, J. Inorg. Nucl. Chem. 1973, 35, 2207.
- J. Tirouflet, J. Besancon, B. Gautheron, F. Gomez and D. Fraisse, J. Organometal. Chem. 1982, 234, 143.