

# Organometallic Chemistry

## Trimethylaminedichlorogallane ( $\text{Cl}_2\text{Ga} \cdot \text{NMe}_3$ )<sub>2</sub> with the Ga—Ga intermetallic bond

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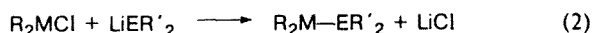
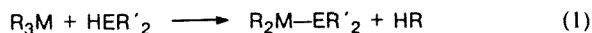
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The reaction of  $\text{GaH}_3 \cdot \text{NMe}_3$  with  $\text{ClPBu}_2$  in ether occurs through the exchange of ligands followed by reduction of  $\text{Ga}^{3+}$  to  $\text{Ga}^{2+}$  to yield  $(\text{GaCl}_2 \cdot \text{NMe}_3)_2$ . X-ray structural analysis demonstrated that gallium atoms in this compound form a direct metal—metal bond with the length of 2.421 Å.

**Key words:** gallium, gallanes, metal—metal bond, structure.

The renewed interest in the chemistry of volatile alkyl and hydride compounds of aluminum, gallium, and indium, which has been particularly notable in the last 5–7 years, arises from the active use of these compounds for the preparation of semiconducting films by the CVD method.<sup>1–5</sup> Among these compounds, the complexes with covalent M—E bonds of composition  $\text{R}_2\text{M}—\text{ER}'_2$ , where M = Al, Ga, or In; E = N, P, or As; R = R' = Alk or R' = H, are of particular interest. These compounds can be used in the most convenient single-source (single-component) version of CVD<sup>6,7</sup> and make it possible to obtain films of the  $\text{A}^{\text{III}}\text{B}^{\text{V}}$  type with the electrophysical characteristics, which are difficult to achieve when multicomponent gaseous mixtures are used.

The methods, which are most generally used for the synthesis of compounds of composition  $\text{R}_2\text{M}—\text{ER}'_2$ , are based on reactions of metal alkyls with hydrides of the Group V elements (Eq. (1)) or on exchange reactions of the corresponding halides with lithium derivatives of the Group V elements (Eq. (2)).

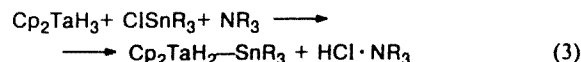


Complexes of virtually all possible types, except for, probably, compounds with R = H, were obtained by these methods.<sup>5</sup> Most of these compounds occur as dimers in the crystalline and gaseous states,<sup>6,7</sup> but when steric hindrances at the M and E atoms increase, for example when R = R' = Bu<sup>t</sup>, dimerization is suppressed and monomeric compounds form,<sup>8,9</sup> which are, apparently, of most interest from the practical standpoint. However, the synthesis of these compounds is rather complicated because compounds of the  $\text{HER}'_2$  type are hardly available. Therefore, in this line of investigations, the problem associated with the development of a simpler method for the synthesis of complexes containing M—E covalent bonds, among them complexes containing M—H bonds, is still a rather high-priority task.

### Results and Discussion

Reactions of insertion of tin, silicon, phosphorus, and a number of other elements (hereinafter referred to as elements) into the M—H bond (M is a transition metal), which afford compounds with the M—E covalent bond, are well known in the chemistry of hydrides.<sup>10–13</sup> When element chloride is used as a reagent,

the reaction proceeds much more easily in the presence of acceptors of hydrogen chloride.<sup>10</sup> In this case, stoichiometry of the reaction, for example, the reaction between  $\text{Cp}_2\text{TaH}_3$  and  $\text{ClSnR}_3$  in the presence of tertiary amine, is described by Eq. (3).



One would expect that reactions of nontransition metal hydrides, which also contain tertiary amines (for example, like  $\text{MH}_3 \cdot \text{NR}_3$ , where M is a Group IIIA metal), with more readily available  $\text{ClER}'_2$ , which are intermediates in the synthesis of  $\text{HER}'_2$ , will make it possible not only to obtain complexes with  $\text{M—E}$  and  $\text{M—H}$  bonds but to simplify substantially the procedure for their preparation.

Unfortunately, the experiment carried out with the use of trimethylaminegallane,  $\text{GaH}_3 \cdot \text{NMe}_3$ , and  $\text{ClPBu}'_2$  in diethyl ether on the assumption that reaction (4) is stoichiometric, did not give the desired result. The reaction between the components proceeds without noticeable evolution of gaseous products and produces the complex of composition  $\text{GaCl}_2 \cdot \text{NMe}_3$  (**1**) in a rather good yield (~30 %). Based on the IR spectral data, this complex does not contain metal—hydride  $\text{Ga—H}$  bonds. However, when **1** was treated with acidified water, hydrogen evolved, which indicates that the  $\text{Ga—Ga}$  bond exists in the complex, i.e., the reaction between  $\text{GaH}_3 \cdot \text{NMe}_3$  and  $\text{ClPBu}'_2$  is redox in character and results in a compound with the gallium atom in the 2+ oxidation state.



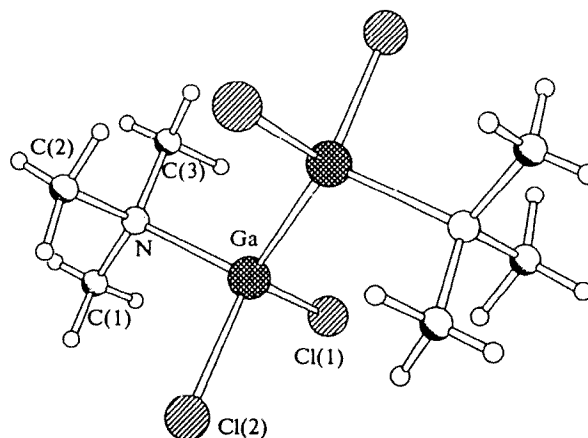
The reaction between  $\text{GaH}_3 \cdot \text{NMe}_3$  and  $\text{PCl}_3$  proceeds with the evolution of gas, which is spontaneously combustible in air (apparently, phosphine) and results in complete precipitation of gallium from the solution as a brick-red compound (**2**) insoluble in organic solvents. Based on the data of IR spectroscopy, product **2**, like **1**, contains no  $\text{Ga—H}$  bonds, but, unlike **1**, product **2** does not eliminate hydrogen upon acidic decomposition and, therefore, does not contain  $\text{Ga—Ga}$  bonds. Besides, the color of compound **2** and its insolubility in organic solvents indicate that polymeric chlorophosphine of approximate composition  $(\text{PHCl})_n$ , which is well known in the chemistry of phosphorus (see, for example, Ref. 14), forms in the course of the reaction; this polymeric chlorophosphine precipitates the gallium compound as a metallopolymer. According to the data of elemental analysis and IR spectroscopy, the composition of **2** may be described by the formula  $(\text{GaCl}_3 \cdot \text{PHCl}_2 \cdot \text{NMe}_3)_n$ . However, note that this formula is tentative because, first, the modes of coordination of phosphorus- and nitrogen-containing ligands to the gallium atom are not clear and, second, experimental element content in **2** substantially differs from the calculated value. However, the latter fact is not surprising taking into account that

**Table 1.** Principal bond lengths ( $d$ ) and bond angles ( $\omega$ ) in the  $(\text{Cl}_2\text{Ga} \cdot \text{NMe}_3)_2$  molecule

Bond	$d/\text{\AA}$	Angle	$\omega/\text{deg}$
Ga—Ga(1)	2.421(1)	Cl(2)GaGa(1)	117.0(1)
Ga—N	2.046(4)	Cl(1)GaGa(1)	116.0(1)
Ga—Cl(1)	2.191(2)	Cl(1)GaCl(2)	106.4(1)
Ga—Cl(2)	2.189(2)	Cl(2)GaN	101.6(1)
N—C(1)	1.462(7)	NGaGa(1)	112.0(1)
N—C(2)	1.496(8)	GaNC(1)	112.8(3)
N—C(3)	1.484(8)	GaNC(2)	107.3(3)
		GaNC(3)	108.1(4)

the polymer can occlude different impurities, primarily solvent molecules.

The structure of complex **1** was studied by X-ray structural analysis (Fig. 1). In this complex, the gallium atoms are in a distorted tetrahedral environment (Table 1) typical of this element and are bonded to each other through the  $\text{Ga—Ga}$  bond. Therefore, the complex has the composition  $(\text{Cl}_2\text{Ga} \cdot \text{NMe}_3)_2$  (the oxidation state of Ga is 2+), which is supported very well by the data on the chemical properties of this compound. The  $\text{Ga—Ga}$  bond length in **1** (2.421 Å) differs little from those observed in other known molecular complexes of gallium(2+) (2.406 Å in  $(\text{GaCl}_2 \cdot \text{diox})_2$ <sup>15</sup>, 2.395 Å in  $(\text{GaBr}_2 \cdot \text{diox})_2$ ,<sup>16</sup> and 2.421 Å in  $(\text{GaBr}_2 \cdot \text{Py})_2$ <sup>17</sup>) and in anions (2.390 Å in  $\text{Ga}_2\text{Cl}_6^{2-}$ <sup>18</sup> and 2.419 Å in  $\text{Ga}_2\text{Br}_6^{2-}$ <sup>19</sup>). As expected, the interatomic gallium—ligand distances appear to be very sensitive to the change in the oxidation state of the metal atom. Thus, in the complexes of gallium(3+) chloride with different amine ligands, the interatomic  $\text{Ga—Cl}$  distance is generally no more than 2.164 Å,<sup>20,21</sup> whereas in the case of compound **1**, this distance is 2.190 Å (average) and it is not much different from those observed in the complex of gallium(2+) chloride with dioxane (the average value is 2.175 Å)<sup>15</sup> and in the  $\text{Ga}_2\text{Cl}_6^{2-}$  anion (2.196 Å)<sup>18</sup>. Amine ligands in the mol-



**Fig. 1.** Structure of the  $(\text{Cl}_2\text{Ga} \cdot \text{NMe}_3)_2$  complex.

ecule are in a *trans* configuration with respect to the Ga—Ga bond. The Ga—N distance (2.046 Å) is somewhat larger than that in the complex of gallium(2+) bromide with pyridine (2.024 Å)<sup>17</sup> and is substantially larger than the values found in the tetrahedral complexes of gallium(3+) chloride with the monodentate nitrogen atom (no more than 2.01 Å).<sup>20–22</sup> In this respect, the Ga—N bond length in the compound studied approaches the values determined for the dimeric complexes of Ga<sup>3+</sup> with bulky bridging nitrogen-containing ligands, *i.e.*, bidentate ligands (2.024–2.039 Å).<sup>23</sup> As a whole, all these differences in the interatomic distances in the complexes with gallium in the oxidation states of 3+ and 2+ are quite regular and are attributable to the decrease in the acceptor properties of the compound as the oxidation state of the metal atom decreases.

Therefore, the structure considered and the data on the structures of analogous compounds reported previously<sup>15–19</sup> indicate that the complexes with gallium in the oxidation state 2+ are quite stable compounds. However, in the cases reported in Refs. 15–17, the mechanism of formation of these complexes is quite clear (halides of composition Ga<sub>2</sub>Hal<sub>4</sub> were used as the initial compounds), whereas the mechanism of the formation of the (Cl<sub>2</sub>Ga·NMe<sub>3</sub>)<sub>2</sub> complex remains unknown. It can only be stated that the first stage of this reaction occurs as the ordinary replacement reaction of hydride ligands with chlorine atoms to form dichlorogallane, Cl<sub>2</sub>GaH·NMe<sub>3</sub>,<sup>24</sup> which is well known in the chemistry of gallium hydride, and HPBu<sub>2</sub> soluble in organic solvents. An analogous reaction of AlH<sub>3</sub>·NMe<sub>3</sub> with ClPBU<sub>2</sub> yields, depending on the ratio of the reactants, chloroalanes of composition H<sub>2</sub>AlCl·NMe<sub>3</sub> (1 : 1), HAlCl<sub>2</sub>·NMe<sub>3</sub> (1 : 2), AlCl<sub>3</sub>·NMe<sub>3</sub> (1 : 3), which are well studied, and HPBu<sub>2</sub>. It is known<sup>25</sup> that the stability of haloalanes with respect to autocatalytic decomposition into elements increases as the number of chlorine atoms in the structure increases; these compounds are more stable than the corresponding gallium compounds (see, for example, Refs. 26 and 27). Gallium compounds, particularly GaH<sub>3</sub>·NMe<sub>3</sub>, rather readily decompose (often for no apparent reason) in solutions to produce hydrogen and metal. Taking into account the method of preparation of Ga<sub>2</sub>Cl<sub>4</sub> based on reduction of Ga<sub>2</sub>Cl<sub>6</sub> with metallic gallium in a solution,<sup>28</sup> it can be supposed that the analogous reaction occurs in the case under consideration as well, *i.e.*, at the second stage of the reaction, Cl<sub>2</sub>GaH·NMe<sub>3</sub> is reduced with the metal that can appear in the system because of partial decomposition of the initial trimethylaminegallane. However, as in the case of haloalanes, the introduction of chlorine atoms into gallane enhances its stability to autocatalytic decomposition (to reduction) and inhibits further decomposition of 1. Generally, the synthesis of (Cl<sub>2</sub>GaH·NMe<sub>3</sub>)<sub>2</sub> with a direct metal—metal bond can be considered as the first stage of decomposition of hydrides of Groups II—III non-

transition metals and their derivatives, which affords ultimately the metal phase.

### Experimental

All operations associated with the synthesis and isolation of the reaction products were carried out under an atmosphere of dry argon using the vacuum technique, Schlenk vessels, and anhydrous solvents (double distillation over LiAlH<sub>4</sub>).

**LiGaH<sub>4</sub>** was prepared by the known reaction of LiH with GaCl<sub>3</sub> in diethyl ether. Finely dispersed LiH powder (0.5 mol) was added with intense stirring to a solution of GaCl<sub>3</sub> (0.04 mol) in ether (80 mL) at –40 °C. The solution was slowly warmed to –20 °C. Then the suspension was stirred for 5 h. The solution was decanted, and the concentration of LiGaH<sub>4</sub> was determined.

**GaH<sub>3</sub>·NMe<sub>3</sub>** was also prepared according to the known procedure by adding the calculated amount of dry NMe<sub>3</sub>·HCl to a solution of LiGaH<sub>4</sub> with the known concentration (1 : 1). The suspension was stirred for 1 h after the evolution of hydrogen ceased. The precipitate of LiCl was filtered off, and the concentration of gallane was determined.

**Synthesis of (Cl<sub>2</sub>Ga·NMe<sub>3</sub>)<sub>2</sub> (1).** ClPBU<sub>2</sub> (1.8 g, 0.01 mol) was added dropwise to a solution of GaH<sub>3</sub>·NMe<sub>3</sub> (1.3 g, 0.01 mol) in ether (100 mL). The transparent solution was stirred at –20 °C for 2 h, concentrated to 1/3 of the initial volume, and diluted with benzene (150 mL). The precipitated crystals were removed from the mother liquor by decantation, washed with pentane, and dried *in vacuo*. The compound (0.6 g) was obtained as single crystals. Found (%): Ga, 34.6; Cl, 35.3. C<sub>3</sub>H<sub>9</sub>Cl<sub>2</sub>GaN. Calculated (%): Ga, 34.90; Cl, 35.5.

**Synthesis of metallopolymer (2).** Dry PCl<sub>3</sub> (4 mL, 0.045 mol) was added dropwise to a solution of GaH<sub>3</sub>·NMe<sub>3</sub> (4.6 g, 0.035 mol) in ether (80 mL). The flocculent beige precipitate formed and gas evolved instantaneously; the gas is spontaneously combustible in air. As phosphorus trichloride was added, the precipitate turned reddish, and after completion of the reaction, the color of the precipitate was brick-red. The precipitate was separated from the mother liquor, washed with ether, and dried *in vacuo* at –20 °C. Based on the data of elemental analysis, the colorless filtrate contained no chlorine and gallium. Found (%): C, 10.32; H, 2.77; Cl, 51.5; Ga, 19.4; N, 3.83. C<sub>3</sub>H<sub>10</sub>Cl<sub>5</sub>GaN. Calculated (%): C, 10.64; H, 2.95; Cl, 52.43; Ga, 20.67; N, 4.13.

**X-ray structural analysis of the single crystal of the (Cl<sub>2</sub>Ga·NMe<sub>3</sub>)<sub>2</sub> complex** sealed in a glass tube was performed on an automated Nicolet P3 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, 2θ<sub>max</sub> = 50°). The crystals are monoclinic: *a* = 7.835(1), *b* = 9.549(2), *c* = 10.416(2) Å, *g* = 86.84(2)°, *V* = 778.1(4) Å<sup>3</sup>, space group

**Table 2.** Atomic coordinates (×10<sup>4</sup>) and temperature factors (*U*) for the (Cl<sub>2</sub>Ga·NMe<sub>3</sub>)<sub>2</sub> molecule

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> · 10 <sup>3</sup> /Å <sup>2</sup>
Ga	4461(1)	5921(1)	4285(1)	35(1)
Cl(1)	1800(2)	5803(2)	3665(2)	75(1)
Cl(2)	4745(3)	8086(1)	4909(2)	79(1)
N	5731(6)	5883(4)	2569(4)	49(1)
C(1)	5146(9)	7022(6)	1711(5)	68(2)
C(2)	7587(9)	6009(8)	2858(7)	86(3)
C(3)	5488(11)	4508(7)	1949(7)	88(3)

$P2_1/n$ ,  $Z = 4$ ,  $\rho = 1.110 \text{ g cm}^{-3}$ . A total of 954 reflections with  $I \geq 3\sigma(I)$  were used in calculations. Absorption was ignored ( $\mu = 43.10 \text{ cm}^{-1}$ ). The structure was solved by the direct method and refined by the full-matrix least-square method with anisotropic thermal parameters of heavy atoms (Table 2). Coordinates of hydrogen atoms of methyl groups were calculated from geometric considerations and were included in the refinement. The final value of the  $R$  factor was 0.039 ( $R_w = 0.041$ ). The principal bond lengths and bond angles are given in Table 1.

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