



Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

ISSN: 0094-5714 (Print) 1532-2440 (Online) Journal homepage: http://www.tandfonline.com/loi/lsrt19

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To cite this article: L. I. Zakharkin & V. V. Gavrilenko (1999) A Simple Synthesis of Non-Solvated Trimethylgallium and Triethylgallium, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 29:7, 1243-1247, DOI: 10.1080/00945719909349525

To link to this article: http://dx.doi.org/10.1080/00945719909349525

Published online: 14 Apr 2008.



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# A SIMPLE SYNTHESIS OF NON-SOLVATED TRIMETHYLGALLIUM AND TRIETHYLGALLIUM

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#### **ABSTRACT**

A simple synthesis of non-solvated trimethylgallium and triethylgallium is proposed based on the reaction of alkyl iodides with a mixture or an alloy of magnesium and gallium in the absence of a solvent or in aliphatic hydrocarbons as solvent

## **INTRODUCTION**

Trimethylgallium and triethylgallium of high purity are used for the preparation of gallium arsenide semiconducting films by chemical vapor deposition of organometallic compounds.<sup>1-3</sup> The conventional methods by which they are synthesized, by the reaction of gallium trihalides with organolithium, organomagnesium, organozinc, or organomercury compounds, require complicated additional purification of the target products from impurities of starting organometallic compounds.<sup>3</sup> The

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more convenient procedure for the preparation of  $Me_3Ga$  from  $GaCl_3$  and  $Me_3Al$  also has disadvantages.<sup>4</sup>

### **RESULTS AND DISCUSSION**

A simple synthesis of gallium trialkyls consists in the interaction of Ga-Mg alloys or Ga-Mg mixtures with alkyl halides in ethers, sulfides, or amines<sup>5,6</sup>. In this case, both solvated and non-solvated gallium trialkyls are formed. However, the published results<sup>5</sup> concerning the synthesis of trimethylgallium etherates were not reproduced<sup>3</sup>, and attempts to carry out the reaction of alkyl halides with a mixture of magnesium and gallium in donor-type solvents failed<sup>7</sup>. Contrary to the results presented in the earlier work<sup>5</sup>, gallium trialkyls were not isolated from the reaction of alkyl halides with Ga-Mg alloys or Ga-Mg mixtures in the absence of donor-type solvents<sup>7</sup>. Such contradictions in the literature data (cf. Refs. 3 and 7 vs. Ref. 5) have remained unexplainable until now; especially sinc we obtained trimethylgallium etherate in high yield (independent of the study cited<sup>5</sup>) by the reaction of MeI with a Ga-Mg mixture in dibutyl ether<sup>6</sup>. We believe that these differences can be explained by the fact that the samples of Mg and Ga used in the studies by Russian researchers<sup>5,6</sup> differed in the composition of impurities from those employed in Refs. 3 and 7.

In this work we found that unlike the previous data<sup>7</sup>, MeI and EtI react when heated with either Ga-Mg mixtures or alloys without any solvent or in an aliphatic hydrocarbon to give non-solvated gallium trialkyls. The reaction occurs according to the following scheme:

 $6 \text{ RI} + 3 \text{ Mg} + 2 \text{ Ga} \longrightarrow 2 \text{ R}_3 \text{ Ga} + 3 \text{ MgI}_2$ R = Me, Et

The reaction with EtI is carried out at atmospheric pressure, and the reaction with MeI is performed in an autoclave with stirring and at a temperature above 100° C. The yields of gallium trialkyls are in the range from 57 to 65%.

#### **EXPERIMENTAL**

The commercial magnesium powder of MPF-4 grade contained the following admixtures (%): Fe,  $2 \cdot 10^{-2}$ ; Cu,  $7 \cdot 10^{-3}$ ; Mn,  $5 \cdot 10^{-2}$ ; Zn,  $1 \cdot 10^{-4}$ ; Ga,  $1 \cdot 10^{-2}$ ; Si, 0.1. The purity of gallium was 99.99% The organic solvent and alkyl iodides were purified using standard procedures and were distilled under argon. The syntheses of gallium trialkyls were carried out in an atmosphere of pure argon.

**Trimethylgallium.** Gallium (36 g, 0.52 mol), magnesium (21 g, 0.87 mol), and MeI (227 g, 1.6 mol) were placed into a rotating 0.5 L autoclave in an atmosphere of an inert gas. Steel balls with diameters of 5 to 10 mm were placed into the autoclave for better stirring. The autoclave was gradually heated to 100° C with rotation; 2 h later the temperature was increased to 120-160° C. The reaction was conducted for 12 h. When the autoclave was chilled, the reaction product was distilled off directly from the autoclave. Me<sub>3</sub>Ga was obtained in a yield of 38.6 g (65%), b.p. 55-56° C (*cf.* Ref. 8: b.p. 55.7° C). From Me<sub>3</sub>Ga and NaH NaGaMe<sub>3</sub>H was obtained, m.p. 151-152° C (Et<sub>2</sub>O-toluene) (*cf.* Ref. 6). Anal. found: C 25.86; H 7.08; Ga 49.98%, calculated for C<sub>3</sub>H<sub>10</sub>GaNa: C 25.80; H 7.16; Ga 49.90%.

**Triethylgallium.** Procedure A. Gallium (15 g, 0.21 mol) and Mg (8 g, 0.33 mol) in the form of fine cuttings or filings were placed in a threenecked flask, and a crystal of  $I_2$  was added. The mixture was heated *in* vacuo at 150° C and chilled, and the flask was then filled with pure argon. Ethyl iodide (100.7 g, 0.65 mol) was added at 50-70° C for 1 h, and the resulting mixture was heated at 90° C for 4 h. Pure Et<sub>3</sub>Ga was distilled off from the reaction mixture, yield 20.5 g, (61%), b.p. 34-35° C (10 Torr), (cf. Ref. 8; b.p. 142.6° C). From Et<sub>3</sub>Ga and NaH NaGaEt<sub>3</sub>H was obtained, m.p. 40-41° C (hexane) (cf. Ref. 9). Anal. found: C 39.58; H 8.88; Ga 38.45%, calculated for C<sub>6</sub>H<sub>6</sub>GaNa: C 39.63; H 8.80; Ga 38.37%.

**Procedure B.** Gallium (15 g, 0.21 mol) and Mg (8 g, 0.33 mol) were placed in a three-necked flask, a crystal of  $I_2$  was added, and the

mixture was evacuated. Hexane (50 mL) was added to the reaction mixture, and EtI (100.7 g, 0.65 mol) was added dropwise while the hexane was boiling. When the reaction was completed, the solvent was distilled off from the flask, and triethylgallium was isolated by distillation, b.p.  $34-35^{\circ}$  C (10 Torr), yield 21.9 g (65%).

**Procedure C.** Cuttings (9.0 g) of a Ga-Mg alloy (Ga, 35%, Mg, 65%) were placed in a reaction flask, and a crystal of  $I_2$  was added. The reaction mixture was heated in vacuo to 150° C and chilled. Ethyl iodide (69 g, 0.44 mol) was then gradually added to the resulting mixture, and it was heated to 85° C. Triethylgallium was distilled off; b.p. 34-35° C (10 Torr), yield 4.49 g (57%).

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Received: 31 March 1998 Accepted: 25 March 1999 Referee I: O. T. Beachley, Jr. Referee II: L. K. Krannich