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Organogallium compounds from metallic gallium through using metal-vapor synthesis

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The first syntheses of organogallium compounds utilizing metallic gallium and alkyl halides (bromides and iodides) are presented. Metal-vapor synthesis methods were used, and it is proposed that gallium atoms are the reactive species involved.

Gallium also reacted with alkyl halides as fine particles in slurry form, but only when deposited in, or co-deposited with, alkylaluminum compounds. Rationale for this finding is based on irregularity of the clusters due to incorporation of aluminum (or its compounds) and probably also on smaller particle sizes.

Keywords: Metal-vapor synthesis, ethylgallium sesqui-iodide, ethylgallium sesquibromide, gallium atoms, gallium clusters

INTRODUCTION

Preparative methods used in the synthesis of organogallium compounds are based on standard procedures used in organometallic chemistry, for example:[1,2]

(1) Reactions with main group organometallics of magnesium, lithium, zinc or silver with gallium trihalides (GaX_3). Although this method is most often used, a disadvantage is the potential reducing power of some of the organometallic reagents (e.g. sodium alkyls), which can cause reduction of some gallium(III) to metallic gallium [Ga(0)]. Another disadvantage is that the obligatory use of a donor solvent usually results in the solvent irreversibly coordinating to the organogallium product.

(2) Reaction of gallium metal with diorganomercury may also be used but this is seldom done because of expense and toxicity.

(3) Hydrometallation of multiple carbon–carbon bonds by gallium hydrides is also used.

(4) Electrochemical methods from gallium metal and organomagnesium compounds in strong donor solvents may also be carried out.[3,4]

The direct reaction of gallium metal with alkyl halides does not work well, although an interatomic compound Mg_5Ga_2 in donor solvents does react giving organogallium compounds in low yield.[4] Earlier synthetic reports using alloys and mixtures of metals[5] are irreproducible according to Holliday.[4] We agree with Holliday, and have been unsuccessful in reacting conventionally prepared alloys and mixtures of gallium with aluminum, magnesium or copper in the absence of donor solvents.[6]

The possibility of using gallium atoms to prepare organogallium halides was suggested by two reports, one from our laboratory showing that methylgallium bromide (CH_3GaBr) formed at low temperature when gallium atoms and methyl bromide were co-deposited.[7] Also, gallium atoms, prepared by laser pyrolysis of trimethylgallium (Me_3Ga), were shown to be reactive with trifluoromethyl iodide (CF_3I) in the gas phase, but only to form gallium(I) iodide (GaI) and trifluoromethyl (CF_3) radicals.[8]

Before describing our current results, it is important to realize the importance of effecting reactions of pure gallium with alkyl halides. In the last few years gallium arsenide (GaAs) semiconductors have played a central role in the development of new electronic devices. One of the most important methods of obtaining these materials is by epitaxial growth of gallium arsenide by metalorganic chemical vapor deposition (MOVCD),[9] also called MOVPE, or by metalorganic molecular beam epitaxy (MOMBE).[10] For these methods, volatile organometallics or elementohydrides of extremely high purity are needed (< 1 ppm impurity). Thus, the interest in synthesis of organogallium compounds has increased in recent years,[3,4,8,11] as well as interest in

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organometallics incorporating gallium and arsenic together.[12,13]

EXPERIMENTAL

Apparatus

Two metal-vapor synthesis (MVS) reactor designs were employed: (1) a stationary reactor where gallium vapor and vapors of reagents were co-deposited at 77 K followed by warming,[14] and (2) a rotary reactor where gallium vapor was evaporated into cooled liquids[15] or onto a solidified film.

Figure 1 illustrates our stationary reactor with modifications so that high-boiling reactants such as triisobutylaluminum (i-Bu_3Al) could be let in. The inlet tube was electrically heated.[16] The entrance for reactant vapors could be regulated by a stopcock (D) connected to a long rod (C) and screw mechanism (F) in the upper part of the reactor. The evacuation tube of the reactor was equipped with side arms (six), stopcocks, and ball joints so that if gases were released during a reaction some could be retained in the trap containing molecular sieves at 77 K. After the reaction was completed, these trapped gases could be released by heating the molecular sieves and analyzed by gas chromatography (GC).

The rotary reactor with either a 1-dm^3 or 2-dm^3 reactor bulb was also modified slightly. A side arm was added so that evolved gases could be trapped if desired.

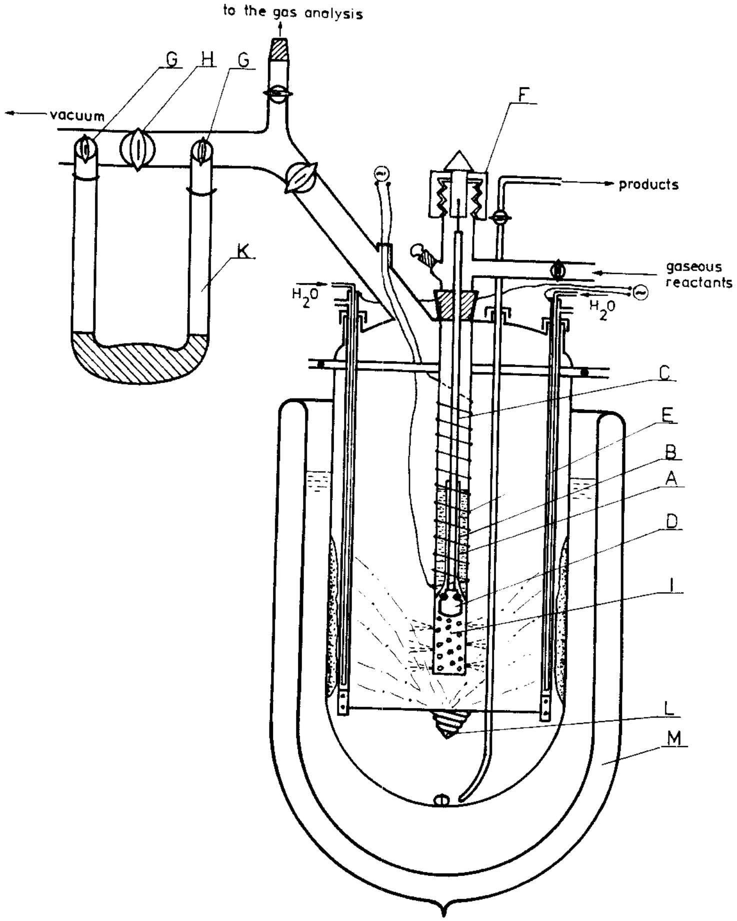


Figure 1 Stationary metal-vapor reactor (MVS) modified for high-boiling reactants: A, 20 cm^3 container; B, duct; C, rod; D, stopcock; E, electrical heating wire; F, screw; G, side arms; H, through-valve; I, reactant inlet 'shower head'; K, trap; L, crucible; M, Dewar flask.

General procedure

Stationary reactor

The tungsten–alumina (W–Al_2O_3) crucible was charged with gallium metal and shielded with molybdenum sheet metal to decrease emitted radiation. The reactor was assembled, evacuated, and the Dewar flask filled with liquid nitrogen. The reactor walls were covered with a few grams of solvent or reagent and metal heating and evaporation was then begun. Evaporation rates varied from 0.01 to 0.5 g h^{-1}. During the reaction the Dewar was removed several times in order to observe the matrix. Reaction time was 1–3 h.

Rotary reactor

The crucible was loaded with gallium and a molybdenum shield put in place. The reactor bulb was attached and purged with nitrogen gas. The liquid reactants were added and the reactor bulb cooled to −110°C with an ethanol slush bath, or to −196°C with liquid nitrogen. It was evacuated to below 10 mTorr and metal evaporation and bulb rotation commenced. Reaction time was 1–3 h.

Analysis

All products and the intermediate fractions during work-up were analyzed quantitatively for gallium and/or aluminum, and qualitatively for halogens. Halogens were absent in the lower fractions of the distillate from the reaction products where triethylaluminum was used. However, as a rule distillates contained 1–10 % of triethylaluminum. In the reactions where toluene was present it was impossible to separate triethylgallium (Et_3Ga) from this solvent: they distilled together at up to 110°C. The product from the reaction of gallium and ethyl iodide displayed 23.6 % of Ga which corresponds to 29.6 % of $(Me_2GaI)_2$ and 70.4 % of $(MeGaI_2)_2$.

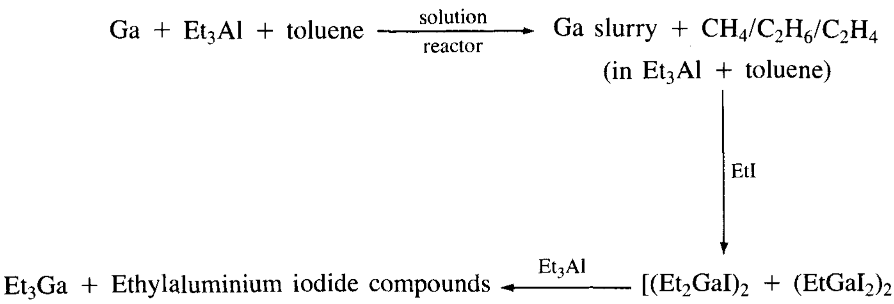
RESULTS

Gallium clusters/particles

We have reported that the deposition of metal vapors with solvents followed by warm-up allows metal atom accretion, and that very fine particles are formed. This is a general way of producing active metal slurries and powders.[17] In the same way we attempted to produce active gallium. We have investigated the influence of metal:solvent ratios, use of different solvents, different reactors (stationary vs rotary), temperature of deposition, and effect of added organoaluminum compounds. Reactivities of the resultant slurries toward alkyl halides were measured.

The results of some of these experiments are collected in Table 1. First, we allowed accretion of gallium atoms in a toluene/triethylaluminum liquid mixture, and later ethyl iodide was added (Scheme 1). Gases were formed as well as a mixture of organogallium and -aluminum compounds. The distilled-off triethylgallium (Et_3Ga) was obtained only in about 20 % yield (based on evaporated gallium) because it was difficult to separate from organoaluminum compounds. The distillate was a mixture of triethylgallium (Et_3Ga) and toluene. Therefore, our next step was to eliminate toluene, and we deposited gallium metal with pure Et_3Al (Eqn [1])

$$\mathrm{Ga} + \mathrm{Et_3Al} \xrightarrow[\text{reactor}]{\text{Stationary}} \underset{\substack{\text{(mixture of Ga and Al}\\ \text{organometallics)}}}{\text{Ga slurry/Et}_3\text{Al} + \text{gases}} \qquad [1]$$



Scheme 1

Table 1 Reactivity of gallium in metal–vapor synthesis

Number	Ratio	Reacting[a] system	Reactor[b]	Temperature of reaction (K)[d]	Time of reaction (h)	Yield of organogallium compound (%)
1a	1:50	(Ga + EtCl)	s	77	3	Very small amounts
		+ Et_3Al (excess)		RT		Very small amounts
2b	1:100	(Ga + EtBr)	s	77	4	65
3	1:120	(Ga + EtI)	s	77	4	77
4a	1:100	(Ga + Et_3Al)	s	77	2.5	< 1
4b	—	+ EtI (excess)	f	RT	> 24	Quantitative consumption of slurry
4c	—	Dry slurry + EtI (excess)	f	RT	2	Quantitative consumption of slurry
5a	1:100:3	(Ga + EtCl + Et_3Al)	s	77	3	< 3
5b	—	Dry slurry + EtI (excess)	f	RT	< 10	Quantitative consumption of slurry
6a	1:80:30	[(Ga + toluene) + EtI]	s	77	3.5	Not determined
6b	1:4	+ Et_3Al	f	RT	12	~ 5
7a	1:130:17	[(Ga + pentane) + EtI]	s	77	6	Not determined
7b		+ Et_3Al (excess)	f	RT	12	< 5
8a	1:26:10	(Ga + pentane + EtI)	s	77	2	Not determined
8b		+ Et_3Al (excess)	f	RT	—	Reasonably high, but not determined
9a	1:30:4	[(Ga + toluene + Et_3Al)	r	77[c]	7	Not determined
	1:5	+ EtI]		173		
9b		Consumption of slurry		RT	6	Reasonably high, but not determined

[a] Reactants and solvents co-deposited together are bracketted. All compounds within parentheses were in solution during metal deposition or they were deposited together. Square brackets indicate that immediately after co-deposition the next component was added to the matrix (or to the low-temperature solution for the solution reactor). Compounds outside the brackets were introduced after warm-up of the matrix. The table is arranged in order of increasing complexity of reacting systems.

[b] Abbreviations: s, stationary co-deposition reactor; r, rotary reactor; f, Schlenk tube.

[c] Heated to about 180 K every $\frac{1}{2}$ h, then cooled and more Ga deposited.

[d] RT, room temperature.

A dark opaque black–brown liquid was obtained from which a silver–black precipitate slowly deposited. Only a small amount (1 %) of gallium organometallic was present in the filtered solution. The silver–black precipitate reacted rapidly and quantitatively with ethyl iodide yielding gallium organometallic in ethylaluminum compounds. The liquid distilling at 140–143 °C appeared to be triethylgallium (b.p. 142 °C) contaminated with triethylaluminum (2 %). The yield was *ca* 45 % of triethylaluminum calculated on the evaporated gallium.

Co-deposition of gallium(0) with toluene followed by warm-up of the matrix and then ethyl iodide (EtI) addition yielded no organogallium compounds, even after stirring at room temperature for 48 h. Addition of triethylaluminum to a freshly prepared gallium(0)/toluene slurry followed by ethyl iodide and prolonged stirring gave the same negative results. Furthermore, even when ethyl iodide was added to a freshly deposited gallium(0)/toluene matrix, followed by warming to room temperature and prolonged stirring, no reaction took place.

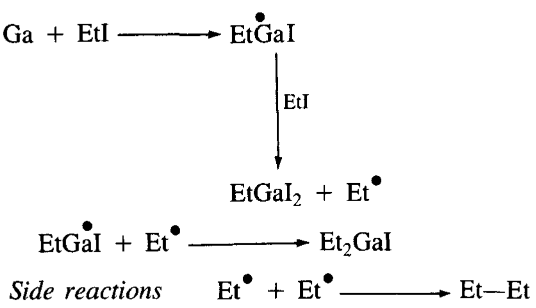
Gallium atoms

The best results were obtained when large excesses of ethyl iodide or bromide were co-deposited with gallium atoms. A ratio of halide to gallium of about 120:1 yielded a bright orange matrix at 77 K which upon warming to room temperature yielded a transparent pale brown solution. During the warm-up period a vigorous reaction took place with generation of heat.

The yield of a mixture of $(Et_2GaI)_2$ + $(EtGaI_2)_2$ from ethyl iodide was 77 % based on metal evaporated, which is essentially quantitative after considering loss of metal vapor to electrode supports, etc. With ethyl bromide the yield was 65 %, whilst ethyl chloride only gave traces of products.

DISCUSSION

On rare occasions small metal clusters/particles exhibit higher chemical reactivity than atoms.[18] This is *not* the case with gallium. According to our results, gallium particles do not react with ethyl iodide. This is true in toluene or pentane. However, when gallium atoms were immersed in excess ethyl iodide or bromide, complete reaction took place giving high yields of $(Et_2GaI)_2$ + $(EtGaI_2)_2$. Treatment of these with triethylaluminum caused alkylation and production of distillable triethylgallium. We believe the reactive species involved are gallium atoms. According to our earlier work,[7] the first step in the reaction is probably insertion to yield an RGaX species. The details of the formation of ethylgallium(III) iodo compounds are not known. One possibility is that upon further matrix warming the radical species abstracts halide (Scheme 2).



Scheme 2

An unusual matrix for gallium atoms was found to be triethylaluminum (as well as triethylaluminum plus toluene). Upon warming these mixtures, reasonably stable colloidal solutions of gallium particles were formed. Slowly a metallic precipitate was deposited that appeared to be a gallium compound which included up to 7 % of aluminum. This material was reactive with ethyl iodide, and is the only known example of gallium particles being so. Organic groups are also contained in these gallium–aluminum (Ga–Al) particles. It seems likely that this comparatively high reactivity is due to an amorphous state with very small particle sizes.

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