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Preliminary communication

Synthesis of tris(trifluoromethyl)gallium and its adducts

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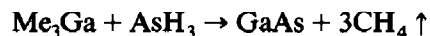
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Abstract

Tris(trifluoromethyl)gallium and its trimethylphosphine and trimethylarsine complexes have been synthesized using the Morrison reagent. Several new materials of potential importance to the microelectronic industry have been produced.

There is currently great interest in gallium arsenide chemistry as a consequence of strong economic incentives in the microelectronics industry [1]. Fueled by new funding made available by many U.S. government agencies, organometallic chemistry as a source of electronic materials precursors stands to become the U.S. organometallic chemical activity of the nineties, comparable in popularity to carbon-hydrogen bond activation in the seventies [2]. Currently gallium arsenide thin film chemistry is best carried out by the OMCVD (organometallic chemical vapor deposition) method for larger scale processes and typically involves the reaction of trimethylgallium with AsH_3 or PH_3 at elevated temperatures (600–700 °C) [3*]:



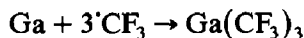
There has been a long standing interest in the synthesis of trifluoromethyl-organometallic compounds in our group and perhaps more such compounds have been prepared at MIT and the University of Texas than in all other laboratories combined [4–8]. Many methods have been employed [4,9,10]. Although trimethyl-aluminum, -gallium, -indium and -thallium [11] derivatives have been known for years, the trifluoromethyl-substituted Group III metals are now unknown.

We report the synthesis of tris(trifluoromethyl)gallium and its trimethylarsine and trimethylphosphine adducts. To accomplish this synthesis we have used the bis(trifluoromethyl)cadmium (glyme) [7,12] pioneered and developed by John Morrison and co-workers. At present the Morrison reagent is the most versatile and effective trifluoromethyl transfer reagent in organometallic chemistry. It is more

* Reference number with asterisk indicates a note in the list of references.

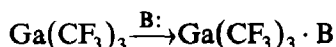
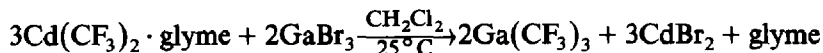
efficient than $\text{Hg}(\text{CF}_3)_2$ which was first used as a transfer reagent by Morrison in our laboratory [8,10].

For this specific synthesis, the most generally applicable synthetic method for trifluoromethyl organometallic compounds [6,13], the condensation reaction of metal atoms with trifluoromethyl radicals:



fails to produce $\text{Ga}(\text{CF}_3)_3$ but gives other gallium fluorocarbon higher polymers [14]. This rare problem is twofold: gallium metal does not vaporize primarily in its monomeric form and gallium vapor is easy to excite electronically when it enters a trifluoromethyl radical plasma region (an uncommon problem) leading to multiple reaction paths.

Bis(trifluoromethyl)cadmium · glyme can be easily prepared by the reaction of CdMe_2 with $\text{Hg}(\text{CF}_3)_2$ in glyme [12]. ($\text{Hg}(\text{CF}_3)_2$ was prepared by the decarboxylation reaction of $\text{Hg}(\text{CO}_2\text{CF}_3)_2$ in the presence of K_2CO_3 at 190°C under vacuum.) Tris(trifluoromethyl)gallium is prepared by the addition of a slight excess of $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ in CH_2Cl_2 to a stirred CH_2Cl_2 solution of GaBr_3 :



B: = trimethylphosphine and trimethylarsine

A dropwise addition of 2.0 g (5.9 mmol) of $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ in 10 ml of CH_2Cl_2 to 1.15 g (3.7 mmol) of GaBr_3 in 10 ml of CH_2Cl_2 led to immediate precipitation of CdBr_2 . The solution was stirred for a few minutes before filtering off the insolubles. Recrystallization from hexane gave 0.32 g (1.2 mmol) of $\text{Ga}(\text{CF}_3)_3$ as a tan solid (31% yield). ^{19}F NMR gave a singlet in the trifluoromethyl substituted metal region (-10 to $+80$ ppm) (see Table 1). A qualitative base hydrolysis of $\text{Ga}(\text{CF}_3)_3$ gave CF_3H which was identified by the infrared spectrum. The mass spectrum of $\text{Ga}(\text{CF}_3)_3$ was taken using field desorption mass spectroscopy and contained molecular ion peaks at 276 and 277 and $M^+ - \text{F}$ peaks at 257 and 258. Analysis. Found: F, 61.87. $\text{Ga}(\text{CF}_3)_3$ calcd.: F, 61.78%. The compound decomposed at 350°C without melting.

Tris(trifluoromethyl)gallium (trimethylphosphine) can be formed quantitatively by the addition of a slight excess of PMe_3 to a solution of $\text{Ga}(\text{CF}_3)_3$ dissolved in methylene chloride. The complexed compound was recrystallized from hexane. The ^{19}F and ^1H NMR data are in Table 1. A high resolution mass spectrum confirmed

Table 1

^{19}F NMR and ^1H NMR data for CF_3 gallium compounds ^a

Compound	^{19}F NMR	^1H NMR	$J(\text{P-H})$
$\text{Ga}(\text{CF}_3)_3$	52.4	—	—
$\text{Ga}(\text{CF}_3)_3 \cdot \text{PMe}_3$	51.7	1.5d	8
$\text{Ga}(\text{CF}_3)_3 \cdot \text{AsMe}_3$	51.4	1.6	—

^a Spectra were recorded for dilute solutions in CD_2Cl_2 at room temperature with external CFCl_3 and SiMe_4 as standards for ^{19}F and ^1H NMR, respectively. Shifts are in ppm and coupling constant in Hz.

the $M^+ - F$ peak, 33 m/e of the gallium 69 isotope with a 2 ppm error. (HRMS: 332.95786 found, 332.95714 calculated.) Analysis Found: F, 48.57. $\text{Ga}(\text{CF}_3)_3\text{PMe}_3$ calcd.: F, 48.48%. Crystals suitable for X-ray crystallography have been grown in THF at 0°C. A structure determination for $\text{Ga}(\text{CF}_3)_3\text{PMe}_3$ is underway.

Similarly, $\text{Ga}(\text{CF}_3)_3$ can be complexed with AsMe_3 to form $\text{Ga}(\text{CF}_3)_3\text{AsMe}_3$. This compound can also be recrystallized from hexane. $\text{Ga}(\text{CF}_3)_3\text{AsMe}_3$ decomposes at 225°C. Analysis Found: F, 43.04. $\text{Ga}(\text{CF}_3)_3\text{AsMe}_3$ calcd.: F, 43.11%.

The $(\text{CF}_3)_3\text{GaAsMe}_3$ adduct appears to be a very good single source precursor for the preparation of Group III–Group IV semiconductor materials such as gallium arsenide under mild conditions [15]. The oligomeric nature of gallium compounds of this class may be unique and crystallographic studies of the adducts are underway. Collaborations in the gallium arsenide film area are also underway.

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