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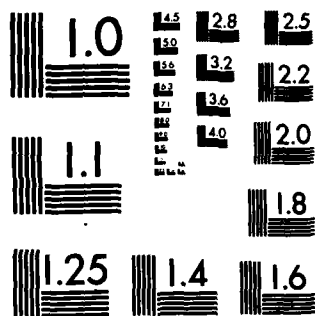
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NEW GALLIUM PRECURSORS FOR THE FORMATION OF HIGH PURITY
GALLIUM ARSENIDE BY METAL ORGANIC VAPOR PHASE DEPOSITION

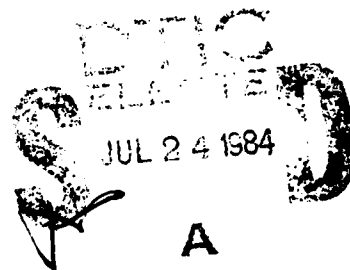
E. P. Schram
Department of Chemistry

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DEPARTMENT OF THE AIR FORCE
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by

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The Ohio State University

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I. ABSTRACT

The reduction of gallium trichloride monoammonia adduct with lithium hydride affords lithium trichlorohydrido gallate whereas the non-coordinated trichloride affords the known species, lithium tetrahydrido gallate.

Attempts to prepare the ammonia adduct of gallane via lithium tetrahydrido gallate and ammonium chloride resulted in decomposition with hydrogen evolution. Exploratory investigation geared towards the formation of gallium perfluoroalkyls, via discharge reactions involving hexafluoroethane and trifluoriodomethane, resulted in the gallium reduction of the pyrex reactors - construction of quartz reactors is therefore necessitated.

INTRODUCTION

The employment of gallium alkyls, towards the formation of epitaxial gallium arsenide (GaAs), via metal organic chemical vapor deposition (MOCVD), invariably results in carbon contamination of the GaAs. This exploratory effort involved screening several synthetic approaches toward the formation of new volatile compounds of Ga which, when employed in MOCVD reactors, may result in less carbon contamination than gallium alkyls.

The principle effort was directed towards the synthesis of an ammonia adduct of gallane, (i.e., $\text{GaH}_3 \cdot \text{NH}_3$), analogous to the known species which contain carbon, $\text{GaH}_3 \cdot \text{N}(\text{CH}_3)_3$.^{1,2} In a related manner, several systems designed to afford gallium amide, $\text{Ga}(\text{NH}_2)_3$, were examined. Finally, several systems were screened with regard to their potential toward the formation of perfluoroalkyl gallium compounds.

Discussion1. Ammonia Adducts of Gallane.

An ideal compound of gallium, to be employed in MOCVD reactors, would be gallane, GaH_3 ; however, this species is known only as the trimethylamine adduct $\text{GaH}_3 \cdot \text{N}(\text{CH}_3)_3$.^{1,2} The synthesis of the latter involves the reduction of galliumtrichloride with lithium hydride, equation 1, followed by hydride elimination by the weak acid, $\text{N}(\text{CH}_3)_3\text{H}^+$, equation 2.



This procedure was duplicated and the product isolated and characterized by its reported vapor tension and gas phase infrared spectrum.

In a related manner, toward the synthesis of $\text{GaH}_3\cdot\text{NH}_3$, NH_4Cl was substituted for $\text{N}(\text{CH}_3)_3\text{HCl}$, equation 2. Three separate reactions were carried out employing diethyl ether as the solvent, without isolation of the intermediate, LiGaH_4 (Table 1). Isolation of the latter is not necessary for the formation of $\text{GaH}_3\cdot\text{N}(\text{CH}_3)_3$, equation 1, and an excess of LiH is employed; i.e., $1\text{GaCl}_3:16\text{LiH}$.⁴

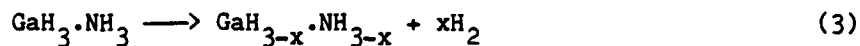
Reaction No.	Equation No.	Reactants				Theoretical Yield of Products and Excess Reagents				
		GaCl_3	LiH	NH_4^+	GaH_4^-	$\text{GaH}_3\cdot\text{NH}_3$	GaH_4^-	H_2	LiH	NH_4^+
1	1	1	20	-	-	-	1	-	17	-
1	2	-	17	30	1	1	-	1	17	29
2	1	1	4	-	-	-	1	-	0	-
2	2	-	-	1.25	1	1	-	1	0	0.25
3	1	1	8	-	-	-	1	-	4	-
	2	-	0	1	1	1	-	1	0	0

TABLE 1.

MOLAR REACTION RATIOS EMPLOYED TOWARD THE FORMATION OF AMMONIA GALLANE

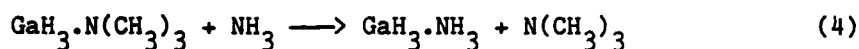
With regard to experimental results, summarized in Table 1, the $\text{GaCl}_3:\text{LiH}$ reaction ratios were varied from 1:20 (reaction 1), 1:4 (reaction 2), and 1:8 (reaction 3) followed by the treatment with excess NH_4^+ (reaction 1), a slight excess (reaction 2), and finally a stoichiometric quantity of NH_4^+ (reaction 3). In all these cases a small amount of H_2 was liberated during the formation of LiGaH_4 , equation 1. With regard to the reaction analogous to that represented by equation 2, reaction 1, in addition to the observed H_2 evolution, NH_3 was liberated, 0.6 mmole/30 mmole NH_4^+Cl^- employed. If the

excess NH_4^+Cl had reacted with excess LiH , a much larger quantity of NH_3 would have been observed. With regard to reaction 2, no NH_3 was observed; i.e., a slight excess of NH_4^+ , but in the absence of LiH . With regard to reaction 3, the produced LiGaH_4 was separated from the reaction products via high vacuum filtration and subsequently treated with NH_4Cl . During the latter procedure H_2 was evolved but NH_3 was absent. Concerning the reaction analogous to that represented by equation 2 (reactions 1 - 3) (Table 1), H_2 was evolved indicating reaction between NH_4^+ and GaH_4^- . Based on the fact that NH_3 was not generally evolved, it must be associated with the white non-volatile reaction product (up to 80°) which resulted from all three reactions. Because this product is non-volatile, unlike $\text{GaH}_3\cdot\text{N}(\text{CH}_3)_3$, it most likely consists of polymeric $\text{GaH}_{3-x}\text{NH}_{3-y}$, arising from the decomposition of $\text{GaH}_3\cdot\text{NH}_3$, equation 3, in an intra- or intermolecular manner.



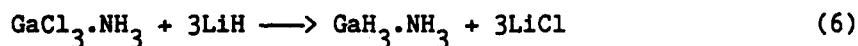
Dihydrogen evolution most likely occurs as a result of increased H^- character associated with GaH_3 as a result of coordination by NH_3 , with simultaneous increased protic character associated with NH_3 as a result of decreased electron density on N. Certainly NH_3 is a strong enough Lewis base to coordinate to GaH_3 because both NH_3 and $\text{N}(\text{CH}_3)_3$ adducts of $\text{Ga}(\text{CH}_3)_3$ are known.^{5,6} One may infer from the reported reaction stoichiometries that NH_4^+ reacts preferentially with GaH_4^- , rather than with the excess LiH .

In an effort to carry out a base displacement reaction, equation 4,



0.4 mmole of gallium adduct were treated with 2.6 mmoles NH_3 (1 atm) with the reaction mixture slowly warmed from -196°C . After 1 minute at 25° all of the H_2 had evolved and $\text{N}(\text{CH}_3)_3$ liberated and identified by gas phase infrared spectroscopy after separation from NH_3 . This result is also consistent with the previous conclusion that $\text{GaH}_3 \cdot \text{NH}_3$ is unstable with respect to elimination of dihydrogen, equation 3.

The final attempt to prepare an ammonia adduct of GaH_3 involved the procedure idealized by equations 5 and 6.



Equal molar quantities of GaCl_3 and NH_3 were combined (equation 5) in diethylether, to afford the adduct which exhibited infrared absorptions, in nujol, at $3280(\text{s})$, $3220(\text{m})$, and $3162(\text{w}) \text{ cm}^{-1}$ with the intensity pattern analogous to that reported for $\text{Ga}(\text{CH}_3)_3 \cdot \text{NH}_3$.⁷

Next the adduct was treated with LiH , 1:3 molar ratio respectively. During a one hour reaction period at 0°C , only a trace of H_2 was evolved. A subsequent 1 hour reaction period at 25°C afforded additional H_2 (~5% of theoretical for complete decomposition of LiH) with NH_3 (3.3% of that initially present in adduct form).

The non-volatile white reaction residue was separated from LiH and LiCl by vacuum filtration employing diethyl ether. LiH was present as unreacted

starting material as determined by its reactivity with H_2O to produce H_2 . The soluble fraction consisted of a mixture of $GaCl_3 \cdot NH_3$ and $LiGaCl_3H$. Diethyl ether is not completely removed from this latter mixture after 24 hours, $25^\circ C$, 10^{-4} torr, but is removed at $60^\circ - 10^{-4}$ torr as determined by stabilization of weight loss with time and confirmed by mass spectroscopy.

A. Mass Spectrum of $GaCl_3 \cdot NH_3 - LiGaCl_3H$.

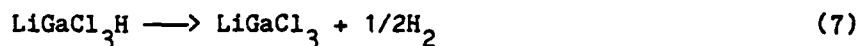
Gallium has two naturally occurring isotopes, mass 68.92 amu (60%) and 70.92 (40%), while chlorine isotopes have masses of 34.96 amu (75%) and 36.98 amu (24%). At $79^\circ C$ the most intense spectrum was due to $GaCl_2 \cdot NH_3$ exhibiting absorptions at 155.8, 157.8, 159.9, and 161.9 amu in the relative expected isotope ratios of $\sim 10.8:18.0:8.5:1$ respectively. (Theoretical: 155.8, 157.8, 159.9, and 161.9 respectively). In a similar fashion weak absorption due to $GaCl_3 \cdot NH_3$, $GaNH_3$, and HCl were observed along with medium intensity absorptions associated with $GaCl_2$ and Ga . The principle mode of decomposition in the mass spectrometer for $GaCl_3 \cdot NH_3$ is loss of Cl . The other component of the produce mixture, $LiGaCl_3H$, is nonvolatile at 79° .

B. Characterization of $LiGaCl_3H$ in the Presence of $GaCl_3 \cdot NH_3$.

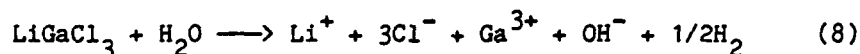
The 1H NMR spectrum consists of a sharp singlet at 1.41 ppm while NH_3 coordinated to $GaCl_3$ exhibits a broad singlet centered at 0.8 ppm from TMS, in the relative ratios 1:3.8 respectively, indicating 43.7 mole percent $LiGaCl_3H$ and 56.3 mole percent $GaCl_3 \cdot NH_3$. The infrared spectrum of $LiGaCl_3H$ exhibits a strong asymmetric absorption at 1985 cm^{-1} assigned to νGaH . This relatively high energy absorption, as compared to νGaH at 1853 cm^{-1} in $GaH_3 \cdot H(CH_3)_3$,¹ is attributed to an increase in the amount of s character in the Ga-H bond as a result of the electronegativity of Cl increasing the p character of the Ga-Cl bonds.

Basic hydrolysis of the $\text{LiGaCl}_3\text{H-GaCl}_3\cdot\text{NH}_3$ mixture (260 mg) afforded 0.6 mmole H_2 and 0.8 mmole NH_3 , indicating the mixture consists of 110 mg LiGaCl_3H and 154.3 mg $\text{GaCl}_3\cdot\text{NH}_3$ (mass balance 98.5%) or 42.8 and 57.2 mole percent composition respectively, compared to the ^1H NMR data, 43.7 and 56.3 mole percent respectively.

In order to determine the thermal stability of LiGaCl_3H and initiate development of its chemistry, a 311 mg sample of the product mixture (0.72 mmole LiGaCl_3H) was pyrolyzed at 140° for 24 hours to afford 0.38 mmole H_2 (theoretical yield 0.36 mmole) with the reductive elimination of H_2 represented by equation 7. The gallium containing product



LiGaCl_3 formally involves Ga(II) , (i.e., $\text{LiCl} + \text{GaCl}_2$), and this 2+ oxidation state should be subject to oxidation by water, equation 8.



The pyrolysis residue was treated with H_2O , pH 12, to afford H_2 (168% yield) and 1.28 mmole NH_3 (133% yield) with the latter arising from the hydrolysis of $\text{GaCl}_3\cdot\text{NH}_3$ remaining after pyrolysis (only 0.6 mmole NH_3 was liberated during pyrolysis). The amount of H_2 collected is indicative of gallium in an oxidation state $< 2+$ perhaps arising as a result of reductive pyrolysis of $\text{GaCl}_3\cdot\text{NH}_3$.

2. Exploratory Investigation.

A. Gallium Amide.

Gallium amide, $\text{Ga}(\text{NH}_2)_3$, has been reported to form when pyrophoric Ga reacts with NH_3 above 100°C ; however, its volatility was not described.⁸ Based on the strong Lewis acid character of Ga, $\text{Ga}(\text{NH}_2)_3$ would be expected to be polymeric and hence nonvolatile at 25°C . This latter suggestion was confirmed. Gallium trichloride was treated with a three fold mole ratio of sodium amide, NaNH_2 , in the mixed solvent system, benzene-toluene, to afford a green gray precipitate (after 4 hours at 25°) which was separated from the soluble components via vacuum filtration. No volatile gallium species other than GaCl_3 could be recovered from the either fraction. The reaction components were recombined and the system heated at 90° for two hours. Again vacuum fractionation of the volatile components afforded only GaCl_3 as a volatile gallium species.

B. Gallium Perfluoroalkyls.

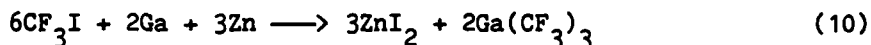
When one subjects hexafluoroethane to a high voltage electric discharge, CF_3 radical are produced which potentially could react with Ga to afford $\text{Ga}(\text{CH}_3)_3$,⁹ equation 9.



A 10,000v vertical H cell was utilized in this exploratory work with the H cell of pyrex construction and Kovar to glass seals that served as electrodes. The gallium was contained in the Kovar while C_2F_6 was allowed to slowly warm from a -196°C trap and condensed in a second -196°C trap, p - 2 torr. Activated gallium was sputtered above the Kovar seal during the purple

discharge, and reduction of the pyrex by Ga resulted in rapid leak formation. It has been reported that pyrex is attacked by Ga at 500°C whereas quartz is quite stable to 1160°C.¹⁰

Several reactions were examined which involved microwave excitation of CF_3I in the presence of Ga. The initial experiments involved subjecting Ga to the tail flame of CF_3I^* which resulted in only the formation of I_2 as a volatile reaction product. Next the microwave cavity was placed directly over the Ga; however, this geometry resulted in reduction of the pyrex reactor. Next the initial geometry was utilized in the presence of Mg to function as an I_2 scavenger. However, the efficiency of the design was low based on the fact that I_2 was again produced. Finally the reaction ideally represented by equation 10 was attempted.



A 5% by weight alloy of Zn and Ga (mp 25°C)¹¹ was prepared (2.6 g Ga) and the stirred liquid alloy treated with CF_3I for one hour at 25° (P = 1 atm). No uptake of CF_3I resulted. Next the reaction mixture was heated for 12 hours at 85°C. The alloy appearance changed to that of a black powder which, when subsequently ground in an effort to prepare a mull infrared sample, yielded metallic droplets. No infrared absorption resulted, and no volatile gallium compounds were obtained from this reaction system.

Future Investigation.

The hydride reduction of $\text{GaCl}_3 \cdot \text{NH}_3$ results in the new species LiGaCl_3H which exhibits remarkable thermal stability. The reaction conditions for its

preparation were quite mild, 25°C. In an effort to increase the H to Cl ratio a less volatile either will be employed at higher reaction temperatures and the chemical properties of the expected series of compounds will be investigated.

With regard to the discharge reactions between CF_3 radicals and Ga - quartz reactor systems need to be fabricated to prevent destruction of the reactor and hence allow investigation of these chemical systems.

Experimental

All reactions were carried out employing standard high vacuum techniques with the quantities of volatile materials measured in the gas phase in a volume calibrated system. Typically reactions were carried out on a mmole scale. Dihydrogen was collected with a Toepler system and identified by combination to H_2 over CuO at 300°C. Infrared spectra were recorded with a Perkin Elmer 457 spectrometer while NMR spectra were obtained with a Bruker WM-300FT instrument. Mass spectral measurements were obtained utilizing a Nicolet FT-MS-1000 spectrometer.

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