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Preparation of Organogallium Compounds from Organolithium Reagents and Gallium Chloride. Infrared, Magnetic Resonance, and Mass Spectral Studies of Alkylgallium Compounds

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Conditions for the preparation of a series of base-free trialkylgallium compounds in benzene solvent by the exchange reaction of alkyllithium compounds and gallium chloride are described. Optimum conditions which favor formation of the trialkyl involve mixing a benzene solution of an appropriate alkyllithium compound and a benzene solution of gallium chloride in exactly a 3:1 molar ratio, heating of the reaction mixture for 12 hr at 70°, filtration to remove by-product lithium chloride, removal of solvent under vacuum, and vacuum distillation of the product: $3RLi + GaCl_3 = 3LiCl + R_3Ga$, where $R = C_2H_5$, n-C_3H_7, n-C_4H_9, i-C_4H_9, s-C_4H_9, and t-C_4H_9. Alkylgallium dichlorides and dialkylgallium chlorides are produced when lithium alkyls and gallium chloride are allowed to react in a 1:1 and 2:1 molar ratio, respectively: $nRLi + GaCl_3 = nLiCl + R_nGaCl_{3-n}$, where $n = 1$ and 2. Reaction of an alkyllithium compound and gallium chloride in a molar ratio in excess of 3:1 results in formation of the corresponding lithium tetraalkylgallate: $4n\text{-}C_3H_7Li + GaCl_3 = 3LiCl + LiGa(n\text{-}C_3H_7)_4$. Trivinylgallium tetrahydrofuranate is produced by the reaction of vinyllithium and gallium chloride in 3:1 molar ratio in tetrahydrofuran solvent. Infrared, proton magnetic resonance, and mass spectra of R_nGaCl_{3-n} compounds where $R = C_2H_5$ to C_4H_9 isomers and $n = 1$–3 are reported and discussed. Proton magnetic resonance spectra reveal that the chemical shifts for protons on α-carbon atoms are sensitive to substitution on the gallium. An explanation for these chemical shift data along with molecular association data for R_nGaCl_{3-n} compounds is given. Mass spectroscopy can be used as a convenient, diagnostic tool for the identification of organogallium compounds of this type. Ion abundance data for all compounds are presented and the fragmentation processes believed to give these ions are discussed.

Introduction

Previously, we reported[1] the preparation of tri-*n*-butylgallium in high yield and purity by the reaction of gallium chloride and *n*-butyllithium in 1:3 molar ratio (eq 1).

$$GaCl_3 + 3n\text{-}C_4H_9Li \xrightarrow{\text{benzene}} 3LiCl + (n\text{-}C_4H_9)_3Ga \qquad (1)$$

Analytically pure tri-*n*-butylgallium was isolated in yields of 90–97% upon dropwise addition of a benzene solution of *n*-butyllithium to a benzene solution of gallium chloride in 3:1 molar ratio, heating at the reflux temperature, filtration to remove lithium chloride, removal of benzene solvent under vacuum, and vacuum distillation of the product. This preparative route to tri-*n*-butylgallium has significant advantages[1] over previously reported routes. We have now developed and wish to report the general reaction of a series of organolithium reagents and gallium chloride in 1:1, 2:1, and 3:1 molar ratio, respectively (eq 2)

$$nRLi + GaCl_3 = nLiCl + R_nGaCl_{3-n} \qquad (2)$$

where $R = C_2H_5$, n-C_3H_7, n-C_4H_9, i-C_4H_9, s-C_4H_9, t-C_4H_9, and C_2H_3(vinyl) and $n = 1$–3.

Infrared, proton magnetic resonance, and mass spectra of R_nGaCl_{3-n} compounds where $R = C_2H_5$ to C_4H_9 isomers and $n = 1$–3 were recorded and interpreted in an effort to develop spectroscopy as a tool for identifying these compounds and to describe bonding characteristics.

Experimental Section

Pyrophoric compounds were handled using Schlenk ware under dry nitrogen, a nitrogen filled drybox and/or a multipurpose vacuum manifold.[2] Thiophene-free, reagent grade benzene was distilled over $LiAlH_4$ prior to use. Vinyllithium (2 *M* in THF) was purchased from Alfa. *n*-Butyl, *sec*-butyl-, and *tert*-butyllithium reagents in hydrocarbon solvent were purchased from MCB Manufacturing Chemists. Lithium metal as $^1/_8$ in. diameter wire with 1–2% sodium was obtained from the Lithium Corporation of America. Ethyl bromide and *n*-propyl and isobutyl chlorides were obtained from Aldrich Chemical and distilled prior to use. The preparation of gallium chloride was described previously.[1]

Analyses. Organometallic gallium compounds were analyzed by methods reported previously.[1] The results of these analyses are given in Table I. The organolithium reagents which were prepared in this laboratory were analyzed by hydrolysis of a small portion of the sample followed by analytical determination of evolved alkane using a multipurpose vacuum line[2] and atomic emission analysis for lithium in the aqueous medium using a Jarrell-Ash instrument.

Preparation of Organolithium Reagents. Benzene solutions of ethyl-, *n*-propyl-, and isobutyllithium were prepared using modified literature preparations.[3,4] Finely divided lithium shot[5] was prepared by rapidly stirring a heated suspension of lithium wire cut into 0.5 in. lengths and dry mineral oil in a Morton flask. The lithium shot was allowed to cool and the mineral oil was removed by washing with dry benzene.

Ethyllithium in Benzene. Ethyl bromide (25 ml, 0.334 mol) was added dropwise to a magnetically stirred suspension of 1.4 mol of lithium shot and 350 ml of dry benzene in a 500-ml three-neck flask fitted with a pressure equalizing addition funnel and water condenser under nitrogen purge. The reaction mixture was stirred at room temperature for 2 hr after completion of the addition. The mixture was cooled and filtered under nitrogen to remove unreacted lithium shot and salts. The salts were washed with three 10-ml portions of dry benzene giving approximately 390 ml of a clear, light yellow filtrate which was found to be 0.42 *M* in ethyllithium. Yield was 50%. Anal. Lithium content = 0.416 *M*; ethyl content (ethane passed through a slush trap cooled with methylcyclohexane, −127°) = 0.422 *M*; R:Li experimental ratio = 1.01:1.00.

Additional Alkyllithium Reagents in Benzene Solution. *n*-Propyllithium and isobutyllithium in yields of 86% were prepared by reaction of *n*-propyl chloride and isobutyl chloride, respectively, with lithium shot using essentially the same procedure described for ethyllithium. Hydrolysis followed by analysis of evolved alkyl and lithium revealed an alkyl:lithium ratio of 1.0:1.0 in both cases.

Preparation of Tri-*n*-propylgallium, Method A. Freshly sublimed gallium chloride (7.18 g, 0.041 mol) was dissolved in 50 ml of dry benzene in a 500-ml one-neck flask which was fitted with a Claisen head to which were connected a 250 ml pressure equalizing addition funnel and water condenser. An atmosphere of dry nitrogen was maintained in the system using a hose-connector attached to the water condenser. The addition funnel was fitted with a septum for introduction of liquids using a syringe. *n*-Propyllithium (127 ml of a 0.956 *M* solution, 0.122 mol) was added dropwise over a period of 1 hr to the magnetically stirred gallium chloride solution. Formation of a white precipitate was noted on initial addition of *n*-propyllithium, but dissolved upon stirring until approximately 15% of the addition had been completed, after which time the precipitate persisted. The reaction was noticeably exothermic as benzene was observed to reflux gently during the entire addition. The reaction mixture was filtered immediately upon completion of the *n*-propyllithium addition and the filtrate was concentrated by removing the majority of the benzene under vacuum. The resulting solution was transferred under nitrogen purge to a 50-ml round-bottom flask which was fitted with a frac-

Table I. Comparison of Calculated and Experimental Weight Percent Composition Data for Organogallium Compounds

Compd	% gallium		% alkyl		% chlorine		Exptl R:Ga ratio
	Calcd	Found	Calcd	Found	Calcd	Found[a]	
$(n\text{-}C_3H_7)_3Ga$	35.0	33.7	65.0	63.6			3.07
$(n\text{-}C_3H_7)_2GaCl$	36.4	36.4	45.0	46.0	18.6	17.6	2.06
$n\text{-}C_3H_7GaCl_2$	38.0	36.8	23.9	23.0	38.6	40.4	1.02
$(i\text{-}C_4H_9)_3Ga$	28.9	28.3	71.1	71.0			3.06
$(i\text{-}C_4H_9)_2GaCl$	31.8	32.1	52.1	49.2	16.1	18.7	1.87
$i\text{-}C_4H_9GaCl_2$	35.3	35.3	28.9	26.5	35.8	38.2	0.92
$(s\text{-}C_4H_9)_3Ga$	28.9	28.3	71.1	67.9			2.93

[a] Determined by difference.

tionating column, distillation condenser, three-neck separator, and collection flasks. The solution was heated using a Woods metal bath and the remaining benzene distilled at 76–78° under 640 Torr. The fractionating column was removed which allowed 2.2 ml of a clear, colorless liquid to distil at 135–140°. This was found to be tri-*n*-propylgallium. Yield was 27% based on the quantity of gallium chloride used. Another fraction of 5.0 ml of a clear, colorless liquid was obtained at 92–93° under 0.20 Torr. This was found to be di-*n*-propylgallium chloride. Yield was 72% based on the quantity of gallium chloride used.

Variables in the reaction sequence were studied systematically in an effort to optimize yields of the trialkyl. These attempts are described in methods B–D below.

Method B. *n*-Propyllithium (92 ml of a 1.10 *M* solution, 0.102 mol) was added to gallium chloride (5.50 g, 0.031 mol) in 30 ml of dry benzene. The molar ratio of the reactants *n*-propyllithium:gallium chloride was 3.4:1.0. The mixture was heated for 12 hr at 70° after completion of the *n*-propyllithium addition and filtered. The solid residue was washed with dry benzene; benzene was removed from the combined filtrate and washings under vacuum giving a solid and a relatively involatile liquid. The liquid distilled in the range 25–26° under 0.5 Torr, yielding 2.2 ml of a clear, colorless liquid. This was found to be tri-*n*-propylgallium by analysis. Yield was 37%. No effort was made to analyze the solid left in the distillation flask; however, the solid was found to be extremely reactive with water.

Method C. The reactants were mixed in the molar ratio *n*-propyllithium:gallium chloride 2.4:1.00, the reaction mixture was heated for 12 hr at 70°, and products were isolated by vacuum distillation. One fraction distilled at 25–26° under 0.030 Torr yielding 3.6 ml of a clear, colorless liquid. This was found to be tri-*n*-propylgallium by analysis. Yield was 32%. A second fraction of 4.0 ml of a material found to be di-*n*-propylgallium chloride by analysis distilled in the range 78–81° under 0.030 Torr. Yield was 41%.

Method D. Reactants were mixed in the molar ratio *n*-propyllithium:gallium chloride of 3.0:1.0 (11.13 g, 0.0632 mol of gallium chloride was used). The reaction mixture was heated at 70° for 12 hr, filtered, and subjected to vacuum distillation. A single product having a volume of 9.0 ml was obtained at 25–26° under 0.025 Torr. This was found to be tri-*n*-propylgallium by analysis. Yield was 74%.

Reaction of Di-*n*-propylgallium Chloride and *n*-Propyllithium. *n*-Propyllithium (6.0 ml of a 1.05 *M* solution, 0.0063 mol) was added dropwise to a magnetically stirred solution of di-*n*-propylgallium chloride (1.34 g, 0.00070 mol) in 10 ml of dry benzene. Appearance of a white precipitate was noted upon addition of the alkyllithium solution. The resulting mixture was filtered to remove the precipitate and the benzene was removed from the filtrate under vacuum. The remaining liquid distilled under vacuum yielding 1.30 ml of a clear, colorless liquid in the range of 25–30° under 0.25 Torr. This was shown to be tri-*n*-propylgallium by analysis. Yield based on the quantity of di-*n*-propylgallium chloride used was 96%.

Reaction of Tri-*n*-propylgallium and *n*-Propyllithium. *n*-Propyllithium (4.25 ml of a 2.01 *M* solution, 0.00854 mol) was added dropwise to a magnetically stirred solution of tri-*n*-propylgallium (1.70 g, 0.0097 mol) in 15 ml of dry benzene in a 50-ml round-bottom flask fitted with a pressure equalizing addition funnel and water condenser. Precipitate formation was noted on initial mixing of the reactants. The mixture was filtered and the solid was washed with two, 15-ml portions of dry benzene using a double Schlenk tube and frit of medium porosity.[6] The sample was dried under vacuum for 2 hr yielding approximately 2 g of material. The sample was found to be soluble in warm benzene and was recrystallized from this solvent. Analysis revealed the sample to be lithium tetra-*n*-propylgallate [$LiGa(n\text{-}C_3H_7)_4$]. Yield was 90%. Anal. Calcd: Ga, 28.1; propyl, 69.1. Found: Ga, 27.2; propyl, 67.3; experimental propyl:Ga ratio = 4.03:1.00.

Preparation of *n*-Propylgallium Chlorides (R_nGaCl_{3-n}, $n = 1$ and 2). Di-*n*-propylgallium chloride was prepared by the reaction of gallium chloride and *n*-propyllithium in 1:2 molar ratio and by the reaction of tri-*n*-propylgallium and gallium chloride in 2:1 molar ratio in yields of 63 and 85%, respectively. *n*-Propylgallium dichloride was prepared by the reaction of *n*-propyllithium and gallium chloride in 1:1 molar ratio and by the reaction of tri-*n*-propylgallium and gallium chloride in 1:2 molar ratio in yields of 95 and 68%, respectively.

Preparation of Triethylgallium in Benzene. Ethyllithium (215 ml of a 0.42 *M* solution, 0.090 mol) was added dropwise to a magnetically stirred solution of gallium chloride (5.2 g, 0.0296 mol) in 15 ml of dry benzene in a 500 ml flask fitted with a pressure equalizing addition funnel and water condenser. The resulting mixture was heated at 70° for 12 hr, allowed to cool to room temperature, and filtered. Solid on the frit was washed with dry benzene. The combined filtrate and washings were subjected to fractional distillation under a nitrogen atmosphere of 650 Torr. After removal of benzene 4.2 ml of a product fraction boiling at 130–135° was obtained. Mass spectral analysis revealed the product to be triethylgallium. Yield was 96%.

Preparation of Tri-*sec*-butylgallium. *sec*-Butyllithium (115 ml of a 1.27 *M* solution in benzene, 0.146 mol) was added dropwise over a period of 1 hr to a solution of gallium chloride (8.4 g, 0.0478 mol) in 50 ml of dry benzene in a 500 ml flask fitted with a pressure equalizing addition funnel and water condenser. The resulting mixture was stirred at room temperature for 12 hr and filtered. Solvent was removed from the filtrate under vacuum yielding 12.0 ml of a relatively involatile liquid which distilled at 49–52° under 0.5 Torr. The product was found to be tri-*sec*-butylgallium by chemical and mass spectral analysis. Yield was 95%.

Preparation of Tri-*tert*-butylgallium. *tert*-Butyllithium (134 ml of a 1.12 *M* solution in benzene, 0.15 mol) was added dropwise over a period of 1 hr to a magnetically stirred solution of gallium chloride (8.80 g, 0.0499 mol) in 50 ml of dry benzene in a 500 ml flask fitted with a pressure equalizing addition funnel and water condenser. The mixture was heated at 70° for 12 hr, allowed to cool, and filtered. Solvent was removed from the filtrate yielding a relatively involatile liquid that distilled at 36–37° under 0.050 Torr. This material was shown to be tri-*tert*-butylgallium by proton magnetic resonance and mass spectroscopy. Yield was 84%.

Preparation of Triisobutylgallium. Isobutyllithium (215 ml of a 1.54 *M* solution, 0.33 mol) was added dropwise to a magnetically stirred solution of gallium chloride (19.4 g, 0.11 mol) in 100 ml of dry benzene in a 500 ml flask fitted with a pressure equalizing addition funnel and water condenser. The resulting mixture was heated at 70° for 12 hr, allowed to cool, and filtered. Solvent was removed from the filtrate under vacuum yielding 19 ml of a relatively involatile liquid which distilled at 37° under 0.13 Torr. This material was shown to be triisobutylgallium by chemical analysis. Yield was 67%.

Preparation of Isobutylgallium Chlorides (R_nGaCl_{3-n}, $n = 1$ and 2). Diisobutylgallium chloride was prepared by the reaction of triisobutylgallium and gallium chloride in 2:1 molar ratio in 88% yield. Isobutylgallium dichloride was prepared by the reaction of triisobutylgallium and gallium chloride in 1:2 molar ratio in 85% yield.

***n*-Butylgallium Compounds.** Compounds of the general formula $(n\text{-}C_4H_9)_nGaCl_{3-n}$ where $n = 1$–3 were prepared as described previously.[1]

Preparation of Trivinylgallium Tetrahydrofuranate. A 500-ml round-bottom flask containing 7.0 g of gallium chloride (0.037 mol) was fitted with a Claisen tube, 250 ml pressure equalizing addition funnel, and water condenser under nitrogen purge. The addition funnel was charged with 25 ml of dry tetrahydrofuran which was added

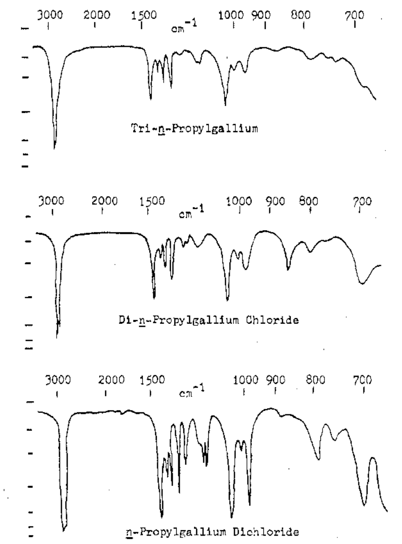


Figure 1. Infrared spectra of *n*-propylgallium compounds (R_nGaCl_{3-n}; n = 1-3).

dropwise to the magnetically stirred gallium chloride cooled with an ice-water bath. Rapid addition of the tetrahydrofuran should be avoided since adduct formation between this solvent and gallium chloride is strongly exothermic. A clear, orange-yellow solution was formed upon completion of the addition. A tetrahydrofuran solution of vinyllithium (100 ml of a 1.16 *M* solution, 0.116 mol) was syringed into the addition funnel and added dropwise over a period of 2 hr to the stirred gallium chloride solution. Precipitate formation was noted upon addition of approximately 5 ml of the vinyllithium solution; however, this precipitate dissolved as more vinyllithium was added. The clear, yellow solution formed upon completion of the addition produced a white precipitate upon stirring at room temperature for 3 days. This mixture was filtered and THF removed from the filtrate under vacuum giving 2.0 ml of a single, colorless fraction at 37-40° under 0.075 Torr. This material was found to be trivinylgallium tetrahydrofuranate by mass spectral and chemical analysis. The experimental vinyl group:Ga ratio was 2.99:1.00. Yield was 35%.

Spectroscopic Characterization of R_nGaCl_{3-n} Compounds Where R = C_2H_5 to C_4H_9 Isomers and n = 1 to 3. All compounds of the general formula R_nGaCl_{3-n} are liquids at room temperature. Infrared, proton magnetic resonance, and mass spectra of the neat liquid samples were recorded.

Infrared spectra were obtained by placing one or two drops of a neat liquid sample between two sodium chloride salt plates in the drybox. Infrared spectra of these samples were obtained on a Perkin-Elmer Model No. 137 instrument over the range 4000-650 cm⁻¹. Infrared spectra for the compounds R_nGaCl_{3-n} where R = *n*-C_3H_7 and n = 1 to 3 are shown in Figure 1.

Proton magnetic resonance spectra were obtained using a Varian A60A instrument and samples of the neat liquids containing trace quantities of benzene or CH_2Cl_2 as internal standard. All samples were prepared in the drybox or on the bench top using a syringe and strong nitrogen purge. All chemical shift values are quoted relative to TMS using literature chemical shift values of τ 2.73 and 4.67 for benzene and CH_2Cl_2, respectively.[7] Proton magnetic resonance spectra of the series of compounds $(i\text{-}C_4H_9)_nGaCl_{3-n}$ where n = 1 to 3 are shown in Figure 2.

Mass spectra were obtained using a Varian EM 600 mass spectrometer. Two to three microliters of trialkylgallium compounds and of trivinylgallium tetrahydrofuranate were injected into the batch oven inlet using a microliter syringe and Varian areograph septa. The oven temperature was maintained at 110°; higher temperatures caused decomposition of the trialkyl compounds. Spectra of alkylgallium halides (R_nGaCl_{3-n} where n = 1 or 2) could not be obtained in the same manner due to decomposition at the relatively higher temperatures needed to cause volatilization of these samples. These materials were introduced by filling a 3 in. length of capillary tube (0.5-0.9 mm i.d.) with one end sealed with 1.0-1.5 µl of a sample in the drybox. The open end of the tube was sealed with tap grease, removed from the drybox, inserted in the direct probe wand of the direct inlet on the EM 600 system, broken slightly above the liquid sample level, and injected immediately. Sample volatility was sufficient to give meaningful spectra without supplying external heat to the samples. All mass spectra were recorded at a total ion current reading of 2-3 and at 70 eV ionizing energy.

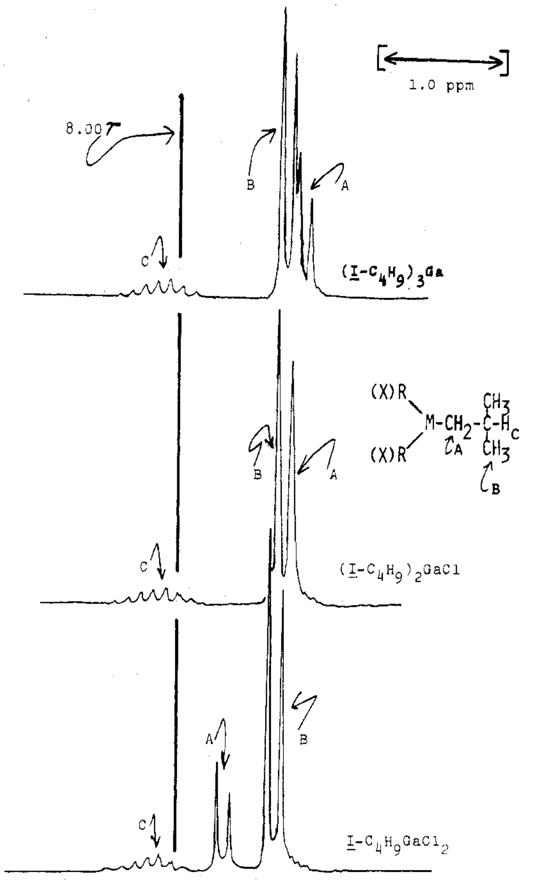


Figure 2. Proton NMR spectra of R_nGaCl_{3-n} compounds: n = 1, 2, and 3, and R = $i\text{-}C_4H_9$.

Table II. Reaction of Gallium Chloride and *n*-Propyllithium in Benzene Under Various Conditions

$$GaCl_3 + nLiR \rightarrow R_nGaCl_{3-n} + nLiCl$$

Method	Rxn temp, °C	Reactant ratio (n/b)	Dist cond	Prdt yield, %	
				R_3Ga	R_2GaCl
A	RT[a]	3.0	Atm pressure[b]	27	72
B	70[c]	3.4	Vacuum	37	0
C	70[c]	2.4	Vacuum	32	41
D	70[c]	3.0	Vacuum	74	0

[a] Reaction mixture filtered upon completion of the *n*-propyllithium addition. [b] Minor decomposition of tri-*n*-propylgallium is expected upon attempted distillation under atmospheric pressure. [c] The reaction mixture was maintained at the temperature specified for approximately 12 hr.

Unsuccessful attempts were made to obtain mass spectra of these compounds using a higher resolution, Varian CH-5 mass spectrometer which was kindly made available by the University of Wyoming Chemistry Department. The mass spectrum of tri-*tert*-butylgallium was obtained by allowing the neat material to bleed into the direct inlet system on the CH-5 instrument. The other samples could not be introduced in this manner due to relative involatility and all samples decomposed (presumably in the inner walls of the batch inlet system) when they were injected with a microliter syringe through a septum into the batch-oven inlet.

Ion abundance data obtained on the EM-600 instrument are given in Table III.[8]

Results and Discussion

Preparation of Base Free Trialkylgallium Compounds. Analysis of Table II reveals that conditions favoring formation of tri-*n*-propylgallium involve mixing *n*-propyllithium and gallium chloride in exactly a 3:1 molar ratio and heating the reaction mixture for 12 hr at 70° (method D). These conditions also favor formation of homologous trialkylgallium compounds in high yield and purity. Triethyl-, tri-*n*-butyl-, triisobutyl-, tri-*sec*-butyl-, and tri-*tert*-butylgallium are produced in yields ranging from 70 to 97% when these reaction conditions are employed.

Analysis of the remaining data in Table II reveals that considerable quantities of di-*n*-propylgallium chloride are produced in a mixture with tri-*n*-propylgallium when *n*-propyllithium and gallium chloride are mixed in a 3:1 molar ratio, respectively, followed by immediate filtration and work-up (method A) or when the ratio of reactants is less than 3:1 (method C, ratio of *n*-propyllithium:gallium chloride = 2.4:1.0). Results in the method A reaction suggest that the metathetical displacement reaction of di-*n*-propylgallium and *n*-propyllithium is relatively slow. This reaction was demonstrated to go to completion, however, in this study. Tri-*n*-propylgallium was produced in 96% yield by the reaction of analytically pure di-*n*-propylgallium chloride and *n*-propyllithium in 1:1 molar ratio (eq 3). Predominant for-

$$n\text{-}C_3H_7Li + (n\text{-}C_3H_7)_2GaCl = LiCl + (n\text{-}C_3H_7)_3Ga \qquad (3)$$

mation of di-*n*-propylgallium chloride in the method C reaction is consistent with a stepwise, metathetical displacement reaction. Support of this conclusion is provided by studies of the reaction of *n*-propyllithium and gallium chloride in 1:1 and 2:1 molar ratios. Major products were found to be *n*-propylgallium dichloride and di-*n*-propylgallium chloride, respectively (eq 4 and 5). Tri-*n*-propylgallium in the relatively

$$n\text{-}C_3H_7Li + GaCl_3 = LiCl + n\text{-}C_3H_7GaCl_2 \qquad (4)$$

$$2n\text{-}C_3H_7Li + GaCl_3 = 2LiCl + (n\text{-}C_3H_7)_2GaCl \qquad (5)$$

low yield of 37% was isolated when *n*-propyllithium and gallium chloride were mixed and allowed to react in 3.4:1.0 molar ratio (method B, Table II). No di-*n*-propylgallium chloride was isolated in this reaction and a hydrolytically active, relatively involatile solid remained in the distillation apparatus at the end of the work-up procedure. This involatile solid is likely lithium tetra-*n*-propylgallate formed by reaction of tri-*n*-propylgallium and excess *n*-propyllithium (eq 6).

$$n\text{-}C_3H_7Li + (n\text{-}C_3H_7)_3Ga = LiGa[(n\text{-}C_3H_7)_4] \qquad (6)$$

Lithium tetra-*n*-propylgallate was produced in 90% yield when *n*-propyllithium and tri-*n*-propylgallium were allowed to react in 1:1 molar ratio (eq 6). This solid substance was found to be relatively insoluble in cold benzene and could be recrystallized from this solvent. Lithium tetra-*n*-propylgallate is relatively involatile and stable at least up to its melting point. Similar alkylates are well known for boron[9,10] and aluminum[9,11] and trimethylgallium has been found to react with methyllithium.[12]

Preparation of Trivinylgallium Tetrahydrofuranate. Efforts to extend the fundamental organolithium–gallium chloride exchange reaction to include reaction in Lewis base solvents have had limited success. The reaction of vinyllithium and gallium chloride in 3:1 molar ratio in tetrahydrofuran has been evaluated as a general route to vinylgallium compounds. A Lewis base solvent must be employed for this reaction due to the insolubility of vinyllithium in hydrocarbon solvents. The reaction in tetrahydrofuran proceeds with two major differences in comparison with alkyllithium–gallium chloride exchange reactions in benzene solvent. First, the reaction in tetrahydrofuran solvent is considerably slower, lithium chloride being formed only after stirring of the reactants at room temperature for several hours. This is likely due to the greater solubility of lithium chloride[13] in the more polar solvent and the corresponding less favorable thermodynamic driving force for the exchange reaction. Second, the major product in tetrahydrofuran solvent is the trivinylgallium–THF, Lewis acid–base adduct (eq 7). This adduct is stable at least up

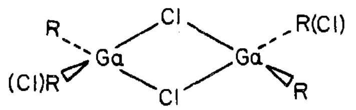
$$3C_2H_3Li + GaCl_3 \xrightarrow{THF} 3LiCl + (C_2H_3)_3Ga{\cdot}THF \qquad (7)$$

to 60° and can be distilled successfully under vacuum. Adduct formation in a basic solvent is expected for organometallic compounds of gallium[14] and amine complexes of trivinylgallium[15] have been described.

Spectroscopic Characterization of Alkylgallium Compounds. Infrared spectra of alkylgallium compounds in the range 4000–650 cm^{-1} did not prove to be diagnostic. The spectra in this range consisted of fairly typical alkyl C–H and C–C stretching and bending absorptions; however, an increase in the intensity of bands attributable to methylene rocking vibrations in the range 700–800 cm^{-1} was observed for all alkylgallium chloride compounds (see Figure 1). Unfortunately, all Ga–C and Ga–Cl vibrations are expected[16] at frequencies lower than 600 cm^{-1}.

The chemical shift of protons on α-carbon atoms of alkylgallium compounds was found to be sensitive to substitution on the gallium atom in proton magnetic resonance spectra. This is most clearly observed in spectra of isobutylgallium compounds (Figure 2). A multiplet consisting of nine peaks centered at τ 7.77, doublet at τ 8.92, and doublet at τ 9.07 is observed in the proton magnetic resonance spectrum of triisobutylgallium. The area ratio of the nine-peak multiplet to combined doublet signals is found to be 1.0:7.7. These signals are assigned to isobutylmethyne, methyl, and methylene protons, respectively. Assignment of the lower intensity, highest field doublet at τ 9.07 to the α-methylene environment is consistent with the polarity of the gallium–α-carbon bond and resulting carbanion character of the α-carbon atom. The α-methylene proton doublet was found to shift to lower magnetic fields in isobutylgallium chloride compounds while the chemical shifts of the other protons remained nearly constant (Figure 2). The α-methylene doublet has merged with the methyl doublet at τ 8.90 in the spectrum of diisobutylgallium chloride and is clearly observed at τ 8.45 in the spectrum of isobutylgallium dichloride.

The shift of α-methylene proton signals to lower magnetic field and relative insensitivity of other signals as isobutyl groups are replaced by chlorine atoms are consistent with strong, local diamagnetic deshielding effects of the electronegative chlorine atoms. These deshielding effects do not appear to be linearly dependent on the number of chlorine atoms present, however. The two chlorine atoms in the dichloride compound are over 3.6 times as effective as the single chlorine atom in the monochloride compound in deshielding the α-methylene protons. The anomalously low deshielding effect of the chlorine atom in diisobutylgallium chloride could possibly be due to a change in the state of aggregation for this compound in comparison with that of the trialkyl. Studies of the molecular association of $(i\text{-Bu})_nGaCl_{3-n}$ compounds in benzene where n = 1–3 reveal that the trialkyl is monomeric while both chloride containing compounds are dimeric over a reasonably wide concentration range (Figure 3). The dimeric compounds likely contain bridging chlorine atoms.



Bridge bonding in this system is believed to arise from mutual overlap between empty metal orbitals, directed toward the bridging chloride ions and filled, valence shell orbitals on the chloride ions.[17] Each bridge bonded chloride ion is thought

Table III. Ion Abundances in Mass Spectra of Alkylgallium Compounds

m/e	Ion	Rel intensity
	A. Tri-*n*-butylgallium	
242	$^{71}GaR_3$	1
240	$^{69}GaR_3$	1
185	$^{71}GaR_2$	66
183	$^{69}GaR_2$	100
170	$^{71}GaRC_3H_6$	23
168	$^{69}GaRC_3H_6$	35
156	$^{71}GaRC_2H_4$	1
154	$^{69}GaRC_2H_4$	3
142	$^{71}GaRCH_2$	7
140	$^{69}GaRCH_2$	9
128	^{71}GaR	23
126	^{69}GaR	38
113	$^{71}GaC_3H_6$	4
111	$^{69}GaC_3H_6$	8
85	$^{71}GaCH_2$	4
83	$^{69}GaCH_2$	7
71	^{71}Ga	66
69	^{69}Ga	93
57	C_4H_9	5
56	C_4H_8	9
55	C_4H_7	5
43	C_3H_7	11
41	C_3H_5	32
29	C_2H_5	14
28	C_2H_4	19
27	C_2H_3	15
	B. Di-*n*-butylgallium Chloride	
222	$^{71}Ga^{37}ClR_2$	1
220	$^{71}Ga^{35}ClR_2$-$^{69}Ga^{37}ClR_2$	6.7
218	$^{69}Ga^{35}ClR_2$	7.1
185	$^{71}GaR_2$	16
183	$^{69}GaR_2$	24
165	$^{71}Ga^{37}ClR$	21
163	$^{71}Ga^{35}ClR$-$^{69}Ga^{37}ClR$	99
161	$^{69}Ga^{35}ClR$	100
129	$H^{71}GaR$	2.4
128	^{71}GaR	3.4
127	$H^{69}GaR$	4.3
126	^{69}GaR	4.9
107	$H^{71}Ga^{35}Cl$-$H^{69}Ga^{37}Cl$	3.6
106	$^{71}Ga^{35}Cl$-$^{69}Ga^{37}Cl$	3.0
105	$H^{69}Ga^{35}Cl$	4.3
104	$^{69}Ga^{35}Cl$	3.4
71	^{71}Ga	32
69	^{69}Ga	46
57	C_4H_9	76
43	C_3H_7	22
29	C_2H_5	15
	C. *n*-Butylgallium Dichloride	
202, 200, 198, 196	$RGaCl_2$ cluster	2
187	$^{71}Ga^{37}Cl_2C_cH_6$	1
185	$^{69}Ga^{37}Cl_2C_3H_6$-$^{41}Ga^{37}Cl^{35}ClC_3H_6$	3.3
183	$^{69}Ga^{37}Cl^{35}ClC_3H_6$-$^{71}Ga^{35}Cl_2C_3H_6$	5.0
181	$^{69}Ga^{35}Cl_2C_3H_6$	2
173	$^{71}Ga^{37}Cl_2C_2H_4$	5
171	$^{69}Ga^{37}Cl_2C_2H_4$-$^{71}Ga^{37}Cl^{35}ClC_2H_4$	37
169	$^{69}Ga^{37}Cl^{35}ClC_2H_4$-$^{71}Ga^{35}Cl_2C_2H_4$	90
167	$^{69}Ga^{35}Cl_2C_2H_4$	70
165	$^{71}Ga^{37}ClR$	7.5
164	$^{71}Ga^{37}ClC_4H_8$	6.7
163	$^{69}Ga^{37}ClR$-$^{71}Ga^{35}ClR$	40
162	$^{69}Ga^{37}ClC_4H_8$-$^{71}Ga^{35}ClC_4H_8$	30
161	$^{69}Ga^{35}ClR$	40
160	$^{69}Ga^{35}ClC_4H_8$	30
145	$^{71}Ga^{37}Cl_2$	6.3
143	$^{69}Ga^{37}Cl_2$-$^{71}Ga^{37}Cl^{35}Cl$	42
141	$^{69}Ga^{35}Cl^{37}Cl$-$^{71}Ga^{35}Cl_2$	100
139	$^{69}Ga^{35}Cl_2$	75
109	$H^{71}Ga^{37}Cl$	1
108	$^{71}Ga^{37}Cl$	4.7
107	$H^{71}Ga^{35}Cl$-$H^{69}Ga^{37}Cl$	5
106	$^{71}Ga^{35}Cl$-$^{69}Ga^{37}Cl$	15
105	$H^{69}Ga^{35}Cl$	5
104	$^{69}Ga^{35}Cl$	15
71	^{71}Ga	38
69	^{69}Ga	57
57	C_4H_9	50
43	C_3H_7	20
29	C_2H_5	5

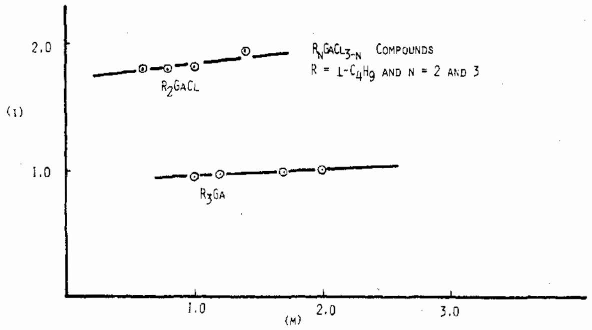


Figure 3. Molecular association of isobutylgallium compounds in benzene solvent. Plot of molecular association number (*i*) against molal concentration (*m*).

to donate four electrons symmetrically to adjacent gallium atoms in the dimer. Each gallium atom of the dimer is thus coordinatively saturated while the monomeric trialkyl is an electron deficient compound. Coordinative saturation in the dimers would have the effect of shielding the α-methylene protons, an effect in opposition to any inductive effect of the electronegative chlorine atoms. Thus, the α-methylene signal is shifted only slightly downfield in dimeric diisobutylgallium chloride and more significantly in dimeric isobutylgallium dichloride.

α-Methylene proton signals of *n*-propyl- and *n*-butylgallium compounds were also found to be sensitive to substitution on the gallium atom; however, the chemical shift of this signal could not always be determined with certainty due to overlapping with other methylene or methyl proton signals.

Ions of the general formulas Ga^+, R_xGa^+, $GaCl_y{}^+$, and $R_xGaCl_y{}^+$ were detected in studies of the mass spectra of R_nGaCl_{3-n} compounds where n = 1–3. Isotopic cluster peaks of relative intensity 3:2, 9:9:2, and 27:36:15:2 separated by two mass units are expected for fragment ions containing a single gallium atom, one gallium and one chlorine, and one gallium and two chlorine atoms, respectively.[18] The relative ratio of intensities of the three most intense peaks of the latter cluster is 9:12:5. All ions appearing in the mass spectra of organogallium compounds were identified according to the masses involved and the isotopic cluster considerations given above (see Table III).

Organogallium compounds of the general formulas

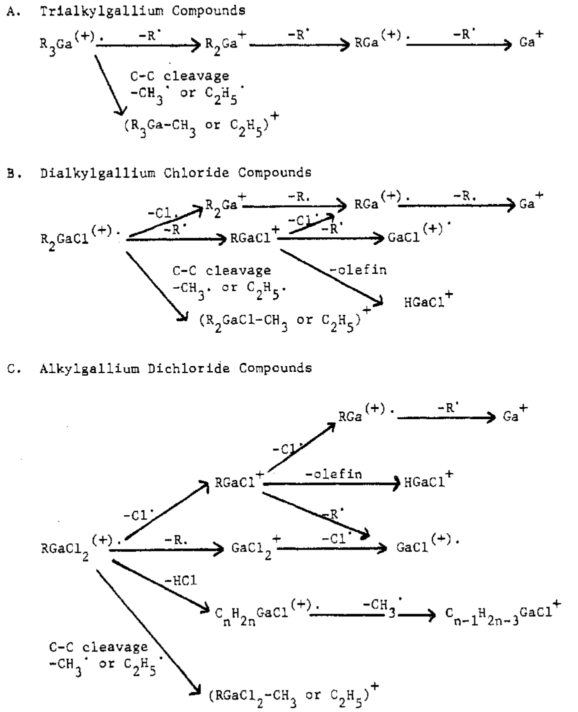


Figure 4. Possible fragmentation modes for R_nGaCl_{3-n} compounds.

R_nGaCl_{3-n} where $n = 1$–3 and R = C_2H_5 to C_4H_9 isomers were found to give characteristic mass spectra. Mass spectroscopy can be used as a convenient, diagnostic tool for the identification of organometallic gallium compounds of this type. Proposed, fundamental fragmentation modes for these compounds are given in Figure 4. Molecular ions for monomeric formula units were relatively weak in intensity and no peaks were observed for aggregated molecules. Even electron ions were found to be more abundant than odd electron ions in agreement with observations of mass spectra of related organoaluminum compounds.[19]

Trialkylgallium compounds showed low intensity monomeric molecular ion peaks, $R_3Ga\cdot^{(+)}$. A primary fragmentation process involves homolytic cleavage of the gallium–carbon bonds and formation of R_2Ga^+, $RGa\cdot^{(+)}$, and Ga^+ fragments (see Figure 4A). In addition, the straight chained trialkylgallium compounds tri-*n*-butyl- and tri-*n*-propylgallium underwent homolytic carbon–carbon bond cleavage producing gallium containing fragments with one or more of the alkyl groups reduced in mass. Elimination of ethylene and formation of an H–Ga bond is an important process occurring in the mass spectrum of triethylgallium (eq 8). A similar process was found to be important in mass spectral studies of ethylaluminum compounds.[19]

$$(C_2H_5)_2Ga^+ = HGaC_2H_5^+ + C_2H_4 \qquad (8)$$

The monomeric molecular ion in mass spectra of dialkylgallium chloride compounds (see Figure 4B) eliminated either a chlorine atom or an alkyl radical in a competitive process forming R_2Ga^+ or $RGaCl^+$ fragments, respectively. Once formed, R_2Ga^+ fragments could undergo fragmentation analogous to that involved in spectra of the trialkyls producing $RGa\cdot^{(+)}$ and Ga^+ ions. $RGaCl^+$ fragments apparently eliminate a chlorine atom, an alkyl radical, or an olefin molecule producing $RGa\cdot^{(+)}$, $GaCl\cdot^{(+)}$, or $HGaCl^+$, respectively.

Alkylgallium dichloride monomeric molecular ions eliminate a chlorine atom, alkyl radical, or an HCl molecule producing $RGaCl^+$, $GaCl_2^+$, or $C_nH_{2n}GaCl\cdot^{(+)}$ fragments, respectively (see Figure 4C). Once formed, $RGaCl^+$ likely fragments in the fashion discussed above producing $RGa\cdot^+$, Ga^+, $HGaCl^+$, and $GaCl\cdot^+$ ions. The fragment ion $C_nH_{2n}GaCl\cdot^{(+)}$ presumably formed by elimination of HCl from the molecular ion eliminates a methyl radical producing $C_{n-1}H_{2n-3}GaCl^+$ as a major process.

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Registry No. Ethyllithium, 811-49-4; *n*-propyllithium, 2417-93-8; isobutyllithium, 920-36-5; *sec*-butyllithium, 598-30-1; *tert*-butyllithium, 594-19-4; vinyllithium, 917-57-7; $GaCl_3$, 13450-90-3; $(n\text{-}C_3H_7)_3Ga$, 29868-77-7; $(n\text{-}C_3H_7)_2GaCl$, 55681-97-5; $LiGa[(n\text{-}C_3H_7)_4]$, 55701-36-5; $n\text{-}C_3H_7GaCl_2$, 6063-84-9; $(C_2H_5)_3Ga$, 1115-99-7; $(s\text{-}C_4H_9)_3Ga$, 55681-98-6; $(t\text{-}C_4H_9)_3Ga$, 55681-99-7; $(i\text{-}C_4H_9)_3Ga$, 17150-84-4; $(i\text{-}C_4H_9)_2GaCl$, 17150-83-3; $i\text{-}C_4H_9GaCl_2$, 55682-00-3; $(C_2H_3)_3Ga\cdot THF$, 55701-37-6.

Supplementary Material Available. Ion abundance data for triethylgallium, tri-*n*-propylgallium, di-*n*-propylgallium chloride, *n*-propylgallium dichloride, triisobutylgallium, diisobutylgallium chloride, isobutylgallium dichloride, tri-*sec*-butylgallium, and tri-*tert*-butylgallium will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50074D-11-75.

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