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Convenient Preparation of Base-Free Tri-*n*-butylgallium, Di-*n*-butylgallium Chloride, and *n*-Butylgallium Dichloride. Molecular Association Studies of *n*-Butylgallium Compounds in Benzene

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A convenient method has been developed for the preparation of base-free R_nGaCl_{3-n} compounds (where R = *n*-butyl and n = 1-3). The one step synthesis involves the metathetical reaction of an appropriate organolithium reagent with gallium chloride in a hydrocarbon solvent according to the stoichiometry shown in the following equation (benzene solvent; n = 1-3; R = *n*-butyl): $GaCl_3 + nLiR \rightarrow nLiCl + R_nGaCl_{3-n}$. The work-up procedure involves filtration to remove by-product lithium chloride, removal of solvent *in vacuo,* and vacuum distillation of the *n*-butylgallium product. In a typical reaction analytically pure tri-*n*-butylgallium was isolated in 97% yield. Alternatively, organogallium chlorides (R_nGaCl_{3-n}, n = 1, 2) are prepared by allowing mixtures of triorganogallium compounds and gallium chloride to react according to the following redistribution reactions: $2GaR_3(l) + GaCl_3(s) = 3R_2GaCl(l)$; $GaR_3(l) + 2GaCl_3(s) = 3RGaCl_2(l)$. No solvent is employed in these reactions and the yields after vacuum distillation are essentially quantitative. Molecular association studies of these compounds in benzene solution over a reasonably wide concentration range have indicated that tri-*n*-butylgallium is monomeric and that both di-*n*-butylgallium chloride and *n*-butylgallium dichloride are dimeric.

Introduction

Organometallic compounds of gallium have received little attention in comparison with those of boron and aluminum, in spite of reports that the reactivity of gallium compounds is unique among group IIIa analogs.[1-5] The relative lack of interest in gallium chemistry can be attributed to the relative high cost of gallium metal (or compounds of gallium in general) and the relative difficulty of preparing organometallic gallium compounds.

In the past, gallium alkyls and aryls have been prepared by metal exchange[6] (eq 1) or by the reaction of organometallic

$$2Ga + 3HgR_2 = 2GaR_3 + 3Hg \qquad (1)$$

compounds with a gallium halide (alkyl-halogen exchange). Among the organometallic compounds used in the alkyl-halogen exchange reactions are Grignard reagents[7] and aluminum,[2] zinc,[8] and lithium alkyls (eq 2-5, respectively).

$$GaX_3 + 3RMgX \xrightarrow{ether} GaR_3{\cdot}ether + 3MgX_2 \qquad (2)$$

$$GaCl_3 + 3R_3Al + 3KCl = R_3Ga + 3K[AlR_2Cl_2] \qquad (3)$$

$$2GaX_3 + 3R_2Zn = 2R_3Ga + 3ZnX_2 \qquad (4)$$

$$>GaX + RLi = LiX + >GaR \qquad (5)$$

Metal-exchange reactions using mercury alkyls or aryls (eq 1) are inconvenient for general use because the alkyls are costly and toxic, and generally (excluding vinyl or allyl cases) the reactions are slow and must be conducted at elevated temperatures with the use of a catalyst. Halogen-alkyl exchange reactions using Grignard reagents (eq 2) are convenient routes to ether solutions of organometallic gallium compounds. However, with the exception of tri-*n*-propyl- and tri-*n*-butylgallium it is not possible to remove ether from the product. Base-free triorganogallium compounds can be prepared using aluminum alkyls (eq 3) or zinc alkyls (eq 4); however, the extreme pyrophoric nature of these alkyls makes the procedures difficult. In the case of the aluminum alkyl reaction it is necessary to add KCl after the initial reaction of gallium chloride and trialkylaluminum has occurred in order to liberate gallium chloride from gallium dichlorodialkylaluminate(III) which is formed as an intermediate (eq 6). The gallium alkyl is often contaminated

$$3KCl + Ga[R_2AlCl_2]_3 = GaCl_3 + 3K[R_2AlCl_2] \qquad (6)$$

with traces of unreacted aluminum alkyl making additional treatment necessary. Even with these difficulties, halogen-alkyl exchange using aluminum alkyls is the most frequently used method to prepare samples for synthetic purposes[5] or for the determination of physical properties.[4]

Only isolated reports concerning the use of lithium alkyls in halogen-alkyl exchange reactions with gallium halides (general eq 5) have appeared. In 1934, Groll reported the metathetical reaction of ethyllithium[9] and diethylgallium chloride (eq 7). Methyllithium has been used to prepare di-

$$(C_2H_5)_2GaCl + LiC_2H_5 = LiCl + Ga(C_2H_5)_3 \qquad (7)$$

methylgallium chloride etherate[10] (eq 8), and, apparently,

$$GaCl_3 + 2CH_3Li \xrightarrow{ether} 2LiCl + (CH_3)_2GaCl{\cdot}O(C_2H_5)_2 \qquad (8)$$

trimethylgallium was generated as an intermediate in the preparation of tetrameric dimethylgallium hydroxide[11] (eq 9).

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(1) G. Coates, M. Green, and K. Wade, "Organometallic Compounds–The Main Group Elements," Vol. 1, Methuen, London, 1967, pp 179-373.

(2) J. J. Eisch, *J. Amer. Chem. Soc.*, 84, 3830 (1962).

(3) Ethyl Corp., British Patent 876,093 (1961); *Chem. Abstr.*, 58, 10322*f* (1963).

(4) K. W. Eggar, *J. Chem. Soc. A*, 3603 (1971).

(5) V. Markova, V. Kormer, and A. Petrov, *J. Gen. Chem. USSR*, 37, 1662 (1967).

(6) The following organometallic mercury compounds have been used in the metal-exchange preparation of organometallic gallium compounds (eq 1): (a) R = CH_3, G. E. Coates, *J. Chem. Soc.*, 2003 (1951); (b) R = C_2H_5, L. M. Dennis and W. Patnode, *J. Amer. Chem. Soc.*, 54, 182 (1932); (c) R = *n*-C_3H_7, *i*-C_3H_7, and vinyl, J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, 24, 953 (1962); (d) *cis*-and *trans*-HC=CH(CH_3), D. Moy, J. P. Oliver, and M. T. Emerson, *J. Amer. Chem. Soc.*, 86, 371 (1964); (e) R = C_6H_5, H. Gilman and R. Jones, *J. Amer. Chem. Soc.*, 62, 980 (1940).

(7) (a) R = CH_3, G. Renwanz, *Ber. Deut. Chem. Ges. B*, 65, 1308 (1932); (b) R = *n*-C_3H_7, H. Hartmann and H. Lutsche, *Naturwissenschaften*, 48, 601 (1961).

(8) R = CH_3, C. A. Kraus and F. Toonder, *Proc. Nat. Acad. Sci. U. S.*, 19, 292 (1933).

(9) H. P. A. Groll, U. S. Patent 1,938,179 (1934); *Chem. Abstr.*, 28, 1053 (1934).

(10) G. E. Coates and J. Graham, *J. Chem. Soc.*, 233 (1963).

(11) M. J. Sprague, G. E. Glass, and R. S. Tobias, *Inorg. Syn.*, 12, 67 (1970).

$$GaCl_3 + 3CH_3Li = \left[\begin{array}{l}\text{solution,}\\ Ga(CH_3)_3\\ \text{not isolated}\end{array}\right] \xrightarrow{H_2O} [Ga(CH_3)_2OH]_4 \qquad (9)$$

These reactions demonstrate the potential of methyl- and ethyllithium alkyls to undergo exchange reactions with gallium halides in ether solution. The present study was undertaken to elucidate the reaction of lithium alkyls and gallium chloride in hydrocarbon solvent according to eq 10.

$$GaCl_3 + nLiR \xrightarrow[n = 1-3]{\text{hydrocarbon solvent}} nLiCl + R_nGaCl_{3-n} \qquad (10)$$

This route to alkylgallium compounds has the potential of providing a relatively general and convenient route to base-free (*i.e.*, ether free) alkylgallium compounds. This paper will summarize primarily our studies of the reaction of *n*-butyllithium with gallium chloride and the preparation of $(n\text{-}C_4H_9)_nGaCl_{3-n}$ compounds, where $n = 1-3$. Molecular association curves for the *n*-butylgallium products in benzene solution will be presented and discussed.

Experimental Section

Handling Procedures. The gallium compounds used in this study decompose upon exposure to air reacting with water forming hydroxides and with oxygen forming alkoxides.[2] Precautions were, therefore, taken to exclude contamination by the atmosphere. Compounds of gallium were handled using Schlenk ware or a drybox under inert nitrogen atmosphere.[12]

General Chemicals. Thiophene-free reagent grade benzene was distilled over $LiAlH_4$ prior to use. *n*-Butyllithium in benzene was obtained from Foote Mineral Co. Gallium metal (99.999%) was obtained from the Alcoa Co. Chlorine was obtained from Matheson and was passed through a P_4O_{10} column prior to use.

Analysis. In a typical analysis a sample of an *n*-butylgallium compound was transferred into a glass ampoule of about 100-ml volume and weighed accurately. This was attached to a multipurpose vacuum line[12] by means of an O-ring joint and an excess of $HCl-H_2O$ mixture was condensed onto the evacuated sample using liquid nitrogen. The ampoule was then sealed under vacuum by heating a constriction in the joint connection with a small hand torch. Complete hydrolysis of the sample was accomplished by heating in a 120–140° oven for at least 48 hr. After this period the tube was allowed to cool to room temperature and reconnected to the vacuum line. The gaseous contents were admitted to the vacuum line by breaking a break-seal in the ampoule with a small glass-encased magnet. Butane was separated from the other gases present by fractional condensation using a slush prepared from ethyl acetate (−83.6°). Butane was determined quantitatively by measuring the pressure and temperature in a region of known volume. Butane was identified by measuring the vapor pressure at −45.2° (chlorobenzene slush). The vapor pressure at this temperature was found to be 94 ± 1 Torr for all samples. This compares with a literature value of 94 Torr.[13] Gallium was subsequently determined from the same sample by EDTA titration in the pH range 2.5–2.8 using gallocyanine as indicator.[14] Chloride content in the butylgallium chlorides was estimated by difference.

A solid sample of gallium chloride was hydrolyzed by adding water at room temperature followed by analysis for gallium as described above. Chloride was determined using a modified Volhard procedure.

All analytical results are summarized in Table I.

Table I. Comparison of Calculated and Experimental Weight Per Cent Composition Data for R_nGaCl_{3-n} Compounds (R = *n*-butyl, n = 0–3)

	% gallium		% alkyl		% chlorine	
Compd	Calcd	Found	Calcd	Found	Calcd	Found
R_3Ga	29.0	28.3	71.0	72.8		
R_2GaCl	31.8	32.0	52.1	52.1	16.2	15.9[a]
$RGaCl_2$	35.2	34.4	28.8	28.9	35.9	36.7[a]
$GaCl_3$	39.6	39.3			60.4	59.8

[a] Determined by difference.

Preparation of Gallium Chloride ($GaCl_3$). Existing literature methods for the preparation of gallium chloride involve reactions of gallium metal (generally on a scale of 0.0014–0.20 mol) with either HCl or Cl_2 at elevated temperatures.[2,15,16] These methods proved unsatisfactory in our efforts to prepare gallium chloride in larger quantities (1–2 mol) due to difficulties encountered in collecting the light, finely divided product and because of physical obstruction caused by deposition of the voluminous quantities of gallium chloride in key sections of the apparatus. Several unsuccessful attempts were made to collect the finely divided product quantitatively, including (1) cooling a section of the apparatus with liquid nitrogen, (2) passing the product through diethyl ether or benzene, or (3) allowing the product to settle in a closed section of the tube. In all of these cases a significant quantity of the product was always lost through the bubbler incorporated into the system to prevent buildup of excessive internal pressure.

Up to 2 mol quantities of gallium chloride were prepared using a special glass ampoule consisting of a bulb of approximately 250-ml capacity. Two glass tubes of 10-mm diameter were connected to the top portion of the bulb. One of these tubes was 5 cm in length and allowed the introduction of chlorine gas through a 5-mm tube which extended down to the bottom of the ampoule. The other tube (30 cm in length) was wrapped with heating tape and connected to a mercury-filled bubbler. The bottom of the ampoule was fitted with a 100-ml heating mantle.

In a typical reaction the apparatus was charged with 100.0 g of gallium metal (1.45 mol) under N_2 purge. Dry chlorine was introduced at a moderate rate. The reaction proceeded at a reasonable rate when the heating mantle and tape were maintained at approximately 150°. The heating tape and 30 cm tube served to melt the finely divided product which formed in the lower section preventing loss of product from the system. At an intermediate stage in the reaction (when the reaction was estimated to be one-fourth complete) the ampoule contained unreacted gallium and liquid product in two layers. The system was actually at a slight negative pressure even though chlorine was being introduced indicating rapid reaction with the two-layer system. As the reaction proceeded, the product layer increased in volume relative to the gallium layer until after approximately a 4-hr reaction time only the product layer was present. The system remained at a slight negative pressure for approximately 3 additional hr, indicating rapid reaction of chlorine and this liquid product. The product layer increased in volume by 30% during this period. After approximately 7 hr of total reaction time the product turned light yellow and chlorine began to escape through the mercury bubbler indicating the end of the reaction. The product was transferred to the drybox for analysis and subsequent use. A yield of 240 g (94% of theoretical) was obtained. The product melted sharply in the range 78–79° compared to the literature value of 77.9°. The analysis of a solid sample is included in Table I.

Alternatively, liquid gallium chloride can be poured under N_2 purge into tared round-bottom flasks directly from the reactor using Schlenk techniques. These can be stoppered and stored for subsequent use. In one experiment 0.5 mol of gallium chloride was transferred into a 1-l. round-bottom flask under N_2 purge. Dry benzene (500 ml) was distilled into the flask readily dissolving all of the gallium chloride. Aliquot samples (1.00 ml) were removed with a syringe for hydrolysis and subsequent analysis for gallium and chlorine. The following results were obtained by analysis of the freshly prepared solution: gallium, 0.555 *M*; chlorine, 1.63 *M*; chlorine to gallium gram-atomic ratio, 2.93:1.00. The solution was allowed to stand at room temperature for 60 days. Reanalysis gave the following results: gallium, 0.525 *M*; chlorine, 1.49 *M*; chlorine to gallium gram-atomic ratio, 2.90:1.00.

Larger aliquots of this solution were used in place of freshly sublimed gallium chloride in reactions with *n*-butyllithium. Results using this solution were comparable to those reported below using freshly sublimed gallium chloride.

Preparation of Tri-*n*-butylgallium. Freshly sublimed gallium chloride (10.60 g, 0.0603 mol) was dissolved in 50 ml of dry benzene in a 250-ml Schlenk flask. The flask was fitted with a Claisen tube to which were connected a 250-ml pressure-equalizing addition funnel and water condenser. A solution of *n*-butyllithium (55.3 ml of a 3.27 *M* solution, 0.180 mol) was added dropwise to the magnetically stirred gallium chloride solution over a 1-hr period. This rate of addition was sufficient to maintain moderate reflux of the

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(12) D. F. Schriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(13) Reference 12, p 273.

(14) G. W. C. Milner, *Analyst*, 80, 77 (1965).

(15) W. C. Johnson and C. A. Jaskew, *Inorg. Syn.*, 1, 26 (1939).

(16) N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1965).

solvent. Solid formation was apparent upon addition of the first drops of *n*-butyllithium solution; however, this solid dissolved when the solution was stirred. Precipitate formation was permanent after approximately 10% of the alkyllithium solution had been added. After completion of the alkyllithium addition, the mixture was heated at reflux temperature for 12 hr and then filtered (the solid was washed with three 10-ml portions of dry benzene) yielding a filtrate that was straw yellow. Solvent was removed *in vacuo* yielding 14.0 ml of liquid product. The entire sample distilled at 58-59° under 0.5 Torr yielding 14 g of a clear, colorless liquid. A portion of this sample was analyzed as described above (see Table I). The observed yield of tri-*n*-butylgallium was 97% of theoretical.

In a second preparation, the mixture was not heated at reflux after the addition of *n*-butyllithium. The mixture was filtered as described above and solvent removed *in vacuo*. Vacuum distillation of this crude product gave two fractions. The major component was tri-*n*-butylgallium. The higher boiling component (approximately 5% of the total) was shown to be di-*n*-butylgallium chloride. (See discussion of di-*n*-butylgallium chloride below.)

Preparation of Di-*n*-butylgallium Chloride. Method A. To 3.10 g of tri-*n*-butylgallium (0.0129 mol) was added 1.14 g of solid gallium chloride (0.00646 mol) in the drybox. The ensuing reaction was very exothermic. After the initial reaction had subsided and the sample had begun to cool to room temperature, the sample was heated to 100° for 12 hr to facilitate exchange. The entire sample distilled in the range 110-114° under 0.5 Torr. Analysis of a portion of this sample (see Table I) revealed that the product is di-*n*-butylgallium chloride.

Method B. Gallium chloride (1.7 g, 0.010 mol) was dissolved in 25 ml of dry benzene. A solution of *n*-butyllithium (0.020 mol) was added dropwise over a period of 30 min. The resulting mixture was heated at reflux for 12 hr. The mixture was filtered and solvent removed from the filtrate yielding a liquid which distilled at 111-114° at 0.5 Torr. This was shown to be identical with the di-*n*-butylgallium chloride described in method A by spectral comparison (nmr and infrared) and by analysis.

Preparation of *n*-Butylgallium Dichloride. Method A. To 3.75 g of tri-*n*-butylgallium (0.0156 mol) was added 5.48 g of solid gallium chloride (0.0311 mol) in the drybox. After the gallium chloride had dissolved (approximately 5 min), the product was heated at 100° for 12 hr. The entire sample distilled at 96-99° at 0.5 Torr. Analysis indicated that the product is *n*-butylgallium dichloride (see Table I).

Method B. A single product, identical with that described in method A (by spectral comparison and analysis), was obtained by allowing gallium chloride and *n*-butyllithium to react in 1:1 molar ratio under the exact conditions described in the method B preparation of di-*n*-butylgallium chloride.

Molecular Weight Measurements. Molecular Association in Benzene. Molecular weights of tri-*n*-butylgallium, di-*n*-butylgallium chloride, and *n*-butylgallium dichloride in benzene solution were determined using a cryoscopic method. A glass ampoule fitted with a Beckmann adjustable 5° range thermometer and magnetic stirring mechanism was utilized in this study. The freezing point (relative) of a sample of pure, dry benzene was determined. A known mass of butylgallium compound was then introduced by syringe and the freezing point depression of this relatively concentrated solution determined. Additional portions of dry benzene were introduced with a syringe in order to determine the freezing point depression of relatively dilute solutions.

Molecular weight data are summarized in Table II. A plot of molecular association number (I) against molal concentration for all compounds investigated is shown in Figure 1.

Table II. Association of *n*-Butylgallium Compounds R_nGaCl_{3-n} (n = 1-3; R = *n*-Butyl) in Benzene

Amt, g					
Solvent	Solute	ΔT, °C	Mol wt (exptl)	Assocn, (I)	Concn, m
Tri-*n*-butylgallium (Monomeric Unit Formula Weight 241)					
15.06	1.0274	1.512	244	1.01	0.28
20.97	1.0274	1.099	241	1.00	0.20
28.92	1.0274	0.808	238	0.99	0.15
39.12	1.0274	0.621	228	0.95	0.11
Di-*n*-butylgallium Chloride (Monomeric Unit Formula Weight 219)					
13.96	1.3920	1.23	438	2.00	0.23
18.31	1.3920	0.96	428	1.95	0.18
25.26	1.3920	0.71	419	1.91	0.13
37.26	1.3920	0.49	412	1.88	0.091
n-Butylgallium Dichloride (Monomeric Unit Formula Weight 198)					
16.92	1.4997	1.24	386	1.95	0.23
25.67	1.4997	0.83	380	1.92	0.15
36.73	1.4997	0.59	374	1.89	0.11

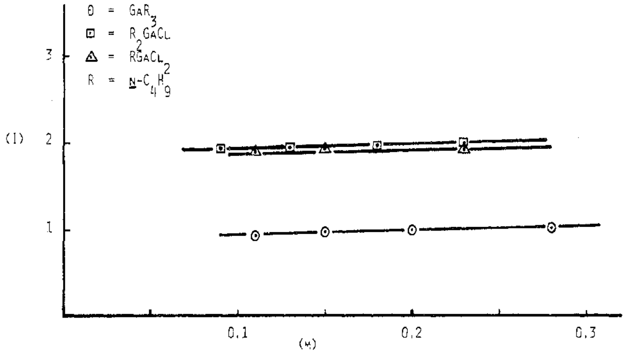

Figure 1. Plot of molecular association number (I) against molal concentration for benzene solutions of R_nGaCl_{3-n} compounds (R = *n*-butyl; n = 1-3).

Results and Discussion

Preparation of Gallium Chloride. A convenient procedure for the large-scale, high-yield preparation of gallium chloride was developed. The entire procedure can be conducted on the bench top using Schlenk techniques. The product can be dissolved in benzene (or other suitable solvent) and stored at room temperature over reasonable periods. Aliquot samples of this solution can be used for synthetic purposes. Alternatively, solid gallium chloride can be transferred to a drybox and stored for subsequent use.

$$2Ga + 3Cl_2 = 2GaCl_3 \qquad (11)$$

$$4GaCl_3 + 2Ga = 3Ga[GaCl_4] \qquad (12)$$

$$Ga[GaCl_4] + Cl_2 = 2GaCl_3 \qquad (13)$$

Observations concerning the rate of chlorine uptake at various stages in the reaction and the presence of two layers at intermediate stages in the reaction (see Experimental Section) suggest the reaction pathway eq 11-13. It is likely that the initial reaction of chlorine and gallium produces a mixture of $GaCl_3$ and $Ga[GaCl_4]$ (eq 11 and 12). In this regard it is important to note that $Ga[GaCl_4]$ is prepared quantitatively by the reaction of gallium chloride and gallium metal in 2:1 molar ratio at 200°.[17] Uptake of chlorine after the liquid gallium layer has disappeared and corresponding increase in volume of the liquid product during the last 3 hr of the reaction are consistent with the occurrence of eq 13.

Preparation of Alkylgallium Compounds. It is now possible to prepare benzene solutions of tri-*n*-butylgallium,[18] di-*n*-butylgallium chloride, and *n*-butylgallium dichloride using techniques which are not very different from those used to prepare Grignard reagents. A benzene solution of *n*-butyllithium is added dropwise to a benzene solution of gallium chloride according to eq 14-16 (where R = *n*-butyl).

$$GaCl_3 + RLi = LiCl + RGaCl_2 \qquad (14)$$

$$GaCl_3 + 2RLi = 2LiCl + R_2GaCl \qquad (15)$$

$$GaCl_3 + 3RLi = 3LiCl + R_3Ga \qquad (16)$$

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(17) L. Foster, *Inorg. Syn.*, **4**, 11 (1953).

(18) It is significant to note that corresponding trialkylgallium compounds are produced when *n*-propyl-, isobutyl-, and *tert*-butyllithium reagents and gallium chloride in benzene are allowed to react in a 3:1 mole ratio (eq 16) under the conditions described in this paper for the preparation of tri-*n*-butylgallium. See R. A. Kovar, Abstracts, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 13, 1973, p 31.

By-product lithium chloride is removed by filtration. All of the procedures to this point can be conducted on the bench top using Schlenk techniques. The products can be isolated by removal of benzene under vacuum and they can be purified further by vacuum distillation.

Alternatively, di-*n*-butylgallium chloride and *n*-butylgallium dichloride can be prepared from gallium chloride and tri-*n*-butylgallium by exchange reactions (eq 17 and 18, respectively).

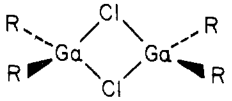
$$2GaR_3(l) + GaCl_3(s) = 3R_2GaCl(l) \quad (17)$$

$$GaR_3(l) + 2GaCl_3(s) = 3RGaCl_2(l) \quad (18)$$

Similar exchange reactions were used to prepare diethylgallium chloride,[2] diisobutylgallium chloride,[5] and diphenylgallium halides and phenylgallium dihalides.[6e] The exchange route to alkylgallium halides is the method of choice if a quantity of trialkylgallium is available because the reactions can be conducted free of solvent.

Molecular Association Studies. Previous reports have established the monomeric nature of trialkylgallium compounds (including tri-*n*-butylgallium) with the exception of trivinylgallium which is dimeric. Mixed alkylgallium halides (R_nGaCl_{3-n}, where R = methyl or ethyl and $n = 0$-2) are dimeric in hydrocarbon solvents.[19]

This study of the association of n-Bu_nGaCl_{3-n} compounds (where $n = 1$-3) in benzene solution is in agreement with previous reports of methyl and ethyl derivatives. Tri-*n*-butylgallium was shown to be monomeric over the concentration range studied while the butylgallium chlorides are dimeric over the same range of concentrations (see Figure 1). Chlorine-bridged structures are tentatively assigned to the dimeric *n*-butylgallium compounds (see structures I and II).[20]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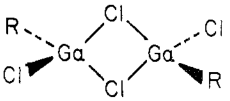
II

These tentative structures are in agreement with the structure assigned to $[RGaCl_2]_2$ compounds (where R = methyl or ethyl) which was based on infrared and Raman studies.[21]

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Registry No. $GaCl_3$, 13450-90-3; tri-*n*-butylgallium, 15677-44-8; di-*n*-butylgallium chloride, 17712-71-9; *n*-butylgallium dichloride, 43067-92-1; *n*-butyllithium, 109-72-8.

(19) For a general review of molecular association data see K. A. Yusada and R. Okawara, *Organometallic Chem. Rev.*, **2**, 255 (1967).

(20) For simplicity the trans form of dimeric-*n*-butylgallium dichloride is shown. The present study cannot rule out the cis form or a mixture of both cis and trans forms.

(21) C. Faraglis, F. Maggio, R. Cefalu, R. Basco and R. Barbieri, *Inorg. Nucl. Chem. Lett.*, **5**, 473 (1969).

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Indium-115 and Halogen Nuclear Quadrupole Resonance in Organoindium Halides and Related Compounds

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^{115}In and halogen nqr have been observed in several dimethylindium compounds, two monoalkylindium dihalides, and indium tribromide. The nqr data indicate that Me_2InI and Me_2InBr have the Me_2TlBr type of structure with linear dimethylindium groups equatorially surrounded by a square-planar arrangement of halogens. The structure of Me_2InCl is indicated to be distorted from this and Me_2InF appears to have a nonlinear dimethylindium group like Me_2InOAc, whose nqr parameters are consistent with its known structure. $MeInI_2$ is confirmed by its nqr spectrum to be $[Me_2In][InI_4]$ whereas those of $MeInBr_2$ and $EtInI_2$ are consistent with halogen-bridged dimers, $[RInX_2]_2$. The ^{115}In nqr spectrum of $InBr_3$ indicates its structural similarity with InI_3 rather than with $InCl_3$.

Introduction

For suitable nuclei, nuclear quadrupole resonance[1,2] (nqr) represents a convenient way of gaining information on structure and bonding in the solid state. The structural information is often less ambivalent than that provided by other methods, save of course single-crystal diffraction methods, and is relatively easily obtained.

The abundant (96%) indium isotope, ^{115}In, is an eminently suitable subject for nqr studies. Its nuclear spin of $^9/_2$ allows both the asymmetry parameter, η, and the nuclear quadrupole coupling constant, e^2Qq/h, to be obtained from simple frequency measurements on polycrystalline samples.[1,2] These frequencies are often in ranges convenient for current instrumentation[3] and the large magnetic moment of ^{115}In produces relatively large transition probabilities.

Organoindium compounds are the least studied of all group IIIb organometallics and thus we turned to ^{115}In and ligand nqr as a means of gaining information on these compounds and allowing them to be placed in better perspective with those of thallium, gallium, and aluminum. In the case of aluminum there is a substantial body of nqr information[4,5] with which to compare the indium data.

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(1) T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, 1, (1958).

(2) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969.

(3) G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instrum.*, 35, 698 (1964); 36, 702 (1965).