186. *An Investigation of Some Aryl-aluminium and -gallium Compounds.*

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The preparation of the new compounds Ph_nGaX_{3-n} ($X = Cl, Br$; $n = 1, 2$) is reported. Both these and the corresponding aluminium chlorides are shown to be dimeric in benzene, and halogen-bridged structures are suggested. Confirmatory evidence is presented for the association of triphenylaluminium in solution as previously observed. The electrical conductances of triphenylgallium, diphenylgallium chloride, and phenylgallium dichloride have been determined over ranges of temperature; the results indicate that these compounds are mainly covalent.

IN recent years considerable interest has been focused on the alkyl and halogeno-alkyl compounds of aluminium.[1] In addition trimethylgallium has formed the subject of much work.[2] However, until lately scant attention has been paid to triphenylaluminium and triphenylgallium and their halogeno-derivatives. Surtees [3] has now reviewed the chemistry of arylaluminium compounds and whilst the present paper was in preparation Mole [4] reported a further study of the phenylaluminium chlorides.

A recent revival of interest in arylgallium compounds also is shown by the synthesis of triphenyl-, tri-*o*-tolyl-, and tri-*m*-tolylgallium and their dioxan adducts by Viktorova and her co-workers.[5] This work apart, only the dipole moment, molecular weight, and solubility in selected organic solvents [6] of triphenylgallium have been measured since its original preparation by Gilman and Jones.[7] Nor has any reference been made in the literature to any arylgallium halide.

Accordingly we have prepared triphenylgallium and triphenylaluminium and from these have derived diphenylaluminium chloride, phenylaluminium dichloride, and the halides of general formula Ph_nGaX_{3-n} ($X = Cl$ or Br). All have been isolated highly pure and the last four are new compounds. Their degree of molecular association in benzene or naphthalene has been determined cryoscopically; all but triphenylgallium are dimeric in the particular solvent used. Bridge structures are suggested for the dimers.

The specific electrical conductances of triphenylgallium, diphenylgallium chloride, and phenylgallium dichloride have been measured over ranges of temperature in the solid and liquid states. The results reveal that, whereas the first two compounds are weak conductors in both phases, the last exhibits marked conductance, comparable in magnitude with that of weak electrolytes such as mercuric chloride and bromide.[8] An ionic conduction process is considered to operate and the high conductivity of phenylgalliumdichloride can be ascribed to its relatively greater electrolytic dissociation.

RESULTS AND DISCUSSION

A determination of the molecular weight of triphenylaluminium in benzene indicated that the compound was dimeric in this solvent. However, we considered this evidence to be inconclusive because of the low solubility of the compound in benzene at its freezing point and consequent possible precipitation of solute. The use of naphthalene as solvent obviated this difficulty, the value 7·0 being taken for the cryoscopic constant. A check

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[1] Ziegler, " Organometallic Compounds," ed. H. Zeiss, Reinhold, New York, 1960, p. 194.

[2] Coates, " Organometallic Compounds," 2nd edn., Methuen, London, 1960, pp. 144—151, p. 158.

[3] Surtees, *Rev. Pure Appl. Chem.* (*Australia*), 1963, **13**, 91.

[4] Mole, *Austral. J. Chem.*, 1963, **16**, 794, 801, 807.

[5] Viktorova, Sheverdina, Delinskaia, and Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1963, **152**, 609.

[6] Strohmeier and Hümpfner, *Chem. Ber.*, 1957, **90**, 2339; *Z. Elektrochem.*, 1957, **61**, 1010; Strohmeier, Hümpfner, Miltenberger, and Seifert, *ibid.*, 1959, **63**, 537.

[7] Gilman and Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 980.

[8] Janz and McIntyre, *J. Electrochem. Soc.*, 1962, **109**, 842.

determination of the molecular weight of triphenylgallium in this solvent gave good agreement with the formula weight of the monomer.

The specific electrical conductance κ of solid and liquid triphenylgallium, diphenylgallium chloride, and phenylgallium dichloride was measured over a range of temperature appropriate to each compound. The results are listed below.

Electrical conductivities.

Ph_3Ga between 60 and 192°

Temp.	60·0° †	90·8 †	127·7 †	159·8 †	161·0 †	163·5 †	165·0 †
$10^9\kappa$ (ohm^{-1} cm.$^{-1}$)	0·285	0·499	0·661	0·950	1·16	1·42	1·87
Temp.	165·2° *	165·8 †	165·8	167·0	167·5	168·0	168·5
$10^9\kappa$ (ohm^{-1} cm.$^{-1}$)	2·77	2·05	2·64	2·94	2·79	2·82	2·99
Temp.	169·7°	170·5	173·0	176·0	179·0	182·0	184·0
$10^9\kappa$ (ohm^{-1} cm.$^{-1}$)	3·11	2·97	3·13	3·29	3·42	3·59	3·83
Temp.	184·8°	188·0	191·0	192·0			
$10^9\kappa$ (ohm^{-1} cm.$^{-1}$)	3·73	3·89	3·87	4·12			

* Supercooled liquid. † Solid.

Ph_2GaCl between 197 and 229°

Temp.	196·9° ‡	197·0	197·0	198·2	199·8	204·9	205·0
$10^8\kappa$ (ohm^{-1} cm.$^{-1}$)	1·11	1·28	1·20	1·33	1·33	1·51	1·54
Temp.	210·0°	210·5	215·5	219·5	219·5	225·0	229·5
$10^8\kappa$ (ohm^{-1} cm.$^{-1}$)	1·81	1·78	2·08	2·34	2·39	2·81	3·22

‡ Melting point of sample.

$PhGaCl_2$ between 26 and 146°. *Run* 1

Temp.	90·4°	97·0	110·5	117·0 *	118·6 *	118·6 *	119·3 *
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	0·498	0·651	0·967	1·94	2·01	2·02	2·05
Temp.	120·8° *	121·9 *	122·1 *	122·2	122·5	122·5	122·8
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	2·12	2·17	2·19	1·15	1·56	2·54	3·53
Temp.	123·4°	123·6	123·8	124·0	124·9	125·9	126·0
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	10·0	22·7	22·7	22·8	23·4	23·9	23·9
Temp.	128·9°	132·8	134·7	135·0			
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	25·4	27·0	28·2	28·8			

Run 2

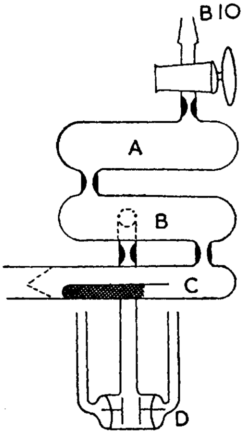
Temp.	25·8°	52·0	83·4	87·4	95·0	100·9	106·1	110·6
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	0·010	0·069	0·306	0·360	0·472	0·564	0·663	0·732
Temp.	113·7°	115·8 *	118·0	119·9 *	120·5	121·4	122·1	124·2
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	0·750	17·6	0·802	19·4	0·943	1·13	1·50	21·5
Temp.	124·7°	125·1	125·3	128·2	131·2	135·2	141·7	
$10^6\kappa$ (ohm^{-1} cm.$^{-1}$)	21·8	22·0	22·0	23·6	25·2	27·5	31·4	

* Supercooled liquid.

Triphenylgallium.—A preliminary conductivity run revealed that, after first melting, the compound had a conductance which decreased with time. This feature was largely eliminated by keeping the compound molten for some hours before readings were taken. In succeeding experiments the change of log κ with $1/T$ (°K) from 60° to the melting point (166°) is represented by a curve which has a point of inflexion at ~9° below the melting point. Here the conductance rises sharply until the compound is fully molten when the slope again diminishes. For the liquid range the conductivity data were not as reproducible as is usual with this type of measurement and slight drift of the values with time was still evident. The activation energy E_κ for the conduction process in the solid is temperature dependent and decreases continuously from 7·3 kcal. mole^{-1} at the lower temperature to ~2 kcal. mole^{-1} at ~40° below the melting point. For the liquid range a least-squares evaluation of the experimental points led to an activation energy of 7·0 kcal. mole^{-1}, with a probable error of 0·6 kcal. The conductivity of the fused compound at its melting point is $2·8 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$ and that 10° below the melting point is $8·0 \times 10^{-10}$ ohm^{-1} cm.$^{-1}$. There is thus a $3\frac{1}{2}$-fold increase of conductivity on melting.

Diphenylgallium Chloride.—In this case the specific conductivity was reproducible over the liquid range from the melting point (197°) to 230° and showed no variation with time. A plot of log κ against $1/T$ (°K) for this region is linear and gives a value of 14·0 kcal. mole^{-1} for E_{κ}. The conductivity of the liquid at the melting point is $1{\cdot}20 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ and a single measurement made on the solid just before fusion indicates that, as with triphenylgallium, there is little increase in conductance on melting.

Phenylgallium Dichloride.—Results for a first liquid run using a slightly impure specimen (m. p. 2° below that of the best) are best fitted by a slightly curved line, the mean slope of which corresponds to an E_{κ} value of 4·7 kcal. mole^{-1}, the conductivity at the melting point being $6{\cdot}7 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$. A fresh, purer sample (m. p. 123°) was used in a cell topped by a vessel (B, Figure) to trap any volatile hydrolytic impurity remaining after transference of the material and sublimation. For the solid compound, between 26 and 123°, the plot of log κ against $1/T$ (°K) is curved and has a point of inflexion about 2° below the melting point. When melting is complete the slope decreases corresponding to $E_{\kappa} = 6{\cdot}5$ kcal. mole^{-1} for the normal liquid. When the temperature was lowered the liquid supercooled and in this region E_{κ} is slightly higher. The conductivity at the melting point is $2{\cdot}24 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$, i.e., about one-third of that of the first impure sample. In a second run the vessel B was sealed off and the cell totally immersed in the thermostat. This time the conductivities obtained were 5—6% lower for the liquid and ~15% lower for the solid compound. These results were reproducible on successive heating and cooling; no drift with time was evident. We consider that the latter are more accurate and ascribe the former higher values to a trace of hydrolytic impurity introduced in the transfer of material after zone refining and not completely eliminated by subsequent sublimation. This reveals the difficulty encountered with this type of compound when minute traces of impurity, undetectable by depression of the melting point, are present. The energy of activation for the solid is again temperature dependent and changes from 14·1 kcal. mole^{-1} at 25·0° to a minimum of 6·0 kcal. mole^{-1} at the inflexion point. The conductivity of the liquid at the melting point is $2{\cdot}11 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ and E_{κ} for the liquid region is 6·9 kcal. mole.$^{-1}$. Before the compound melts, at 112°, the conductance is $7{\cdot}25 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$ and there is thus a 30-fold increase on melting. This contrasts with triphenylgallium and diphenylgallium chloride.



Conductivity apparatus.

The first point to consider is the degree of association in solution of the compounds. This work confirms that triphenylgallium is monomeric in benzene and naphthalene, the former as previously observed.[6] Krause and Dittmar[9] and Mole[4] reported that triphenylaluminium is about 80% associated to dimer in benzene even at the boiling point of

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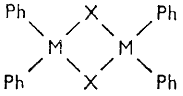
[9] Krause and Dittmar, *Ber.*, 1930, **63**, 2401.

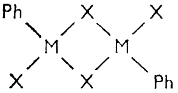
the solvent and we find that the same is true of the compound in molten naphthalene. It is also significant that the order of decreasing melting point in the series Ph_nAlCl_{3-n} is the same as the decrease in molecular weight over the series if all the compounds have dimeric molecular lattices. This is not paralleled in the gallium case, the monomeric triphenylgallium falling midway in the series. The slight dissociation of triphenylaluminium at ~80° implies that, if an entropy change of 20—30 cal. deg.$^{-1}$ mole^{-1} is assumed for the dissociation procession in solution then the heat of dissociation of the dimer is 7—10 kcal. mole.$^{-1}$. The most likely means of association of two monomer units is *via* bridging phenyl groups although there is as yet no evidence as to how this can occur. It is noteworthy however that trivinylgallium, in which also all carbon atoms are unsaturated, has recently been shown to be dimeric,[10] and a bonding scheme has been proposed involving bridging vinyl groups. In addition the proton magnetic resonance spectrum of triphenylthallium gives evidence of rapid intermolecular exchange of phenyl groups [11] presumably also *via* a bridged intermediate. The same could also apply to triphenylaluminium; in this case one of the bridge-ring carbon atoms would be involved in a three-centre bond holding together this ring and both aluminium atoms.

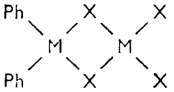
The compounds Ph_2AlCl, $PhAlCl_2$, Ph_2GaCl, $PhGaCl_2$, Ph_2GaBr, and $PhGaBr_2$ are all dimeric in benzene and in the light of the preceding discussion the possibility of an organic bridging group cannot be ruled out. However, in those dimeric organoaluminium halides which have been studied in detail, it seems that in no case does the organic group perform this function although this conclusion has not been reached easily.[12] If it is accepted that internal co-ordination takes place through halogen atoms then the diphenylmetal halides in solution will have the structure:



D_{2h}

When the compounds $PhMX_2$ are considered more possibilities arise of which perhaps the most important are:





X = Cl, Br

C_{2h} C_{2v}

At present it is not easy to decide between these although the analogous dimer of methylaluminium dichloride has the *trans*-configuration in the solid.[13] We are therefore undertaking further work in this direction.

The main feature which emerges from the conductivity studies on triphenylgallium is that the solid is a weak conductor of electricity and this situation is but little changed on melting. Thus triphenylgallium, as expected, is mainly covalent in nature. The mechanism of conductance in the regions investigated appears most likely to be ionic and not electronic as (*a*) an increase of conductivity on melting is observed, and (*b*) the activation energies for the process do not exceed 10 kcal. mole^{-1} (0·44 ev). The corresponding quantity

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[10] Oliver and Stevens, *J. Inorg. Nuclear Chem.*, 1962, **24**, 953.

[11] Maher and Evans, *J.*, 1963, 5534.

[12] Smidt, Groenewege, and De Vries, *Rec. Trav. chim.*, 1962, **81**, 729; Glick and Zwickel, *J. Inorg. Nuclear Chem.*, 1960, **16**, 149; Yamamoto, *Bull. Chem. Soc., Japan*, 1962, **35**, 619; Mach, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2295; Van der Kelen and Herman, *Bull. Soc. chim. belges*, 1956, **65**, 362; Brockway and Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287; Groenewege, *Z. phys. Chem. (Frankfurt)*, 1958, **18**, 147.

[13] Allegra, Perego, and Immirzi, *Makromol. Chem.*, 1963, **61**, 69.

for semi-conduction would be expected to be rather larger than this because the first electronic transition band, to which the energy gap is related, must arise from transitions between states separated by at least 3 ev since the compound is colourless. We conclude therefore that the principal charge carriers are most likely to be negative phenyl ions.

In Group III the compounds of type R_2MX differ markedly when M is boron or thallium. Thus Ph_2BCl is a covalent, monomeric compound and is readily hydrolysed whilst the Ph_2Tl^+ ion is stable even in aqueous solution and forms a variety of salts.[2] From the conductivity results reported herein diphenylgallium chloride resembles its boron analogue more closely and like triphenylgallium is principally covalent in the molten state. The conductivities of the latter two compounds differ only by a factor of ~ 10 and although specific rather than molar conductivities are being compared it is unlikely that any radical error in interpretation is introduced by this.

If diphenylgallium chloride is monomeric in the fused state then the observed conductance is surprisingly small in view of the considerable polarity of the Ga–Cl bond and consequent ease of chloride ionisation. Indeed the observed conductance of fused gallium trichloride itself, in which a similar situation would be expected to arise because of terminal Ga–Cl bonds, is almost 100 times greater at its melting point.[14] If, however, the former is dimeric with the chlorine atoms tied in bridging positions then the release of each requires the scission of two bonds. An alternative mode of ionisation in the dimer involves the release of terminal phenyl groups as negative ions as in triphenylgallium and explains the similarity in conductance. The latter view is encouraged by the fact that the compound is dimeric in solution. In both cases very little ionisation actually takes place and the small rise in conductance at the melting point is consistent with increased mobility of the few charge carriers which do occur in the liquid.

Whereas for gallium trichloride there is a sharp decrease in conductivity on melting,[14] when the phenyl group is substituted for chlorine; as in $PhGaCl_2$, the same behaviour is no longer observed, there being, in fact, a 30-fold increase in conductivity. It is significant that this increase and the conductivities themselves are very much greater for this compound than for either of the others we studied. The magnitudes of these and the activation energies for the solid and the liquid are comparable with the corresponding quantities observed in electrochemical studies of solid and fused mercuric chloride and bromide.[8] In these cases the results have been interpreted as showing that the conduction process is ionic and the compounds are electrolytically dissociated to a small extent ($\sim 10^{-4}\%$) into kinetically free ions. The same conclusions apply equally well to $PhGaCl_2$; whether monomer or dimer form is assumed for $PhGaCl_2$, its superiority in conductance over Ph_2GaCl is attributable to the occurrence in the former of terminal chlorine atoms. Thus the easy release of chloride ions is effected and the auto-dissociation

$$2Ph_2Ga_2Cl_4 \rightleftharpoons Ph_2Ga_2Cl_3^+ + Ph_2Ga_2Cl_5^-$$

in which no net Ga–Cl bonds are broken allows the conduction process to proceed by migration of chloride ions from one neutral dimer molecule to the next. This means that appreciable differences should be evident in the activation energies for conductivity and viscous flow since the latter process is dominated by the larger ions. Alternative ionisation schemes are possible in which this difference is lessened and viscosity measurements on the liquid would help to decide between them.

EXPERIMENTAL

Since all the compounds described are readily hydrolysed or oxidised in air all operations were carried out either in a conventional vacuum apparatus or in a dry nitrogen-filled glove-box. The preparation and purification of gallium trichloride, gallium tribromide, and aluminium

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[14] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

trichloride has been described previously.[15-17] Triphenylaluminium and triphenylgallium were prepared by reaction of the high purity metal (Messrs. Johnson Matthey) with the stoicheiometric proportion of diphenylmercury (B.D.H. Ltd.) under the conditions prescribed by Gilman and Jones.[7] The purified products had m. p.'s 239—241° (Laubengayer, Wade and Lengnick,[18] 223—227°; Wittenberg,[19] 225—228°; Nesmeyanov and Novikova,[20] 237°) and 166° (Gilman and Jones,[7] 166°), respectively. On first sublimation of triphenylaluminium samples at ~200° a brown residue remained but succeeding treatments, even at temperatures up to 240°, left only a small quantity of a light powder. The compound decomposed slightly on melting as witnessed by a decrease in melting point of 2—3°. However, we believe that, if the compound were purified even more rigorously, no decomposition should be observed. Any impurity present is most likely due to the extreme sensitivity of the compound to oxygen and moisture. For triphenylaluminium in 1·88, 2·85 wt.-% naphthalene solution *M* was 480, 487 (Calc. for Ph_3Al: *M*, 258) and for triphenylgallium in 1·78 wt.-% benzene and 2·12 wt.-% naphthalene, *M* was 318, 306 (Calc. for Ph_3Ga: *M*, 301).

Purification of Reaction Products.—The two methods most generally useful were (*a*) repeated sublimation *in vacuo*, (*b*) recrystallisation from benzene. Of the two we consider that the former yields a purer product. An important further stage in the refinement of those compounds used in conductivity studies was zone melting. A heating coil was passed downwards over the sample tube (1 cm. diameter) at a rate of 2 cm. per hr., the temperature being adjusted to give a 1 cm. molten zone. The apparatus allowed for recycling and the melting was usually repeated 20—25 times.

Analyses.—(*a*) *Gallium compounds.* Small, glass-stoppered bulbs containing weighed samples were broken under water. Complete solution was achieved by addition of a small quantity of concentrated nitric or hydrochloric acid followed by boiling of the mixture. Gallium was then determined gravimetrically as the trisoxinate. Chlorine and bromine were readily estimated as the silver salts.

(*b*) *Aluminium compounds.* Hydrolysis of these was violent and care was necessary to minimise loss of hydrogen chloride from the mixture. Any precipitate formed at this stage dissolved easily in a few drops of acid. Aluminium and chlorine were then determined as before for gallium compounds.

Diphenylgallium Chloride, Ph_2GaCl.—The reaction between equimolar quantities of hydrogen chloride (0·0394 mole) and triphenylgallium at room temperature *in vacuo* evolved heat and gave a coloured solid. When reaction had ceased a liquid from the vessel condensed in a second trap at −80°. The i.r. spectrum of this liquid showed it to be benzene (0·0404 mole). The remaining solid melted at 180° to a homogeneous yellow liquid which, after resolidification and sublimation at 160° in a dynamic vacuum, yielded a pale yellow solid, m. p. 195°. Finally, when this was zone-refined, white crystalline *diphenylgallium chloride* (m. p. 197°) resulted (Found: Ga, 27·1; Cl, 13·7%; *M* in 3·01, 0·81 wt.-% benzene solution, 518, 514. $C_{12}H_{10}GaCl$ requires Ga, 26·9; Cl, 13·7%; *M*, 260).

Phenylgallium Dichloride, $PhGaCl_2$.—This was prepared in a similar way to that employed for diphenylgallium chloride. Hydrogen chloride (0·1195 mole) reacted with triphenylgallium (0·0597 mole) producing benzene (0·124 mole) and a coloured solid. This melted to a brown liquid which gave two fractions on sublimation. The larger fraction, a white crystalline compound, melted at 120°. On further treatment by zone-refining the melting point rose to 122·4—123·4° (Found: Ga, 31·9; Cl, 32·3%; *M* in 3·88, 2·52 wt.-% benzene solution, 425, 437. $C_6H_5GaCl_2$ requires Ga, 32·0; Cl, 32·6%; *M*, 218). The compound could also be obtained by heating theoretical quantities of triphenylgallium and gallium trichloride at 160° for 4 hr. The product was purified as already described. *Phenylgallium dichloride* is very readily hydrolysed and turns brown even on short exposure to air.

Diphenylgallium Bromide, Ph_2GaBr.—Bromine (0·0073 mole) was distilled on to triphenylgallium (0·0074 mole) in an evacuated vessel. When the mixture was brought to room temperature a vigorous reaction caused it to become heated. The volatile products (0·565 g.) were

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[15] Greenwood and Wade, *J.*, 1956, 1527.
[16] *Inorg. Synth.*, ed. E. G. Rochow, McGraw-Hill, New York, 1960, **6**, 31.
[17] Biltz and Wein, *Z. anorg. Chem.*, 1922, **121**, 257.
[18] Laubengayer, Wade, and Lengnick, *Inorg. Chem.*, 1962, **1**, 632.
[19] Wittenberg, *Annalen*, 1962, **654**, 23.
[20] Nesmeyanov and Novikova, *Bull. Acad. Sci. U.S.S.R.*, Classe sci. chim., 1942, 372.

distilled out and identified as benzene and bromobenzene together with a small quantity of *p*-dibromobenzene. When the remaining solid sublimed three fractions of progressively purer material were obtained. The melting point of the best sample was 212—214° (Found: Ga, 22·8; Br, 25·0%; *M* in 1·36 wt.-% benzene solution, 597, 597. $C_{12}H_{10}GaBr$ requires Ga, 23·0; Br, 26·3%; *M*, 304). A second synthesis of the *bromide* was effected by heating stoicheiometric quantities of triphenylgallium and gallium tribromide for 2 hr. at 200°. The purified product melted at 219—220° (Found: Ga, 23·2; Br, 26·5%).

Phenylgallium Dibromide, $PhGaBr_2$.—Reaction of the stoicheiometric quantities of triphenylgallium and gallium tribromide at 170° for 3—4 hr. produced a light brown solid from which a white compound sublimed. This was *phenylgallium dibromide* (m. p. 129—130°) and, like $PhGaCl_2$, it is rapidly hydrolysed in air (Found: Ga, 22·6; Br, 52·0%; *M* in 3·43, 2·08 wt.-% benzene solution, 617, 624. $C_6H_5GaBr_2$ requires Ga, 22·7; Br, 52·1%; *M*, 307).

Diphenylaluminium Chloride.—This was obtained pure by either of the foregoing methods. It had m. p. 149—151° (Eisch and Kaska,[21] 145—148°; Mole,[4] 149—152°) (Found: Al, 12·4; Cl, 16·2%; *M* in 1·17, 1·51 wt.-% benzene solution, 428, 431. Calc. for Ph_2AlCl: Al, 12·5; Cl, 16·4%; *M*, 217).

Phenylaluminium Dichloride.—This was prepared as already described. It was a white solid, m. p. 94—96° (Von Grosse and Mavity,[22] 94—95°) (Found: Al, 15·5; Cl, 41·0%; *M*, in 1·69, 1·25 wt.-% benzene solution, 352, 354. Calc. for $C_6H_5AlCl_2$: Al, 15·4; Cl, 41·5%; *M*, 175).

A.C. Electrical Conductance.—This was measured at 1592 c./sec. on a Wayne–Kerr universal bridge (model B221). The conductivity cells used for the three compounds consisted of 10-mm. glass tubes in which platinum foil or tungsten rod electrodes were sealed. The cell constants were 0·1979, 0·6503, and 0·4650 cm.$^{-1}$. The procedure for conductivity experiments is exemplified by the following: a zone-refined sample of phenylgallium dichloride was sealed in tube C (Figure) under a slow stream of nitrogen. Evacuation and immersion of B and C in an oil-bath at 125° caused sublimation of the first fraction into A which was then sealed off. Sublimation of the main mass of material was continued into B and, when enough had transferred, C was sealed off. Finally the pure $PhGaCl_2$ was run into the conductivity cell D. Effective control of temperature during the experiments was readily achieved by manual adjustment of a "Variac" transformer connected to an electrical heater.

Molecular Weights.—These were determined cryoscopically in a simple Beckmann apparatus modified to maintain a dry nitrogen atmosphere. The Beckmann thermometer was read to ±0·001° by means of a lens. The results proved satisfactory even for those compounds such as phenylgallium dichloride and dibromide which are extremely moisture sensitive. Benzene and naphthalene were used as solvents and all solutions were made up in the glove-box.

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[21] Eisch and Kaska, *J. Amer. Chem. Soc.*, 1962, **84**, 1501.

[22] Von Grosse and Mavity, *J. Org. Chem.*, 1940, **5**, 106.