# Reactions between organic derivatives of group III elements and acids

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# REACTIONS BETWEEN ORGANIC DERIVATIVES OF GROUP III ELEMENTS AND ACIDS

by

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A thesis submitted for the Degree of Doctor
of Philosophy in the University of Durham.

This dissertation is being presented to the University of Durham, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Unless otherwise stated, the work described is that of the author and has not been submitted in part or otherwise for a degree to this or any other University.

Part of the work described has been the subject of a publication with Professor Coates (Dimethylaluminium cyanide and its gallium, indium and thallium analogues; beryllium and methylberyllium cyanide, J. Chem. Soc., 1963, 229-233).

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## ABSTRACT

The cyanides $Me_2MCN$(M = Al, Ga, In or Tl) were prepared from the trimethylmetal and hydrogen cyanide. In contrast to the polymeric boron cyanides, $R_2BCN$, the aluminium, gallium, and indium compounds are tetrameric in benzene, and dimethylthallium cyanide is a salt in aqueous solution. Reactions between dimethylberyllium (and its trimethylamine complex) and hydrogen cyanide were also investigated.

The phosphinates, thiophosphinates, sulphinates, one arsinate and carboxylates of many of the Group III metals were prepared from reactions between the trimethylmetal and the corresponding acid in an inert solvent (ether or benzene). These were sufficiently volatile to be purified by vacuum sublimation. The compounds were air-sensitive. Molecular weights were determined cryoscopically in benzene and the compounds were found to be dimers. The structures of these dimers were established on the basis of their infrared spectra, as eight-membered ring compounds in which the P = O or similar groups participated in co-ordinate bond formation.

The dithiophosphinates of aluminium, gallium and indium were prepared from reactions between the trimethylmetal and dimethyldithiophosphinic acid in an inert solvent. These were purified by vacuum sublimation as colourless crystals.

Molecular weights were determined cryoscopically in benzene and the compounds were found to be monomers (compare the phosphinates, sulphinates etc. which were found to be dimers).

Dimethylaluminium methane-sulphonate and the corresponding gallium compound were prepared by similar reactions. They were purified by vacuum sublimation as white crystalline solids. Molecular weights were determined cryoscopically in benzene and the compounds were found to be trimers.

The infrared spectra of all the compounds prepared were investigated and several new assignments for different structural features were made.

# INTRODUCTION

# INTRODUCTION

In this section preparative methods for the trialkyls of group III elements are discussed with special reference to trimethyls. The properties of these trimethyls are also included. This is followed by a review of the interaction of group III trialkyls with donor molecules not containing reactive hydrogen. Much interesting work has been done on the co-ordination chemistry of the halides and hydrides of group III elements, but discussion of these compounds is not directly relevant to the subject of the present investigation. The reactions of group III trialkyls with donor molecules containing reactive hydrogen are then reviewed. Finally the objects of the present investigation are described.

## Preparative Methods for the Trialkyls of Group III Elements.

The trimethyl derivatives of group III elements are spontaneously inflammable, sometimes with explosive violence, on exposure to air. Therefore, their preparations demand careful attention to safety and a good deal of precautions regarding the design of apparatus employed, use of a protective atmosphere of pure inert gas like nitrogen or argon, and the maintenance of rigorously anhydrous conditions. Different preparative methods are available for these alkyls, and they usually differ in economy, convenience, and yield. All the trimethyl derivatives are volatile, and therefore the choice of a method from the point of view of purification is no problem. A suitable choice can sometimes avoid the tedious separation of the trialkyl from large quantities of the solvent. A preparative method may also be decided on the end use of the product. Thus, for example, pure trimethylaluminium can not be obtained by the Grignard reaction, but the etherate can be prepared and used for the study of displacement reactions with stronger donors (e.g. bipyridyl). A method involving the use of free metal and another organometallic compound can be represented by the reversible equilibrium:

$$M + M'R \rightleftharpoons MR + M'$$

The reaction which is not applicable to transition metals, proceeds to the right if M is more electropositive than M'. As a result, a more reactive compound is obtained from a less reactive compound. In theory, a number of organometallic derivatives should be able to participate in this reaction leading to a group III trialkyl. In practice, the dialkyls and diaryls of mercury are the only suitable reagents. These mercury compounds are extremely easy to prepare, purify and handle because they are stable in air due to small affinity of mercury for oxygen. A disadvantage is that the displacement reactions with group III elements are rather slow (boron and thallium cannot be used), a further limitation of the method is the instability of higher and branched-chain mercury alkyls. Another method of general application is the reaction between the trihalide and the alkyl of a more electropositive metal. The Grignard reagents or the lithium alkyls are most commonly employed. In these reactions, a less reactive compound is formed from a more reactive compound.

A survey of the methods available for the synthesis of the trialkyls of the individual elements, with special reference to their trimethyl derivatives follows.

Trialkyls of Boron.

The general methods for the preparation of the trialkyls of boron are given below:

(a) In recent years the alkyls of aluminium have been shown to be a very convenient reagent for the preparation of the trialkyls of boron(1). An attractive feature of this synthesis is the exclusion of large quantities of solvents. The formation of quaternary salts is also avoided (these are easily formed when lithium reagents are employed and sometimes even with Grignard reagents in the aryl series). Reactions between boron trifluoride and aluminium alkyls do not easily go to completion. Triethylborane can be obtained in about

90% yield by the reaction between the etherates of triethylaluminium and boron trifluoride. Other variations of this method have been described,(2) the most satisfactory method is the reaction between a borate ester and an alkyl of aluminium. Triethylaluminium exothermically reacts with ethyl orthoborate to give triethylborane in over 90% yield.

$$B(OEt)_3 + AlEt_3 \;=\; Al(OEt)_3 + BEt_3$$

(b) The trialkyls of boron can be prepared by the reaction between a borate ester and Grignard reagents. The use of boron trifluoride etherate is less satisfactory.

$$B(OMe)_3 + 3MeMgBr \;=\; BMe_3 + 3(MeO)MgBr$$

Thus, trimethylborane can be very conveniently obtained by the slow addition of a solution of borate ester in di-n-butyl ether to the Grignard reagent prepared in the same solvent. Unlike the other trimethyl derivatives, trimethylborane (m.p. - 159.85°C, b.p. - 21.8°C) is a gas at room temperature. Therefore, the storage of large quantities of the material is rather inconvenient. It can be easily stored in combination with trimethylamine. The adduct $Me_3N.BMe_3$ can be purified by sublimation and the trimethylborane regenerated by treatment with less than the calculated amount of dry hydrogen chloride.(3,4,5) The method (a) described above is more useful for the preparation of triethyl or higher derivatives because the corresponding aluminium alkyl can be more easily obtained, on a large scale, by the reaction between an olefin, hydrogen and activated aluminium metal (described later).

(c) The higher alkyls of boron can be obtained by the reaction between diborane and a suitable olefin. In a typical reaction, tri-n-hexylborane was obtained in 91% yield by bubbling diborane into a solution of 1-hexene in diglyme $[(CH_3OCH_2CH_2)_2O]$ at room temperature(6)

$$B_2H_6 + 6CH_2 = CH(C_4H_9) = 2B(C_6H_{13})_3$$

(d) The displacement reaction between the boron isobutyl derivative and a higher olefin is another useful preparative method for higher alkyls, as shown below:

$$B[CH_2CHMe_2]_3 + 3CH_2 = CHC_8H_{17} \xrightarrow{\text{above } 120^\circ C} B(C_{10}H_{21})_3 + 3CH_2 = CMe_2$$

In general, a more volatile shorter chain olefin is displaced by a less volatile longer chain olefin.(1,7)

Trialkyls of Aluminium.

The general methods for the preparation of trialkyls of aluminium are given below:

(a) By heating (80-90°C) excess of aluminium with a dialkyl of mercury, the trialkyl can be obtained.(8) The exothermic reaction goes to completion in about a day or two.

$$2Al + 3HgMe_2 = 2AlMe_3 + 3Hg$$

This method has been particularly useful in the past in the alkyl or aryl(9,10) series, when other methods for preparing these compounds were less developed.

(b) Alkylaluminium sesquihalides can be obtained by the reaction between aluminium metal (activated by iodine or a little aluminium alkyl) and an alkyl halide.(11)

$$2Al + 3RX = R_3Al_2X_3$$

These sesquihalides are air sensitive liquids at room temperature, without any sharp boiling points, due to the following disproportionation:

$$2R_3Al_2X_3 \rightleftharpoons R_2Al_2X_4 + R_4Al_2X_2$$

The trialkyl derivatives can be obtained by reduction with sodium, and sodium-potassium alloy during the final stages of the removal of halogen.

$$R_3Al_2X_3 + 3Na = AlR_3 + 3NaX + Al$$

The use of an alloy of aluminium and magnesium has been described.(12)

$$Al_2Mg_3 + 6RCl = 2AlR_3 + 3MgCl_2$$

The method was originally used to prepare the etherate of of trimethylaluminium.(13)

It has been shown that alkylaluminium sesquiiodides disproportionate more easily than the chlorides or bromides, giving a reasonable yield of the trialkyl. Thus, for example, the products from a reaction between methyl iodide and aluminium, can be distilled slowly and the trimethylaluminium taken off (at reduced pressure) from the top of a fractionating column.(14)

Dialkylaluminium chlorides can be obtained by distillation from the corresponding sesquichlorides. From these, the trialkyls can be obtained,(15) as shown by the following equations.

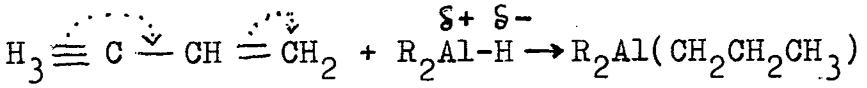
$$R_2AlCl + NaF = R_2AlF + NaCl$$

$$R_2AlF + NaF = Na[R_2AlF_2]$$

$$3Na[R_2AlF_2] \xrightarrow{200\text{-}300^\circ C} 2AlR_3 + Na_3AlF_6$$

The method is very useful for the large-scale preparation of trimethylaluminium.

(c) The reactions of aluminium hydride and lithium aluminium hydride with olefins, together with those between an olefin, hydrogen and aluminium metal were investigated in the last decade.(16,17) Reactions of aluminium hydride with terminal olefins is similar to that described for diborane. It does give a trialkyl but the method is not very useful because aluminium hydride is not easy to prepare free from ether. In contrast with boron hydrides, the reactions of aluminium hydrides with non-terminal olefins are extremely slow. A dialkylaluminium hydride can be used to prepare a mixed trialkyl. The aluminium atom of an Al-H bond is positively polarised, therefore, in reactions with a terminal olefin, the alkylated carbon is attacked by the negatively polarised hydrogen atom, as shown below:



$$H_3 \equiv C \overset{\vee}{-} CH = CH_2 + R_2\overset{\delta+}{Al}-\overset{\delta-}{H} \rightarrow R_2Al(CH_2CH_2CH_3)$$

These mixed trialkyls usually disproportionate into the individual trialkyls. A reaction between lithium aluminium hydride and ethylene at about 100°C, under pressure, gives a quaternary salt.

$$LiAlH_4 + 4C_2H_4 = LiAlEt_4$$

The quaternary salt may be washed with cold pentane to remove any polymer formed, and treated with a suspension of aluminium chloride in an inert solvent, to form the triethyl.

$$3LiAlEt_4 + AlCl_3 = 4AlEt_3 + 3LiCl$$

The higher alkyls, for example, the triethyl can be obtained by a high pressure reaction at about 100°C, between an olefin, hydrogen and aluminium (suitably activated, for example, by agitation with triethylaluminium).

$$2Al + 3H_2 + 6C_2H_4 = 2AlEt_3$$

This method is very useful for the preparation of many of the trialkyls particularly the triethyl and tri-isobutyl, but trimethylaluminium cannot be obtained by this reaction.

### Trialkyls of Gallium.

The general methods for the preparation of the trialkyls of gallium are given below:

(a) Good yields were reported(18) for triethylgallium (80%) from the transalkylation reaction between gallium trichloride and triethylaluminium. A typical reaction sequence is shown below:

$$GaCl_3 + 3AlEt_3 = GaEt_3 + 3AlEt_2Cl$$

$$GaCl_3 + 3AlEt_2Cl = Ga[AlEt_2Cl_2]_3$$

$$2GaCl_3 + 3AlEt_3 = GaEt_3 + Ga[AlEt_2Cl_2]_3$$

$$Ga[AlEt_2Cl_2]_3 + 3KCl = GaCl_3 + 3K[AlEt_2Cl_2]$$

$$GaCl_3 + 3AlR_3 + 3KCl = GaR_3 + 3K[AlR_2Cl_2]$$

Final purification of $GaR_3$ from admixed $AlR_3$ was achieved by preferential complexation of the $AlR_3$ with alkali fluorides.

(b) The displacement reaction(18) between the metal isobutyl derivative and a higher olefin is a useful preparative method for higher alkyls, as shown below:

$$Ga[CH_2CHMe_2]_3 + 3CH_2 = CHC_8H_{17} \xrightarrow{155 - 60^{\circ}C} Ga(C_{10}H_{21})_3 + 3CH_2 = CMe_2$$

The displacement of the alkyl groups branched in the $\beta$- position, by reaction with an $\alpha$-olefin went smoothly according to the above equation. The higher indium alkyl was, however, unstable at the necessary reaction temperature. The ease with which isobutyl derivatives of group III elements participate in the displacement reaction appear to decrease in the order $Al > B > Ga > In$.

(c) The trialkyls can be obtained by the reaction of gallium metal with dialkylmercury.

$$2Ga + 3HgR_2 = 2GaR_3 + 3Hg$$

Trimethylgallium(19) can be conveniently obtained by this method (see experimental section).

(d) The reaction between gallium trichloride and the corresponding Grignard reagent in ether has been described.(20,21)

Trialkyls of Indium.

The trialkyls of indium can be obtained by the following general methods.

(a) The transalkylation reaction(18) between indium trichloride and triethylaluminium gives a good yield of triethylindium.

$$InCl_3 + 3AlEt_3 + 3KCl = InEt_3 + 3K[AlEt_2Cl_2]$$

Excess of triethylaluminium was removed by preferential complexation with alkali fluorides.

(b) Trimethylindium(22) can be prepared by the action dimethylmercury on indium metal (see experimental section).

$$2In + 3HgMe_2 = 2InMe_3 + 3Hg$$

(c) The trialkyls can also be prepared by the reaction between an ethereal solution of indium trichloride and a Grignard reagent.(23) Though they form co-ordination complexes with diethyl ether, these dissociate sufficiently to allow the ether-free alkyls to be separated by fractional distillation or condensation.

Trialkyls of Thallium.

Reaction between a Grignard reagent and thallic chloride, introduces only two organic groups in the molecule giving $R_2TlX$. These can react further with a lithium alkyl to give a trialkylthallium derivative(24)

$$Me_2TlBr + LiMe = TlMe_3 + LiBr$$

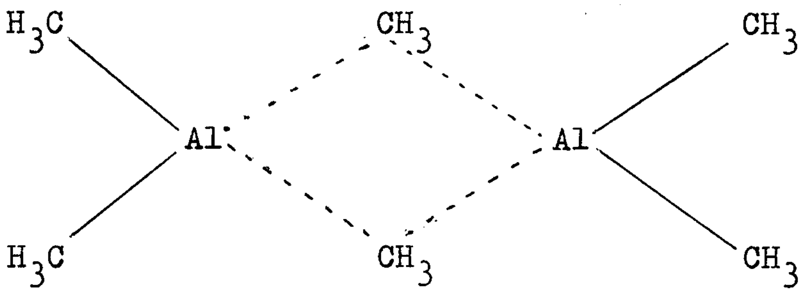
Trimethyl thallium can also be made from the following reaction.

$$TlI + MeI + 2LiMe = TlMe_3 + 2LiI$$

## Properties of the Trimethyl Derivatives of Group III Elements.

Except trimethylborane, all other trimethyls react with water at room temperature to give hydroxy derivatives. These trialkyls usually react with halogens. Trimethylborane has a very sharp smell. It is monomeric in the vapour phase. Electron diffraction, infrared and Raman spectra(25) show that in the vapour phase the $B(CH_3)_3$ molecule is planar and symmetrical with angles of $120^o$. It has been suggested that lack of association may be due to the small size of the boron atom relative to the surrounding organic groups(26) or due to trigonal hyperconjugation.(27) These trialkyls can combine with a suitable ligand (e.g. LiMe) to give a salt (e.g. $LiBMe_4$). Trimethylthallium cannot act in this way. Most of these trimethyls can be used up to about 200°C without any thermal decomposition (trimethylthallium explodes on heating to 90°C; also it is photosensitive).

Trimethylaluminium (m.p. 15.0°, b.p. 126°C) is a colourless mobile liquid. It is dimeric as vapour(28) at 70°C, and in benzene(14) solution. The heat of dissociation to two moles of monomer is 20.2 kcal.(28) The infrared spectrum(29), and x-ray crystal analysis(30) indicate a bridge structure, as shown below:



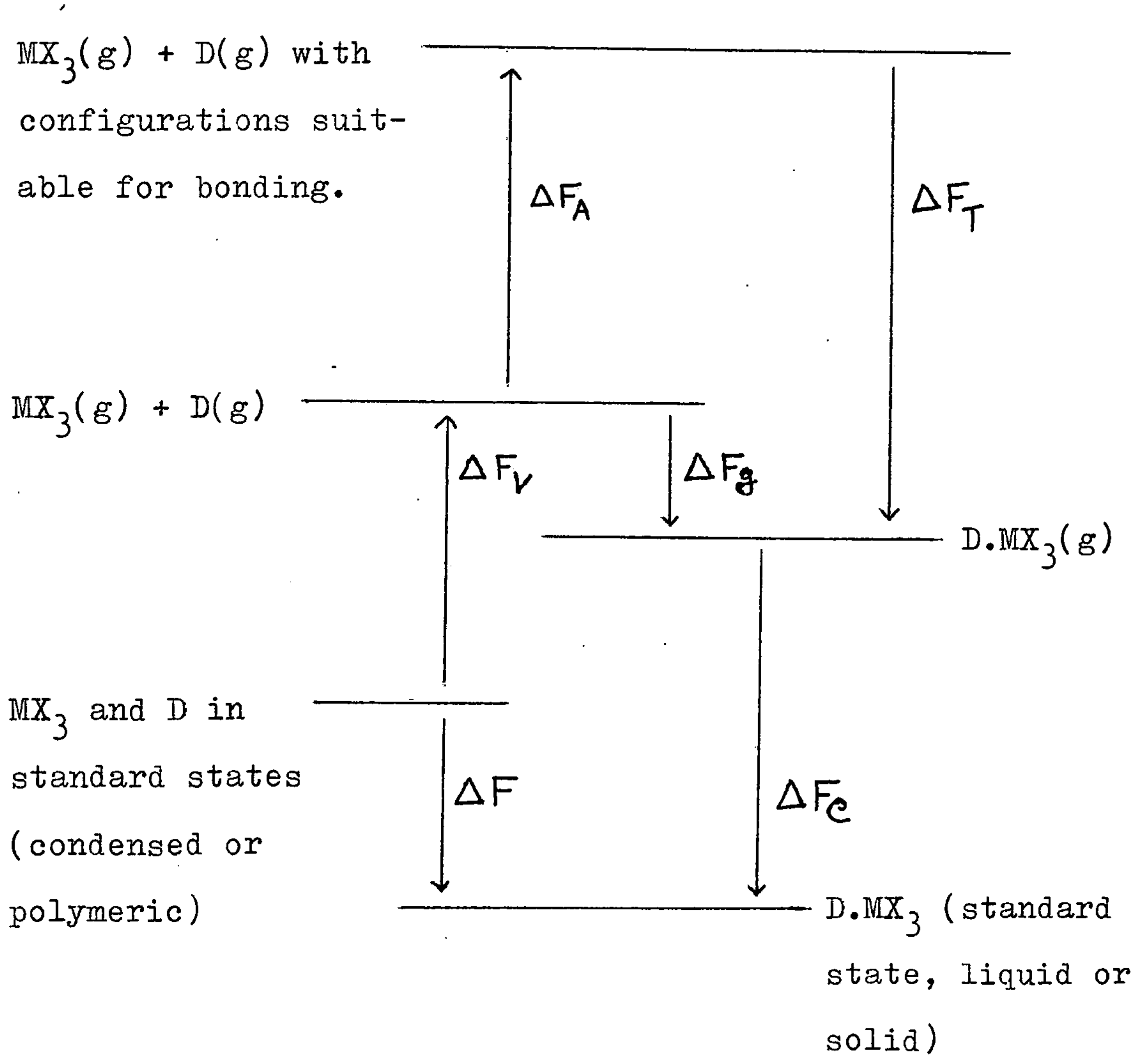
The nature of the bonds in this electron deficient dimer has been a subject of much controversy. At present, the

Al - C - Al bridge bonds are regarded as formed by bent three-centre molecular orbitals (Al $sp^3$ + C $sp^3$ + Al $sp^3$). Thus, each Al - C - Al three centre bond occupied by two electrons can be regarded as a single bond or the Al - C bridge bond as a half-bond. It is of interest to note that the Al-Al distance (2.55 A°) is slightly greater than the calculated Al-Al single bond distance (2.52 A°). Some Al-Al bonding has been suggested from theoretical considerations.(30) Proton magnetic resonance spectra can distinguish between the two types of methyl groups at -75°C, but not at room temperature(31) since rapid exchange occurs.

Trimethylgallium (m.p. -16°; b.p. 56°C), trimethylindium (m.p. 88.4°; b.p. 135.8°C) and trimethylthallium (m.p. 38.5°; extrapolated b.p. 147°C) are monomeric in the vapour phase. Trimethylthallium is monomeric while trimethylindium is tetrameric in benzene solution and in the crystalline state.(32)

These electron deficient molecules can usually combine with ligands able to provide a donor site. The possibility of the donor-acceptor bond being formed can be qualitatively considered in terms of an energy cycle.

Energy steps in the formation of adducts.(33)



$\Delta F_V$ = vapourisation energy required to convert donor and acceptor to the gas phase from their standard states.

$\Delta F_A$ = adjustment energy required to convert gaseous donor and acceptor to moieties having configurations present in the final product, e.g. deformation from trigonal to tetrahedral forms.

$\Delta F_T$ = total energy released in dative-bond formation, giving the adduct in the gas phase.

$\Delta F_g$ = gas-phase energy of formation.

$\Delta F_C$ = energy released when addition compound condenses to standard state.

$\Delta F$ = free-energy change accompanying the reaction $MX_3 + D \longrightarrow D.MX_3$, reactants and products being in their standard states.

If the rehybridisation energy ($\Delta F_A$) is greater than $\Delta F_T$ then no adduct will be formed. Furthermore, if the final ($D.MX_3$) standard state lies above the initial ($D + MX_3$) standard state, then no compound will be formed. In the case of trimethylaluminium, a further complication is introduced by the necess~~as~~ity of 20.2 kcal. for breaking the dimer.

## Review of Interaction of Group III Trialkyls with Donor Molecules not containing Reactive Hydrogen.

A qualitative or quantitative understanding of the relative stability of a metal-ligand bond has provided much valuable information. Thus, for example, it was possible to arrange the trimethyls of group III elements in the order of decreasing Lewis acidity ($Al > Ga > In > B > Tl$) from gas phase dissociation equilibrium studies on their addition compounds with trimethylamine. From an investigation of the dissociation,

$$D.MX_3(g) \rightleftharpoons MX_3(g) + D(g)$$

it is possible to determine the $K_p$ values. From this, the free energy change can be calculated.

$$\Delta F^o = - RT \ln K_p$$

If the $K_p$ values are known at two different temperatures $T_1$ and $T_2$ then the heat content (enthalpy) change $\Delta H$, accompanying the formation of the donor-acceptor bond can be calculated by using the integrated form of the van't Hoff equation.

$$\ln \frac{(K_p)_2}{(K_p)_1} = - \frac{\Delta H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

With $\Delta H$ in calories, R is 1.987, and therefore,

$$\log \frac{(K_p)_2}{(K_p)_1} = - \frac{\Delta H}{4.576} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

It should be mentioned that in a heterogeneous system, the active mass of solid substances present in a reversible equilibrium should be regarded as constant, irrespective of the amount present. Therefore, no terms for any solid present at equilibrium need be included in the expression for the equilibrium constant. For the following dissociation,

$$D.MX_3\ (s) \rightleftharpoons MX_3\ (s) + D\ (g)$$

the equilibrium constant will depend on the partial pressure or pressure of D, depending on whether the system contained any inert gas or not.

$$K_p = p_D$$

Now, the integrated form of van't Hoff equation can be used, but the value of $\Delta H$ derived will be for the complete reaction including solid phases. This value of $\Delta H$ will differ from that for a reaction entirely taking place in the gas phase by the heats of sublimation of the solids.

$$\ln \frac{p_2}{p_1} = - \frac{\Delta H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\text{or } \log \frac{p_2}{p_1} = - \frac{\Delta H}{4.576} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

Calorimetric methods have been employed for systems which dissociate to a great extent or not at all at reasonable temperatures. Another method frequently used is the displacement reaction,

$$D_1.MX_3 + D_2 \rightleftharpoons D_2.MX_3 + D_1$$

to get some qualitative indication of the relative stability of the metal-ligand bond. These reactions depend on a decrease in the free-energy of the system. Therefore, from the following equation,

$$\Delta F = \Delta H - T\,\Delta S$$

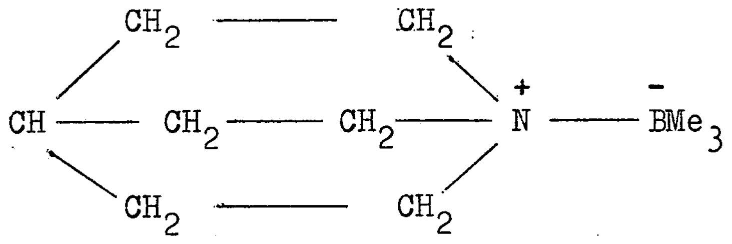
it can be concluded that a displacement reaction does not necessarily give an indication of the relative differences of the values of the enthalpy changes accompanying the formation of the donor-acceptor bond, due to complications resulting from possible differences in the entropy of the two systems. Complications due to volatility effects and lattice energy are also important.

A large number of 1:1 addition compounds of trimethylborane with donor molecules ammonia, methylamine, dimethylamine, trimethylamine, many other higher amines, pyridine and substituted pyridines, trimethylphosphine etc. have been described(33). Phosphine and trimethylstibine forms no compound with trimethylborane even at -78°C. Many of these addition compounds have been investigated by the gas phase dissociation equilibrium methods.(34) In the amine series,(35) it was found that substitution of one methyl group for hydrogen in ammonia made methylamine a better donor (due to electron releasing power of the methyl group), substitution of one more methyl group slightly increased the donor power of dimethylamine, but the substitution of third methyl group made trimethylamine a weaker donor ($\Delta H$ = 13.75, 17.64, 19.26 and 17.62 kcal./mole for the $BMe_3$ addition compounds with $NH_3$, $NH_2Me$, $NHMe_2$ and $NMe_3$ respectively). As the inductive effect increases continuously, this observation was explained by suggesting steric strain due to the interference of the three methyl groups attached to nitrogen with those attached to boron (F-strain). However, this was only part of the explanation because in aqueous solution the same order is found for changes in the basic strengths of these amines.

$$Me_2NH > MeNH_2 > Me_3N > NH_3$$

unlike the bulkyl $BMe_3$, the proton was too small to interfere sterically with the methyl groups attached to nitrogen. It was suggested that the formation of the fourth bond to proton or trimethylborane causes the three methyl groups attached to nitrogen, to move closer together and interfere sterically among themselves (B-strain). Both F-strain and B-strain are effective in co-ordination compounds of trimethylborane.

It has been reported(36) that the addition compound of trimethylborane with triethylamine is too unstable to permit a gas phase dissociation equilibrium study. This is due to steric interference of bulky ethyl groups with the methyl groups attached to the boron atom. However, the compound with quinuclidine in which the carbon atoms are held back from nitrogen, the adduct is more stable.



The comparable stability of $Me_3N.BMe_3$ and $Me_3P.BMe_3$ ($\Delta H$ = 17.62 and 16.47 kcal./mole respectively) may be due to greater F-strain in the trimethylamine adduct, because the boron-nitrogen bond is shorter than boron-phosphorous bond. Absence of F-strain will make ammonia a better donor than phosphine. Relative to trimethylphosphine, phosphine may be a much weaker donor due to the absence of inductive effects, thus, explaining the non-existence of $Me_3B.PH_3$. However, in trimethylphosphine and phosphine the appropriate bond angles are $100^\circ$ and $93^\circ$ respectively (for ammonia and trimethylamine, $107^\circ$ and $108^\circ$ respectively). Therefore, the weaker donor power of phosphine may be due to a large readjustment energy involved for changing into a tetrahedral model.

The co-ordination compounds of trimethylaluminium with ligands such as, dimethylamine, trimethylamine, dimethylphosphine, trimethylphosphine, dimethyl ether, dimethyl sulphide, dimethyl selenide and dimethyl telluride have been described.(37,19,38) The adducts with trimethylamine, trimethylphosphine and dimethyl ether are not appreciably dissociated at 150°C and 40 mm. pressure. From displacement reactions it was established that the stability of the donor-acceptor bond decreased in the order:

$Me_3N.AlMe_3 > Me_3P.AlMe_3 > Me_2O.AlMe_3 > Me_2S.AlMe_3$

It was shown that dimethylaluminium chloride was a stronger Lewis acid than trimethylaluminium. The adducts $Me_2S.AlMe_3$ and $Me_2Se.AlMe_3$ were sufficiently dissociated in the gas phase to permit the determination of relative stability, but $Me_2Te.AlMe_3$ was highly dissociated. It was found that the donor power decreased with increasing size of the ligand atom ($O > S > Se > Te$). The adduct $Me_2HP.AlMe_3$ dissociated appreciably at 150°C, so towards trimethylaluminium as reference acid, trimethylphosphine is a better donor than dimethylphosphine.

Trimethylgallium forms 1:1 addition compounds with most of the ligands mentioned above in connection with aluminium, methyl cyanide and acetone.(39) Trimethylbismuth does not react. The heats of formation of adducts with trimethyls of Group V elements progressively decreases from nitrogen to antimony (measured in gas phase).(40)

$NMe_3$, 21 > $PMe_3$, 18 > $AsMe_3$, 10 > $SbMe_3$ too weak to measure. Oxygen, in dimethyl ether is a stronger donor to trimethylgallium than sulphur, but S, Se and Te are similar (in dimethyls).(40)

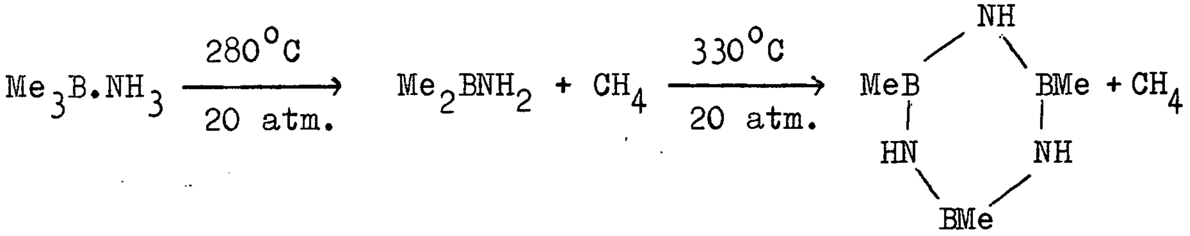
Addition compounds of trimethylindium with trimethylamine and trimethylphosphine have been described, those with trimethylarsine, dimethyl ether and dimethyl sulphide dissociate extensively in the vapour phase.(41)

Co-ordination compounds of trimethylthallium(41) with trimethylamine, trimethylphosphine, dimethyl sulphide and dimethyl selenide have been described, it was mentioned that dimethyl ether was a very weak donor and in the case of trimethylarsine and dimethyl telluride there was hardly any evidence for reaction. The trimethylphosphine and dimethyl sulphide adducts had nearly sharp melting points (27-8°C and -0.5°C respectively), the others melted a little below 0°C.

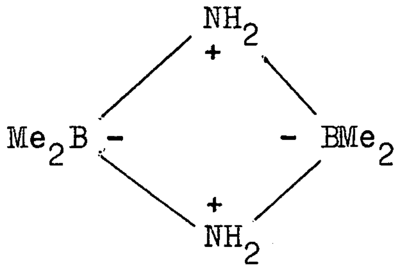
## Review of Reactions of Group III Trialkyls with Donor Molecules Containing Reactive Hydrogen.

Many of the addition compounds of the trimethyls of group III elements with ligands containing a reactive hydrogen can eliminate methane on heating under ordinary conditions or under pressure if the adduct tends to dissociate. Sometimes, a reaction with a suitable ligand can result in elimination of methane spontaneously at room temperature, the hypothetical adduct presumably having only a transitory existence. Donation of a pair of electrons by the ligand increases the protonic character of the hydrogen, and elimination of methane occurs due to nucleophilic attack by one of the negatively polarised methyl groups attached to the acceptor atom.

(a) A discussion of reactions in which the reactive hydrogen is attached to the donor atom follows. The adduct of trimethylborane with ammonia can be thermally decomposed under high pressure, as shown below.(33)

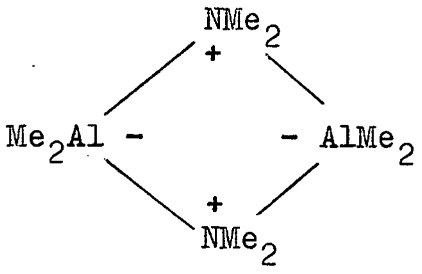


The compound $Me_2BNH_2$ is interesting because it can exist as a monomer, and also a dimer.(42) In the monomer, co-ordination saturation is attained by $p_\pi - p_\pi$ bonding between boron and nitrogen ($Me_2\overset{-}{B} = \overset{+}{N}H_2$). The following structure can be written for the dimer

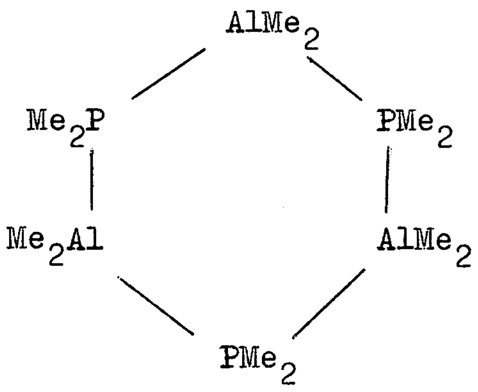


A monomer-dimer reversible equilibrium can be observed in gas phase at room temperature. The compound $Me_2\bar{B} = \overset{+}{N}Me_2$ is also monomeric.(42,43,44)

The double bond formation is entirely confined to boron chemistry and has not been observed with any other element under discussion. Thus, the addition compound of trimethylaluminium with dimethylamine decompose on heating to give $Me_2Al.NMe_2$, which is dimeric in the gas phase.(37) The following structure has been assigned for this compound.



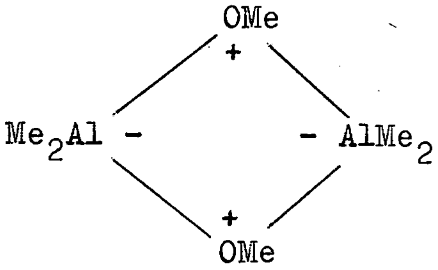
The compound $Me_2AlPMe_2$ was however, found to be trimeric in the gas phase.(37)



Unlike the formation of these amino and phosphino derivatives which require heating, the reactions of trimethylaluminium with MeOH or MeSH go spontaneously at room temperature with elimination of methane.

$$Me_6Al_2 + 2MeOH = 2Me_2AlOMe + 2CH_4$$

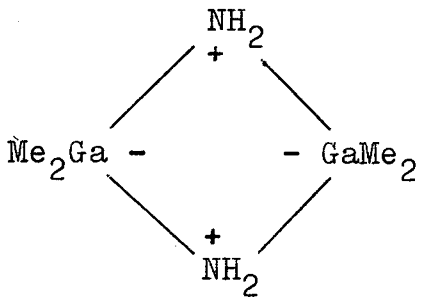
These compounds were found to dimeric, a typical structure is shown below.



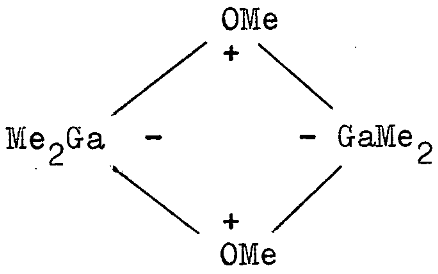
The compound $(Me_2AlSMe)_2$ reacts with trimethylamine.

$$(Me_2AlSMe)_2 + 2NMe_3 = 2Me_2\overset{-}{Al}(SMe).\overset{+}{N}Me_3$$

Trimethylgallium amine decomposes on heating to give the bis-amino derivative and methane.(19)



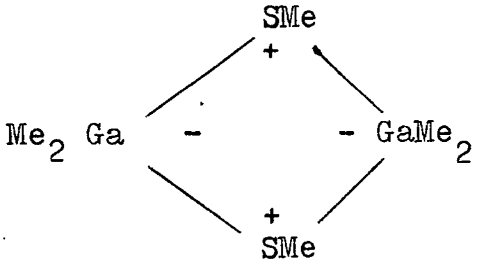
Similar compounds can be obtained by the decomposition of adducts with methylamine and dimethylamine.(19) Methanol reacts spontaneously at room temperature with elimination of methane, to give a dimer, which has been assigned the following structure.(39)



The dimer does not react with trimethylamine or dissociate in the vapour phase. Methanethiol reacts with trimethylgallium.

$$GaMe_3 + MeSH = Me_2GaSMe + CH_4$$

The compound which is a dimer, has been assigned the following structure.



An analogous selenium compound has been described.(39) Unlike the dimeric methoxide, the sulphur and selenium dimers react reversibly with trimethylamine.

$$(Me_2GaSMe)_2 + 2NMe_3 \rightleftharpoons 2Me_2\overset{-}{Ga}(SMe).\overset{+}{N}Me_3$$

Compounds with phenols, thiophenols and selenophenol were found to be similar. They reacted with trimethylamine in a reversible manner. At 20°C the dissociation pressures for the compounds $(Me_2GaSMe)_2$, $(Me_2GaSeMe)_2$, $(Me_2GaO.C_6H_4Bu^t\text{-}p)_2$, $(Me_2GaOPh)_2$, $(Me_2GaO.C_6H_4Cl\text{-}p)_2$, $(Me_2GaSPh)_2$ and $(Me_2GaSePh)_2$ in combination with trimethylamine were found to be 10.3, 4.5, 14, 6.1, 1.5, 0.4 and 0.1 mm. respectively. Increase in dissociation pressure is an indication of stronger donor power of the ligand in these compounds which are very similar, and therefore, other effects may be comparable. From the above data it can be concluded that both in the methyl and the phenyl series the donor power decreases from oxygen to selenium. Substitution of phenyl for methyl makes the ligand a weaker donor. Furthermore, the inductive effects are apparent from the dissociation pressures of the trimethylamine adducts of $(Me_2GaO.C_6H_4Bu^t\text{-}p)_2$ and $(Me_2GaO.C_6H_4Cl\text{-}p)_2$ when compared with those of the analogous phenyl compound.

Trimethylgallium reacts with hydrogen halides to give a monochloride or a dichloride depending on the relative proportions of the reactants used.(45)

$$2GaMe_3 + 2HCl = (Me_2GaCl)_2 + 2CH_4$$

$$2GaMe_3 + 4HCl = (MeGaCl_2)_2 + 4CH_4$$

Both these compounds were found to be dimeric as vapour.

The reactions of trimethylindium have been less extensively investigated than those of trimethylgallium. The unstable ammine, $Me_3InNH_3$, loses methane slowly at room temperature$^{(41)}$ and rapidly on heating (70-80°C) giving a polymer $(Me_2InNH_2)_x$. A dimer $(Me_2InNMe_2)_2$ was obtained on heating (140-60°C) the adduct of trimethylindium with dimethylamine. The compounds $(Me_2InOMe)_x$ and $(Me_2InSMe)_2$ obtained from the reactions of trimethylindium with methanol and methanethiol respectively have been described.

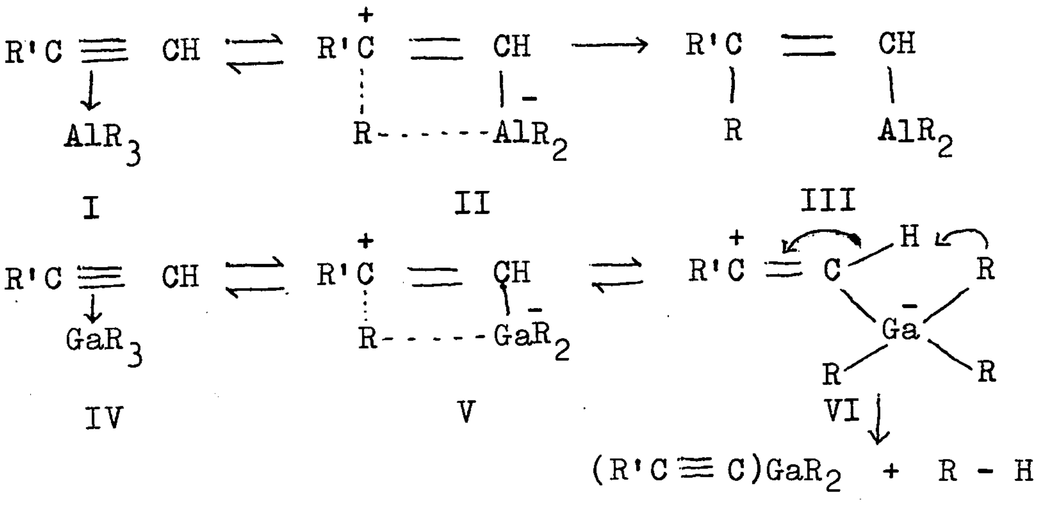
A striking difference between triethylaluminium and triethylgallium is their reactions with acetylene,$^{(46)}$ as shown below:

$$AlEt_3 + HC \equiv CH \xrightarrow{40\text{-}60^\circ C} AlEt_2(CH = CHEt)$$

$$AlEt_3 + HC \equiv CH \xrightarrow{\text{not observed}} AlEt_2(C \equiv CH) + C_2H_6$$

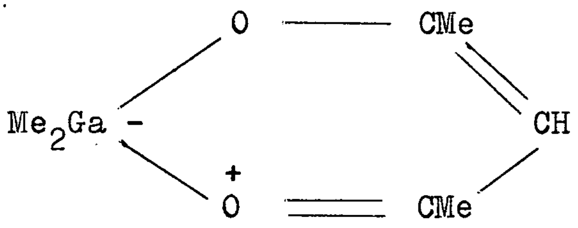
$$GaEt_3 + HC \equiv CH \xrightarrow{50^\circ C} GaEt_2(C \equiv CH) + C_2H_6$$

The suggested mechanisms for these reactions are shown below:

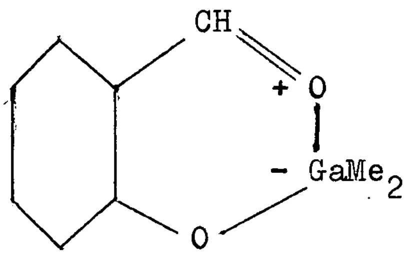


Structure V may be less favoured than structure VI due to decrease in bridging tendency in gallium alkyls. Nucleophilic attack on hydrogen by the negatively polarised R group gives the observed product.

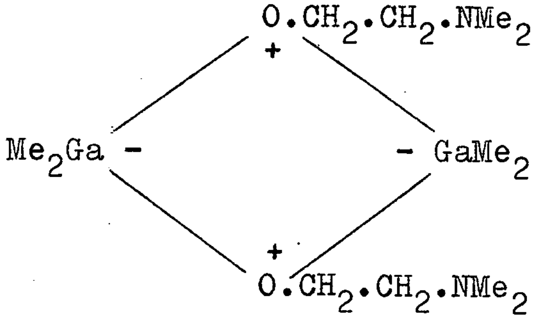
(b) A discussion follows of the reactions of the trialkyls of group III elements with donor molecules in which there are two or more donor atoms. Trimethylgallium reacted with acetylacetone with elimination of methane to form a chelate monomer.(39)



A similar compound was obtained from trimethylindium.(41) The following chelate monomer was obtained from salicylaldehyde and trimethylgallium.



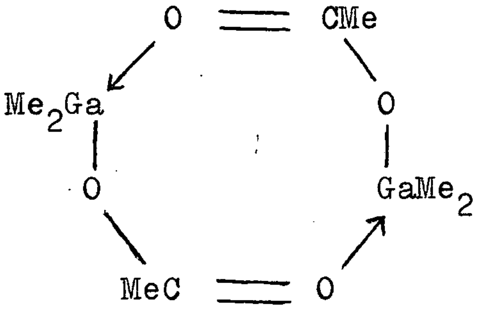
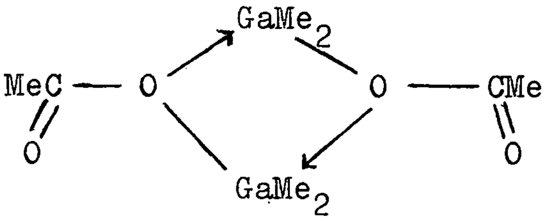
The product obtained from trimethylgallium and dimethylethanolamine is not a chelate compound because it is a dimer which forms a dimethiodide with methyl iodide. The structure is given below.(39)

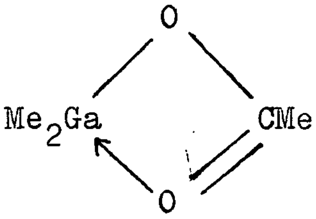


Diethylboron acetate(47) and a dimer dimethylgallium acetate(39) obtained from the reactions of triethylboron and trimethylgallium with acetic acid have been described. However, these compounds were inadequately examined and their structures were not established. A dimer from triethylaluminium and 1:1 dimethylhydrazine has been described.(48)

## Objects of the Present Investigation

There has recently been a growth of interest in bridging ligands in connection with the development of "inorganic polymers" stable to high temperatures. From the review made it is apparent that very little information was available on the reactions of trialkyls of group III elements with weak acids containing two or more donor atoms. These reactions are of interest in connection with the problem whether, for example, a three-atom donor group acts as a chelating or a bridging ligand, e.g. in dimethylgallium acetate.



The trimethyls were chosen for these investigations since the reaction products were expected to have higher melting points and simpler spectra than those derived from other trialkyls. Infrared spectroscopy was used to help to establish the structures of the products, andfor making new assignments. Review of any available information in the areas actually investigated will be given in the discussion section.

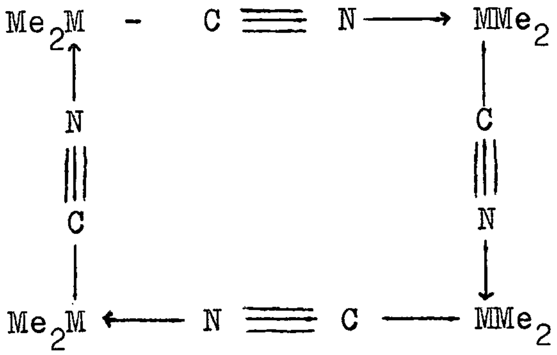
# DISCUSSION

# DISCUSSION

## Cyanides of Group III Elements

Compounds in which an element of Group III is bound to an element of donor character, commonly nitrogen or oxygen, are often associated in order that both elements can become co-ordinatively saturated. Well-known examples are the aminoboron halides, e.g. $(Cl_2B.NMe_2)_2$, and the aluminium alkoxides. Boron cyanides are interesting in this connection since the linear $B - C \equiv N \longrightarrow$ group would not allow the formation of the four- and six-membered rings so frequently found among boron compounds. Boron cyanide is a polymeric solid(49) $[B(CN)_3]_x$ and di-n-butylcyanoborane(50) is an involatile viscous liquid for which cryoscopic measurements in benzene indicate a degree of association of about twenty. Some diarylcyanoboranes have also been found to be polymeric, and both these(51) and $(Bu^n_2B.CN)_x$ are depolymerised by bases such as ammonia and pyridine.

The formation of dimethylaluminium cyanide (m.p. 88°C) from trimethylaluminium and hydrogen cyanide has been mentioned briefly,(52) but without indication of its molecular complexity. In the present work it was found that this compound is tetrameric in benzene solution, and that so are the corresponding gallium and indium compounds (prepared from hydrogen cyanide and trimethyl-gallium and -indium). Aluminium, gallium, indium, and thallium all form compounds, e.g. $(Me_2M.NMe_2)_2$, M = Al,(37) Ga,(19,39) In, or Tl,(41) in which the metal is bound to four ligands and is also part of a four-membered ring, implying easy distortion of the valency angle from 109° to about 90°. Gillespie(53) has shown that distortions from the tetrahedral angle occur much more readily for elements of the second or higher period than for elements of the first period. Thus structure (I; M = Al,Ga, or In) is reasonable, even if $M - C \equiv N \rightarrow M$ group is assumed to remain linear.



(I)

The reactions of the cyanides with trimethylamine were examined, rather than with ammonia or pyridine (whose reactions with $R_2B.CN$ have been studied), because there are data on similar reactions between trimethylamine and $(Me_2M.SMe)_2$ (M = Al(37) or Ga(19,39)), in which $Me_2M(SMe)NMe_3$ is formed. The tetramers (I) absorb four mole of trimethylamine, which doubtless competes with cyanide groups in co-ordination with the metal, forming solid adducts whose dissociation pressures are given by the equations:

$(Me_2AlCN)_4 + NMe_3 : \log_{10} p_{mm.} = 5.288 - 1140/T$ (T in $^{o}K$)

$(Me_2GaCN)_4 + NMe_3 : \log_{10} p_{mm.} = 11.297 - 3330/T$

At $25^{o}C$ the dissociation pressures are 29(Al) and 1.3 mm (Ga), and the above equations correspond to heat content changes of 5.2 and 15.2 kcal. $mole^{-1}$ (of trimethylamine). Thus, relative to trimethylamine, the co-ordination affinity of the cyanide group is greater to gallium than to aluminium, though this conclusion would be invalidated in the event of large disparities between the sublimation energies of the aluminium adduct and tetramer and those of the gallium analogue.

The aluminium compound (I; M = Al) is very sensitive to air and sometimes inflames in the air when touched with a drop of water. The gallium compound slowly liquefies when exposed to the air, smells strongly of hydrogen cyanide, and gradually deposits crystals of the hydroxydimethylgallium tetramer(54) $(Me_2Ga.OH)_4$. The air-sensitivity of the indium compound is very similar to that of $(Me_2Ga.CN)_4$, and is much less than that of $(Me_2Al.CN)_4$.

Reaction between trimethylaluminium and more than one mole of hydrogen cyanide results in the displacement of more than one methyl group from each aluminium atom, but the products appear to catalyse the polymerisation of hydrogen cyanide and isolation of any pure product was not achieved. An excess of hydrogen cyanide may be used in the preparation of dimethyl-gallium and -indium cyanide, without the loss of further methyl groups (reactions under pressure at high temperature were not attempted). Dimethylindium cyanide, however, reacts very slowly with an excess of hydrogen cyanide at room temperature.

Dimethylthallium cyanide was prepared both from trimethylthallium and hydrogen cyanide and from dimethylthallium fluoride and potassium cyanide in aqueous solution. Diphenylthallium cyanide(55) is a high-melting solid [m.p. 318°C (decomp.)], which is sparingly soluble in water, with slight hydrolysis. The dimethyl compound is soluble in water (2.7 gm. in 100 gm. of water at 25°C), in which it behaves as a 1:1 strong electrolyte $[Me_2Tl]^+CN^-$. Its conductance at 25°C is given approximately by the equation:

$$\Lambda_C = 100{\cdot}5 - 51{\cdot}6\sqrt{C} \quad (C = 0.004 - 0.02 \text{ mole } l^{-1})$$

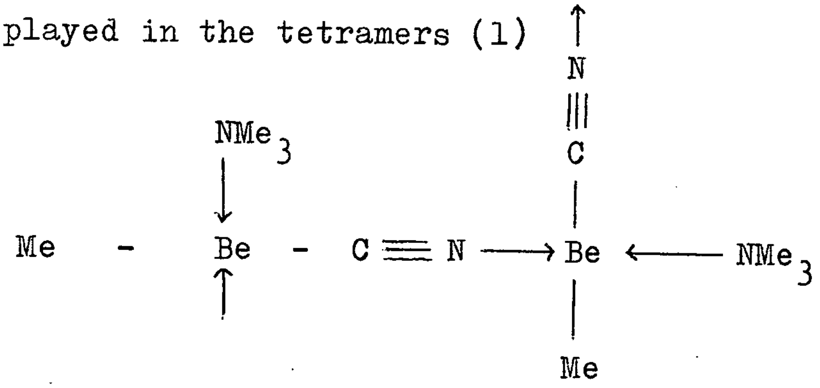
It is insoluble in ether and in benzene.

A brief study was made of the reaction between dimethylberyllium and hydrogen cyanide. Beryllium cyanide does not appear to have been described previously, but it seems to be present in the product of the reaction between beryllium iodide and cyanogen at about 500°C: this substance dissolves in water to a viscous solution which shows reactions characteristic of aqueous cyanide solutions.(56) Beryllium cyanide is precipitated at once when dimethylberyllium is added to an excess of hydrogen cyanide in an inert solvent. It is insoluble in solvents other than those which cause hydrolysis, does not absorb trimethylamine at room temperature or at 70°C, and no doubt has a cross-linked polymeric constitution as would be expected if each beryllium atom had a co-ordination number of four.

If dimethylberyllium and hydrogen cyanide are added simultaneously to ether, some insoluble matter is precipitated but the filtrate evidently contains methylberyllium cyanide. Solutions so obtained are mobile and are unlikely to contain highly polymeric material. The beryllium is co-ordinated to ether, which may be removed by pumping at 70°C, but the residue does not redissolve in ether. Purification of methylberyllium cyanide was not achieved, but the product had a Be:$CH_3$ ratio of 1.00:1, though the analysis indicated a purity of only 97-98%.

Addition of 2,2'-bipyridyl to an ether solution of methylberyllium cyanide gave an orange-yellow solution. Coloured bipyridyl complexes of organoberyllium compounds have been described.(57)

The reaction between hydrogen cyanide and $Me_2BeNMe_3$ was investigated, because the beryllium atom in the hypothetical primary reaction product, $(Me_3N)MeBe.CN$, would have only one vacant co-ordination position, unlike that in MeBe.CN which has two vacant co-ordination positions. The reaction (in benzene solution) resulted in the deposition of a little insoluble matter, but most of the product remained in solution. Removal of benzene gave an apparently amorphous product, very sparingly soluble in benzene and involatile at 200°C/0.01 mm., which evidently is a polymer. Thus trans-association (11) is favoured by both the beryllium and the boron cyanides rather than the cis-association displayed in the tetramers (1)



(11)

Infrared Spectra

The spectra of the cyanides each had a single sharp band in the 2100-2300 $cm^{-1}$ region, clearly due to $\nu(C{:}N)$

(Table 1). The stretching frequencies of the cyanide

Table 1

Cyanide stretching frequencies, $\nu_{\mathrm{C:N}}$ ($\mathrm{cm}^{-1}$) in $\mathrm{R_2MCN}$

| Compound | C:N (stretch) |
|---|---|
| $(\mathrm{Bu}_2^{n}\mathrm{BCN})_n$ (50) | $2280^a$ |
| $(\mathrm{Me_2AlCN})_4$ | $2213^a$, $2224^c$ |
| $(\mathrm{Me_2GaCN})_4$ | $2202^a$, $2216^b$ |
| $(\mathrm{Me_2InCN})_4$ | $2178^a$ |
| $\mathrm{Me_2TlCN}$ | $2101^b$ |
| $(\mathrm{MeBeCN})_n$ | $2222^b$ |
| $[(\mathrm{Me_3N})\mathrm{MeBeCN}]_n$ | $2200^b$ |

$^a$ in $\mathrm{CCl_4}$, $^b$ nujol mull, $^c$ hexachlorobutadiene mull.

group in many metal complexes have been discussed with particular regard to the distinction between terminal and bridging cyanide groups,(58) the former having the lower $\nu$(C:N). In compounds of six elements containing bridging cyanide groups, $\nu$(C:N) was in the range 2164 - 2239 $\mathrm{cm.}^{-1}$, and in the tetramers described here $\nu$(C:N) falls within that range. In agreement with the formulation of dimethylthallium cyanide as a salt, $\nu$(C:N) is quite near the values observed for sodium and potassium cyanide(59) (2085, 2076, respectively, both measured for Nujol mulls).

Examination of the spectrum of the aluminium tetramer at lower frequencies was restricted by the difficulty of finding suitable solvents. The tetramer reacts with, for example, carbon disulphide, forming a yellow substance. Features noted in the spectrum of $(Me_2Al.CN)_4$ in carbon tetrachloride include a prominent band at 1195 $cm^{-1}$ due to $CH_3$ symmetric deformation (compare(60) 1201 $cm.^{-1}$ for $Me_6Al_2$ and 1205 $cm.^{-1}$ for $Me_4Al_2Cl_2$). The assignments for $(Me_2Ga.CN)_4$ are given in Table 2.

Table 2.

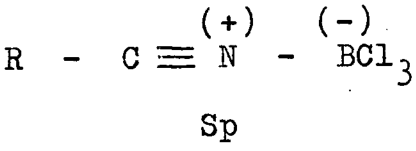
Infrared spectrum in carbon disulphide.

| $(Me_2GaCN)_4$ | Assignments |
|---|---|
| 1207 (ms) | $Ga\text{-}CH_3$ $(d)_{sym}$ |
| 1134 (vw) | 591 + 548 = 1139 ? |
| 766 (s,sh)<br>746 (vs)<br>705 (ms) | Ga-Me (rock) |
| 607 (ms,sh)<br>598 (s)<br>591 (ms,sh) | $GaMe_2$ $(stretch)_{as}$ |
| 548 (m) | $GaMe_2$ $(stretch)_{sym}$ |

The infrared spectra of a number of boron trichloride complexes with aliphatic and aromatic nitriles have been described.(61) It was found that the CN stretching frequencies were 80 ± 9 $cm.^{-1}$ greater in the complexes than in the free nitriles. This was surprising because coordination would have been expected to lower the bond order, with consequent decrease in the nitrile stretching frequency. A decrease in carbonyl stretching frequency is observed in the complexes of carboxylic esters, amides and ketones, where the donors are the carbonyl groups (e.g. $CH_3.CO_2Et$ has $\nu_{C=O}$ at 1740 cm.$^{-1}$ but $CH_3.CO_2Et, BCl_3$ at 1563 cm.$^{-1}$). The observed increase in CN stretching frequency was too great to be due to a mass effect or a coupling between the widely separated CN and BN stretching modes. Therefore, it was suggested that in the complexes the CN bond order is in fact higher than in the free nitriles. The suggestion was based on the hypothesis that in the free nitriles, the CN bond is approximately intermediate between a double and a triple bond (I). A similar situation (involving II and III) is not possible

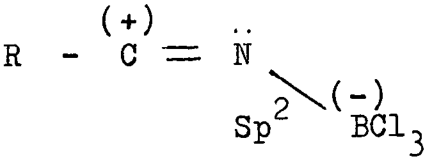
$$R - C \equiv \ddot{N} \longleftrightarrow R - \overset{(+)}{C} = \overset{..(-)}{N}$$

I



$$R - C \equiv \overset{(+)}{\underset{Sp}{N}} - \overset{(-)}{BCl_3}$$

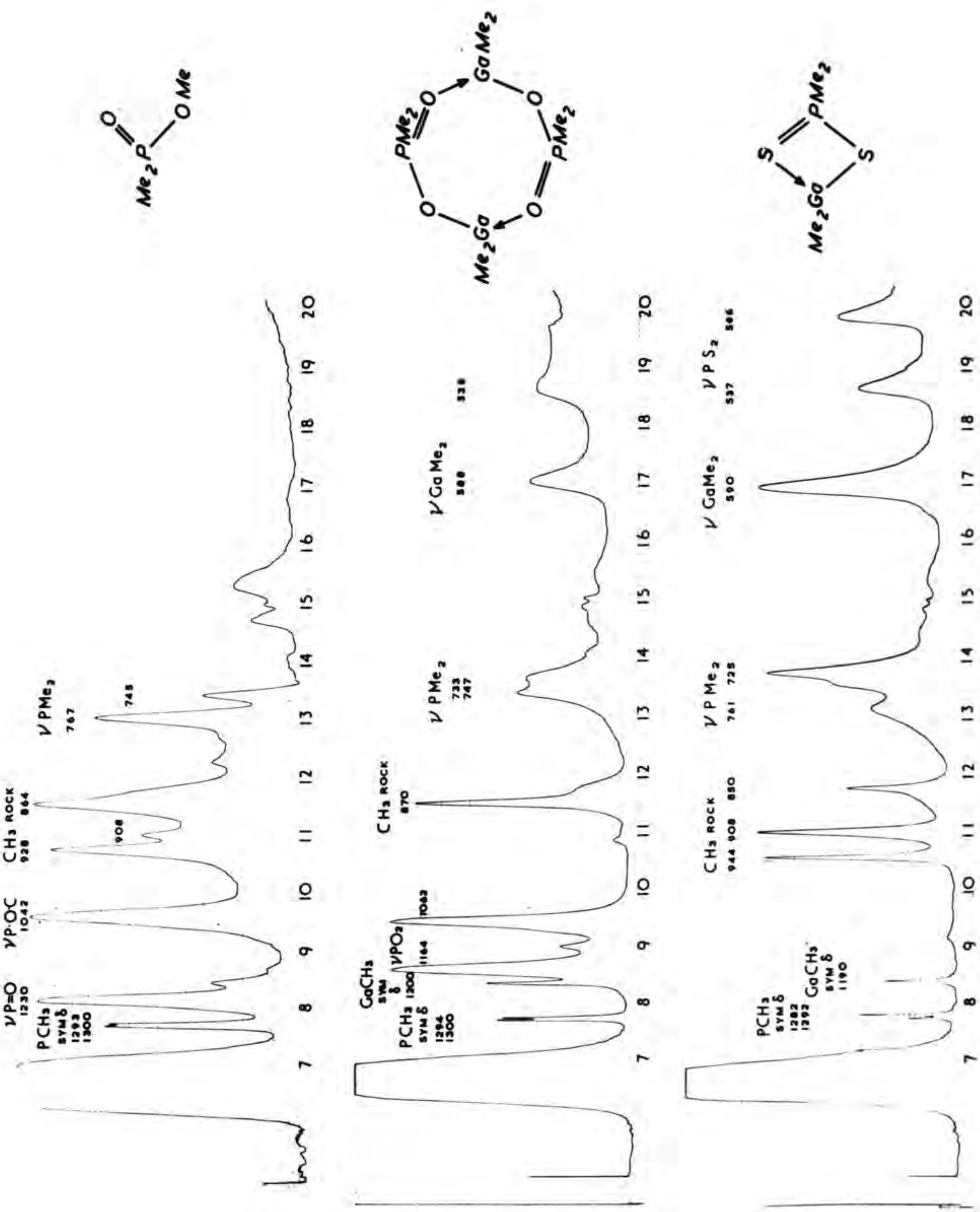
II



III

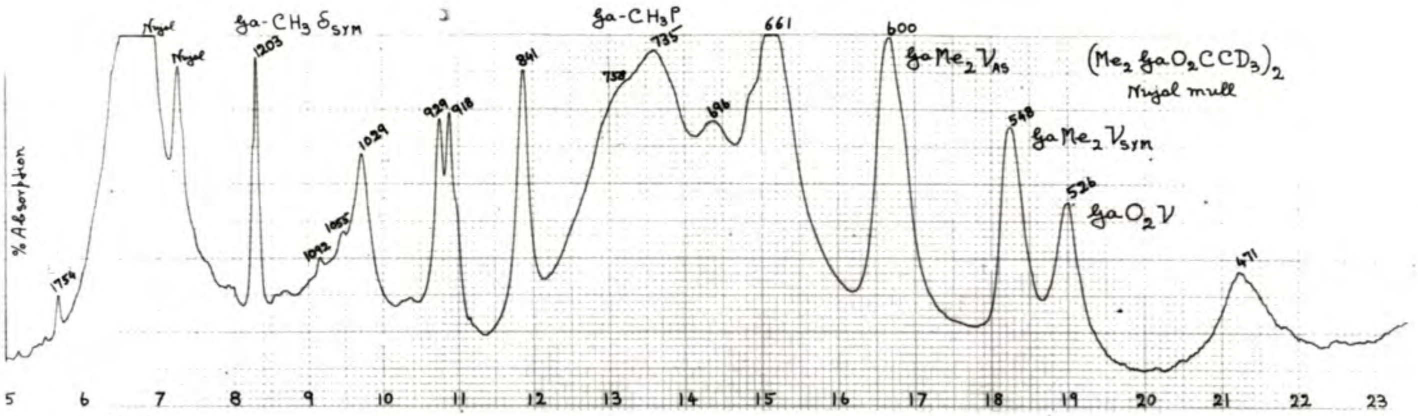
in the complexes because of the very different geometry of (II) and (III). Structure (II) was assumed to represent the co-ordination compounds investigated and is supported by the x-ray analysis of acetonitrile-boron trifluoride complex. Further, the CN bond distances in acetonitrile (1.16Å) and the boron trifluoride complex (1.13Å) indicate that co-ordination shortens bond length and hence increases bond order (although the difference between the two lengths is just outside the quoted mean deviations).

Similar effects have been observed for the isocyanide groups(62). The stretching frequencies of these groups bonded to phenylethynylgold are about 100 cm.$^{-1}$ greater than those of the free isocyanides, the differences $\nu$(bonded) - $\nu$(free) being 103, 98, and 81 cm.$^{-1}$ for n-butyl, p-tolyl, and o-ethylphenyl isocyanide.



νP=O 1230
PCH₃ SYM δ 1293 1300
νP·OC 1042
CH₃ ROCK 928 864
908
νPMe₂ 767
745
GaCH₃ SYM δ 1200
νPO₂ 1164 1062
PCH₃ SYM δ 1294 1300
CH₃ ROCK 870
νPMe₂ 723 747
νGaMe₂ 588
528
PCH₃ SYM δ 1282 1292
GaCH₃ SYM δ 1190
CH₃ ROCK 944 908 850
νPMe₂ 761 725
νGaMe₂ 590
νPS₂ 537 506
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Me₂P
O
OMe
PMe₂
GaMe₂
Me₂Ga
S

Fig. A


(Me$_2$ GaO$_2$CCD$_3$)$_2$
Nujol mull
% Absorption
1754
Nujol
Nujol
Ga-CH$_3$ $\delta_{SYM}$
1203
1092
1055
1029
929
918
841
Ga-CH$_3$ ρ
758
735
696
661
600
GaMe$_2$ $\nu_{AS}$
548
GaMe$_2$ $\nu_{SYM}$
526
GaO$_2$ ν
471
5
6
7
8
9
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11
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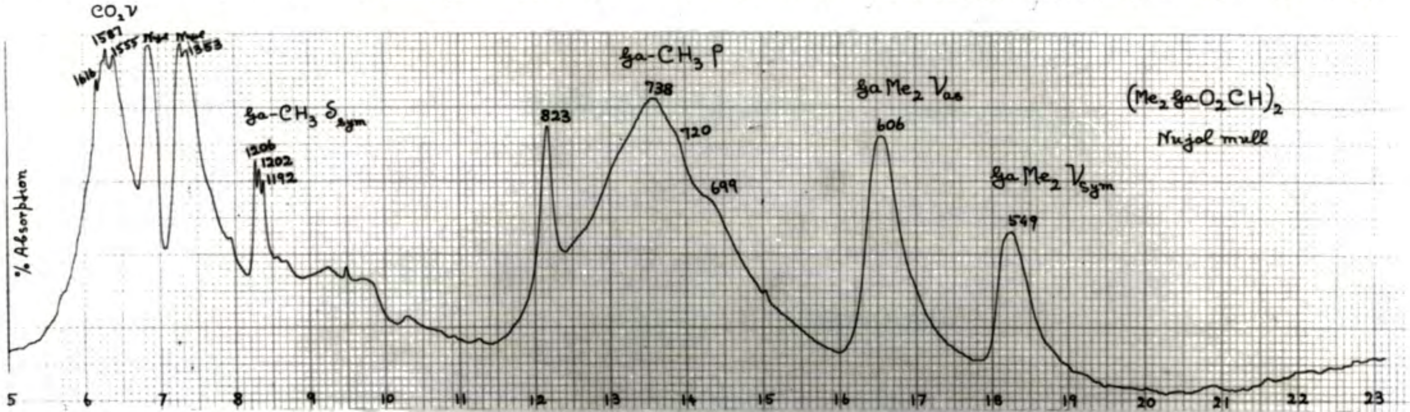
(Me$_2$ GaO$_2$CH)$_2$
Nujol mull
% Absorption
CO$_2$ ν
1616
1587
1555
Nujol
Nujol
1353
Ga-CH$_3$ $\delta_{sym}$
1206
1202
1192
823
Ga-CH$_3$ ρ
738
720
699
GaMe$_2$ $\nu_{as}$
606
GaMe$_2$ $\nu_{sym}$
549
5
6
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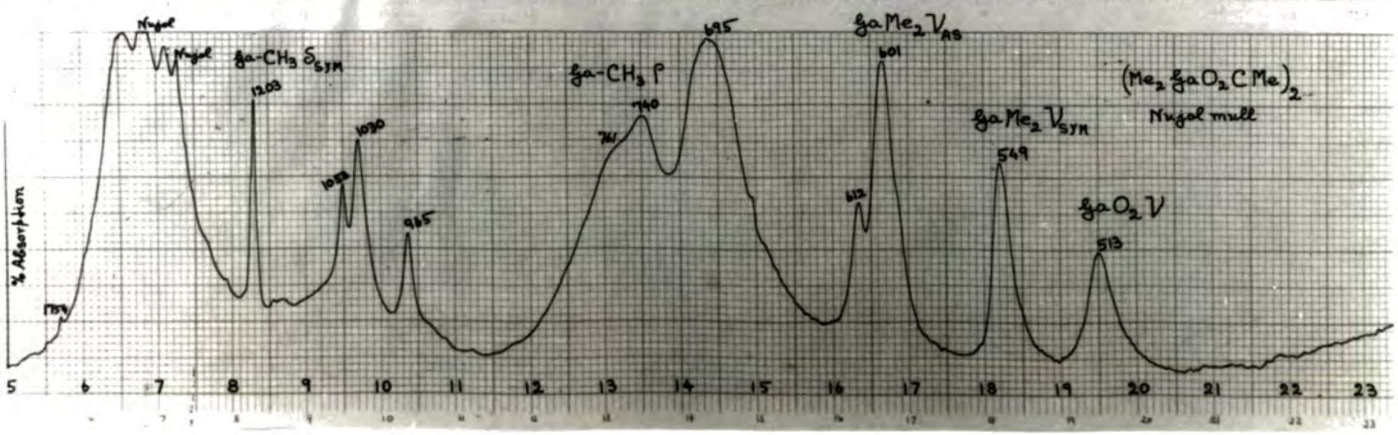

(Me$_2$ GaO$_2$CMe)$_2$
Nujol mull
% Absorption
1754
Nujol
Nujol
Ga-CH$_3$ $\delta_{SYM}$
1203
1053
1030
965
Ga-CH$_3$ ρ
761
740
695
GaMe$_2$ $\nu_{AS}$
612
601
GaMe$_2$ $\nu_{SYM}$
549
GaO$_2$ ν
513
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

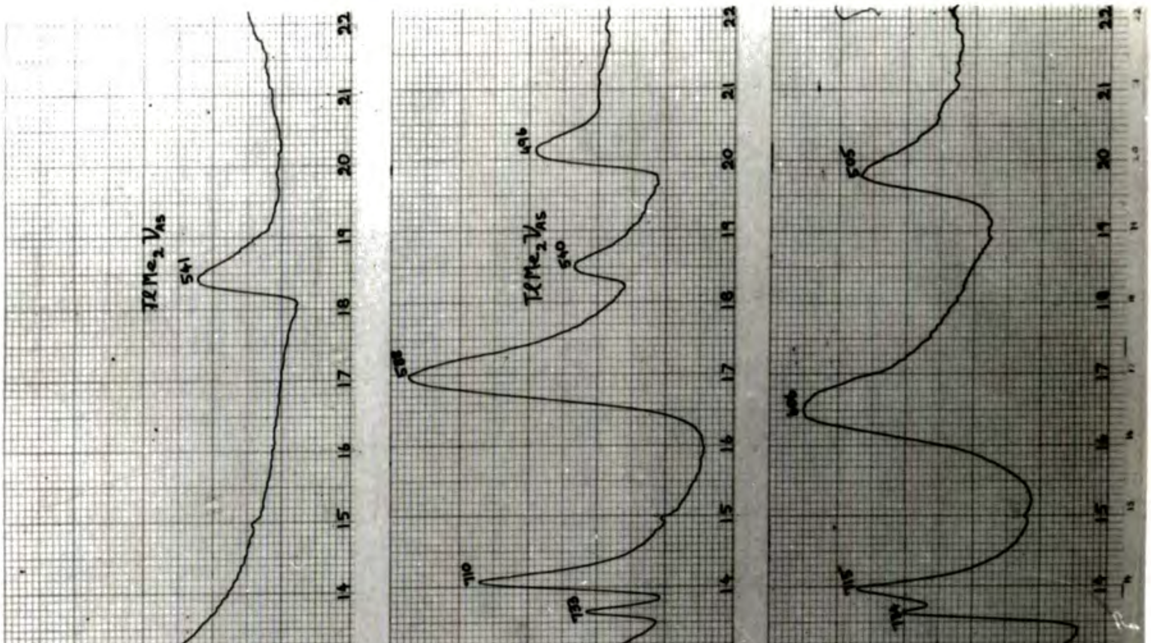
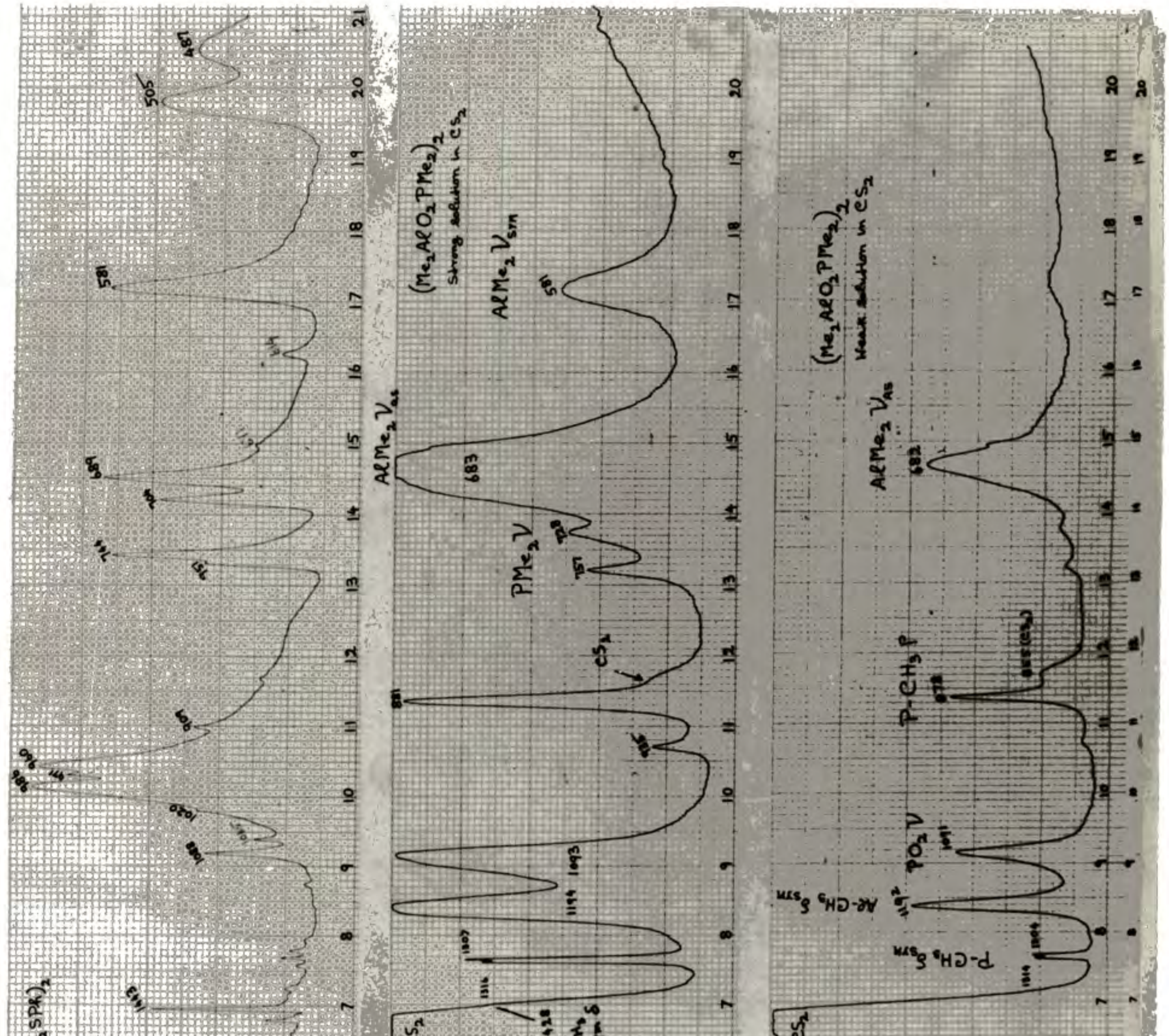

Me$_2$TlBr
potassium bromide disc
%Absorption
Tl-CH$_3$ P
800
1178
TlMe$_2$ $\nu_{AS}$
541
Me$_2$Tl(S$_2$PMe$_2$)
%Absorption
1280
1170
1087
945
909
841
787
733
710
588
TlMe$_2$ $\nu_{AS}$
540
496
Cd(S$_2$PMe$_2$)
%Absorption
1279
1136
932
915
847
734
715
606
505
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

Fig. C



% Absorption
(Me2AlO2PMe2)2 Strong solution in CS2
AlMe2 Vsym
AlMe2 Vas
PMe2 V
CS2
(Me2AlO2PMe2)2 Weak solution in CS2
PO2 V
P-CH3 P
Al-CH3 δsym
P-CH3 δsym
683
581
682

Fig. D

## The Interpretation and Discussion of Spectroscopic Data.

In Tables 1-26 are given suggested assignments of the characteristic absorption bands to the various structural features of the compounds examined. A discussion of these follows (all frequencies are given in wave-numbers).

### P-$CH_3$ Linkage

A sharp band (sometimes a doublet) in the 1280-1320 region has been sometimes erroneously assigned as a $CH_3$ rocking (wagging) vibration, for example, by Corbridge and Lowe.(63) However, other workers are in agreement that this band is due to symmetrical deformation of the methyl group.(64) In the present work, this band (usually a doublet) was found in the regions 1300-1320 and 1280-1300 for dimethylphosphinates (see Tables 3,5 and 6) and dimethyldithiophosphinates (Tables 12-17) respectively. Many other compounds containing a similar structural unit (e.g. X-$CH_3$, where X=C, As,Al,Ga,In and Tl) were investigated. Therefore, it is of interest to discuss in some detail the positional stability of this band, and changes with alteration in the electronegativity or mass and size of X. Present work is in agreement with published material that X remaining the same these bands are fairly stable in position within the ranges quoted, and can be used for diagnostic work. Thus for example, C-$CH_3$ absorbs at 1379 in ethane(65) and within a few wave-numbers in other compounds. As X is progressively replaced by nitrogen, oxygen and fluorine, for example, in methylamine(66), methanol(67) and methyl fluoride(68), the frequency gradually rises to 1426, 1455 and 1475 respectively. There is very little change in the mass or size of X on passing from one atom to its neighbour within the same period. Therefore, presumably the chemical nature of X and in particular its electronegativity influences the considerable changes in observed frequencies. The elements silicon and antimony have the same electronegativity. For these heavier elements the frequency data can only be derived from molecules containing several methyl groups. Under these conditions more than one band may be observed. For the molecules $Me_4Si$ and $Me_3Sb$ the average frequency has been calculated by Sheppard(69) from the separate frequencies and their degeneracies as assigned in the literature. These are 1253 and 1200 for silicon and antimony respectively.

The available normal co-ordinate calculations on several $X(CH_3)_y$ compounds have been summarised.(69) For similar molecules within the same group or across a period the observed frequencies changed in a manner similar to the changes in the force constants controlling the methyl symmetrical deformation mode. It was found that the principal change occurred in the H - C - X deformation force constant, while the H - C - H deformation force constant varied slightly. Therefore, the observed frequency changes as X is progressively replaced by other atoms are not influenced to a great extent by mechanical coupling of the $CH_3$ vibration with other modes of the molecule.

Absorption due to the as~~s~~ymmetrical mode of the methyl group occurs in the 1450 ± 20 region, when X is carbon. With other elements in place of carbon, it varies only slightly in position and is usually found in the region 1380-1480. Hence, the assignments of frequencies due to this mode, in the 1395 - 1420 region for the infrared spectra of dimethyl-phosphinates and -dithiophosphinates are reasonable. These were examined as solution in carbon disulphide, and the bands were usually observed as shoulders on the slope of the strong solvent absorption in that region. It was not possible to examine these air-sensitive phosphinates or dithiophosphinates of Al, Ga or In as pressed potassium bromide discs to obtain a clearer spectrum for this region. Such an investigation was possible for the air-stable dithiophosphinates of Tl and Cs (Tables 16 and 17). Bands at 1404 for the thallium compound, and at 1418 and 1404 for the caesium compound were observed (compare 1417 and 1430, 1440 and

1415, 1450, and 1437 and 1420 for the infrared spectra of trimethylphosphine(70), dimethylphosphine(71), methylphosphine(72) and trimethylphosphine oxide(73) respectively).

Bands due to phosphorus-methyl rocking (wagging) vibrations were observed in the 840-1000 region (compare(74) 947, 960 and 1067; 948 and 960; 977 and 1017; 866, 872, and 950 for the infrared spectra of the series of phosphorus compounds mentioned above). It should be mentioned that for the compounds examined as solution in carbon disulphide, there was no difficulty in assigning a prominent band in the 850 region due to a methyl rocking vibrational mode. For similar cell thickness (0.1 mm) only a weak bump is observed due to absorption by the pure solvent, this being the first overtone of a fundamental in the 400 region.

Absorptions due to phosphorus-methyl bending modes were observed in the 255-295 region (compare(74) 263 and 305, 265 and 318, 256 and 311 for the Raman spectra of trimethylphosphine, dimethylphosphine and trimethylphosphine oxide respectively).

All the compounds investigated had two bands in the 710-760 region due to phosphorus-methyl stretching modes. Thus, for example, caesium dimethyldithiophosphinate had strong bands at 715 and 734 (compare(63) 695 vw and 725 m for $NaPO_2Me_2$). These bands were very close and hence a distinction between symmetric and asymmetric stretching modes is not possible without a detailed mathematical analysis.

P-O Linkage.

A band at 1290 was first observed by Venkateswaran(75) in the Raman spectrum of $POCl_3$. This band disappears(76) in $PSCl_3$ and a new band appears at 750. In various organic derivatives of phosphorus, the P = O and P - O - C (aliphatic) stretching modes cause strong absorption in the 1175-1350 and 990-1050 regions respectively.(77,78) Bands at 1062 and 1164, 1057 and 1171 in the infrared spectra of the dimers $(Me_2GaO_2PMe_2)_2$ and $(Me_2InO_2PMe_2)_2$ respectively were easily assigned to the $PO_2$ stretching modes. Confirmation was obtained from the disappearance of these bands in the spectra of the corresponding dithiophosphinates. In the ester $Me_2PO_2Me$ bands at 1230 and 1042 were observed for the P = O and P - O - C (aliphatic) stretching modes respectively (Fig. A). In the salt $NaO_2PMe_2$ the $PO_2$ stretching modes absorb at 1068 and 1168. Therefore, the bands which are farther apart in the ester move closer together in the salts where the distinction between the two phosphorus-oxygen bonds disappear, giving rise to symmetric and as~~s~~ymmetric stretching modes of the $PO_2$ group. For the gallium and indium phosphinates a similar behaviour was observed relative to the ester.

This is an indication that the P = 0 groups are not free but acting as donors in these dimers (described later). The aluminium dimer had a strong band at 1091 clearly due to a $PO_2$ stretching mode, which disappeared in the spectrum of the corresponding dithiophosphinate. The other band (compare the corresponding gallium and indium dimers) was probably near 1192 and was masked by the intense band due to the symmetric deformation of the methyl groups attached to the aluminium atom.

This region was more complicated in the spectra of diphenylphosphinates and diphenylthiophosphinates of aluminium and gallium (Tables 7-10), due to the presence of $C_{ar}$-H in - plane - deformation vibrations. It has been shown that mono-substituted aromatic compounds absorb(79) in the regions 1125-1175, 1070-1110 and 1000-1070 due to the in-plane-deformation vibrations of the hydrogen atoms remaining in the ring. The spectra of aluminium and gallium diphenylphosphinate or diphenylthiophosphinate were assigned by comparing the corresponding compounds. It is reasonable to assumethat the bands arising due to aromatic hydrogen motions would be similar in the corresponding aluminium or gallium compounds, while the phosphorus-oxygen stretching modes may be slightly metal-sensitive. Therefore, the bands 1134, 1027 and 998 for the dimer $(Me_2AlO_2PPh_2)_2$, and similar bands 1130, 1024 and 998 for the analogous gallium dimer were assigned to the aromatic hydrogen motions. Hence, for the gallium compound the metal-sensitive strong bands at 1180 and 1048 (together with the medium shoulder at 1067) must be due to $PO_2$ stretching modes. For the aluminium compound one strong band at 1072 was clearly identified as due to this mode, the other was probably masked in a manner similar to that described for the analogous dimethylphosphinate dimer. Similarly, for the dimers $(Me_2AlOSPPh_2)_2$ and $(Me_2GaOSPPh_2)_2$ the almost identical bands (Tables 9 and 10) at 1117, 1026 and 999 must be due to aromatic hydrogen motions. Hence, the metal-sensitive bands 1064 and 1047 for the aluminium compound together with the bands at 1089 and 1066 for the analogous gallium dimer are suggested to be due to phosphorus-oxygen stretching modes. The dimers evidently contain two identical P - O bonds (described later) and therefore the symmetric and as~~s~~ymmetric modes might have caused the observed doublets in each case.

### $C_{ar}$- H Out-of-Plane Deformation Vibrations.

A very strong band in the 730-70 range has been assigned to the $C_{ar}$- H out-of- plane deformation vibrations(80-84) in mono-substituted aromatic compounds. Furthermore, a strong band in the 700 ± 10 region is also observed.(83-85) In the present work, three bands have been assigned to $C_{ar}$- H (o.p.d.) in the range 690-755.

### M - $CH_3$ Linkage (M = Al, Ga, In or Tl)

Bands due to aluminium-methyl as~~s~~ymmetric stretching modes and the methyl symmetric deformation modes were assigned by Hoffmann(60) in the regions 680 and 1200 respectively. Very little information was available on other types of metal-methyl vibrational modes, and the suggested frequencies are based on Hoffmann's and the present work.

In the infrared spectra of dimethylaluminium dimethylphosphinate and analogous gallium and indium compounds, single sharp bands at 1192, 1200 and 1151 respectively were assigned to symmetric deformation modes of the methyl groups attached to these metals. These bands were observed at 1186, 1190 and 1147 respectively, for the corresponding dimethyldithiophosphinates. It seems, then, that the attachment of two sulphur atoms to the metal lowers the methyl symmetric deformation frequency relative to the analogous case with oxygen (a similar effect was observed when the methyl groups attached to phosphorus were considered in the same compounds). The lowering of frequency for this band in the indium compounds relative to the corresponding gallium dimer or monomer may be a mass effect because the electronegativities of these two metals are about the same. Comparison of aluminium and gallium compounds reveal that increased electronegativity has slightly raised the frequency of this band though the mass effect acts in the opposite direction. Furthermore, these conflicting effects are responsible for the observation of this band at 1195 in the Raman spectrum of dimethylthallium nitrate or perchlorate(86) in solution. This clearly indicates that the expected decrease in frequency due to increased mass of thallium relative to aluminium or gallium has been completely balanced by the electronegativity effect tending to raise the frequency. This vibration which is forbidden in the infrared spectrum of linear dimethylthallium ion, is probably responsible for the very weak absorptions at 1170 and 1178 for the salts dimethylthallium dithiophosphinate and dimethylthallium bromide respectively (in the solid state).

The bands due to metal-methyl rocking vibrations in the 700-800 region were found to have a rather characteristic contour (see Fig. B.). These were first identified in simple compounds like dimethylthallium bromide, trimethylgallium, dimethylgallium cyanide and dimethylgallium formate, where this region was not complicated by possible absorptions due to other structural units, for example, aromatic hydrogen out-of-plane motions in compounds containing the phenyl ring (Tables 18, 4, 2 and 26). Subsequently the assignments were extended to dimethylgallium acetate and $(d^3)$ acetate, and to other compounds.

Bands at 682 and 581, 588 and 538, and 528 and 484 in the infrared spectra of the dimers $(Me_2AlO_2PMe_2)_2$, $(Me_2GaO_2PMe_2)_2$ and $(Me_2InO_2PMe_2)_2$ were assigned to be due to metal-methyl as~~s~~ymmetric and symmetric stretching modes respectively (Tables 3, 5 and 6.). Thus the expected decrease in frequency with increasing mass on moving from aluminium to indium is observed. Further, these bands were fairly stable in position in the various compounds investigated, and therefore, the assignments appear to be reasonably certain. A band due to the as~~s~~ymmetric stretching mode of the dimethylthallium ion was found at 540. The corresponding symmetric stretching mode has been reported to cause a band at 498 in the Raman spectrum(86).

M - O Linkage (M = Al, Ga or In).

Infrared spectra of tris-acetylacetonates of aluminium, gallium and indium were examined by Djordjevic(87). Bands at 496, 446 and 434 were assigned to Al-O, Ga-O and In-O stretching modes respectively.

A strong band at 517 in the infrared spectra of the dimer $(Me_2AlOSPPh_2)_2$ and a doublet (523 and 509) in the same region for the analogous gallium dimer were assigned to be due to phosphorus-phenyl skeletol vibrations on the basis of vibrational analyses of diphenylphosphine and triphenylphosphine(92). Therefore, the metal-sensitive bands at 454 and 403 in the aluminium compound, and at 426 and 389 in the gallium compound are considered to be due to Al-O or Ga-O stretching modes. The dimers evidently contain two identical metal-oxygen bonds, therefore two bands are observed in each case due to symmetric and as~~s~~ymmetric stretching vibrations. Similarly the metal-sensitive lower frequency bands at 355 and 333, and 300 and 274 in the aluminium and gallium compounds respectively are due to metal-sulphur stretching modes (Tables 9 and 10).

In the dimers $(Me_2GaO_2PMe_2)_2$ and $(Me_2InO_2PMe_2)_2$ the metal-oxygen stretching modes were observed at 483 and 439, and 466 and 438 respectively (Tables 5 and 6). Thus for similar compounds In-O stretching modes absorb at slightly lower frequencies than Ga-O stretching modes. In this respect, the observation is similar to that reported for the tris-acetylacetonates of these metals. For the dimer $(Me_2GaO_2AsMe_2)_2$, the $GaO_2$ stretching modes absorbed at 433 and 408, slightly lower than the analogous phosphorus compound (Table 19).

In the carboxylate series, single sharp bands were observed due to this vibration at 513, 526 and 382 in the infrared spectra of the dimers $(Me_2GaO_2CMe)_2$, $(Me_2GaO_2CCD_3)_2$ and $(Me_2GaO_2CH)_2$ respectively. Thus, it was found that in the various compounds investigated with gallium-oxygen bonds, the bands due to $GaO_2$ stretching modes were in the range 380-525.

M-S Linkage (M = Al, Ga or In).

No information was available on bands due to metal-sulphur vibrational modes, which would be expected to be in the 250-400 region. Bands considered due to metal-sulphur vibrations in the monomers $Me_2AlS_2PMe_2$, $Me_2GaS_2PMe_2$ and $Me_2InS_2PMe_2$ were at 348, 314 and 313 respectively (Tables 12, 14 and 15). Thus Al-S vibrations absorbed at higher frequencies than Ga-S and In-S modes, which were similar. Further, in the monomer $Al[S_2PMe_2]_3$ where the co-ordination number of aluminium presumably is six, the aluminium-sulphur vibrational frequency dropped to 328. In the dimers $(Me_2AlOSPPh_2)_2$ and $(Me_2GaOSPPh_2)_2$, bands 355 and 333, and 300 and 274 were assigned to metal-sulphur stretching modes.

S-O Linkage.

Infrared spectra of benzene sulphinic acids, esters and salts have been measured by Detoni and Hadzi(88). Bands at 1090, 1126-36 and 1020 are due to S = O stretching or $SO_2$ $(\text{stretch})_{as}$ in the compounds benzene sulphinic acid, methylbenzene sulphinate and potassium benzene sulphinate respectively. Similarly, bands at 860, 960 and 980 respectively in these compounds must be due to

S-O stretching or $SO_2$ symmetrical stretching modes. The positions of these bands correspond well to those of Raman bands, wherever there has been duplication of the work of Houlton and Tarter(89). The assignments given in Tables 21-23 are based on the above investigations.

### C-O Linkage.

The assignments for $CO_2$ stretching modes were made by comparing the spectra of different compounds examined with this structural unit, and also taking into consideration the published data on the spectra of esters,(90) and acetate ions (these will be described later in connection with the structures of dimethylgallium acetate and related compounds).

### P-S Linkage.

A strong band at 654 in the infrared spectrum of the monomer $MeAl(S_2PPh_2)_2$ was assigned to the P = S stretching mode (compare 656 for $Ph_2PS_2H$).

Strong bands at 588 and 496, and 606 and 505 in the infrared spectra of dimethylthallium dimethyldithiophosphinate and caesium dimethyldithiophosphinate were assigned to $PS_2$ as~~s~~ymmetrical and symmetrical stretching modes, because in these simple molecules absorption in this region due to any other vibrational mode was unlikely (Tables 16 and 17). Bands at 233 and 220 in the thallium and caesium compounds respectively were assigned to $PS_2$ bending motions.

For many other compounds investigated with phosphorus-sulphur bonds, the frequencies for $PS_2$ as~~s~~ymmetric and symmetric vibrations were similar to those quoted above.

### Miscellaneous Linkages.

The assignments for different structural features of the dimer $(Me_2GaO_2AsMe_2)_2$ involving arsenic, are described later.

The assignments of P - Ph skeletal vibrations are based on published evidence(92) (compare 420 and 520 in $Ph_3P$ and $Ph_2PH$ respectively). Sulphur-phenyl skeletal vibrations were assigned by analogy with the phosphorus compounds.

## Table 3.

Infrared spectrum in carbon disulphide (below 2000cm.$^{-1}$)

| $(Me_2AlO_2PMe_2)_2$ | Assignments |
|---|---|
| 1428 (s,sh) | $P\text{-}CH_3$ $(d)_{as}$ |
| 1316 (s)<br>1307 (s) | $P\text{-}CH_3$ $(d)_{sym}$ |
| 1192 (vs) | $Al\text{-}CH_3$ $(d)_{sym}$ |
| 1192 (vs) ?<br>1091 (vs) | $PO_2$ (stretch) |
| 935 (w)<br>878 (s) | P-Me (rock) |
| 757 (m)<br>728 (m) | $PMe_2$ (stretch) |
| 682 (vs) | $AlMe_2$ $(\text{stretch})_{as}$ |
| 581 (m) | $AlMe_2$ $(\text{stretch})_{sym}$ |

## Table 4.

Infrared spectrum as vapour (pressure 15 mm.).

| Trimethylgallium | Assignments |
|---|---|
| 1408 (vw, broad) | $Ga\text{-}CH_3$ $(d)_{as}$ |
| 1212 (s)<br>1205 (s)<br>1198 (s) | $Ga\text{-}CH_3$ $(d)_{sym}$ |
| 769 (vs)<br>735 (s)<br>727 (s) | Ga-Me (rock) |
| 587 (vs,sh)<br>583 (vs)<br>570 (vs) | $GaMe_3$ (stretch) |

Table 5.

Infrared spectrum in carbon disulphide and benzene.

| $(Me_2GaO_2PMe_2)_2$ | Assignments |
|---|---|
| 1300 (m)<br>1294 (m) | $P-CH_3$ $(d)_{sym}$ |
| 1200 (m) | $Ga-CH_3$ $(d)_{sym}$ |
| 1164 (vs)<br>1062 (vs) | $PO_2$ (stretch) |
| 1112 (w) | |
| 923 (vw)<br>870 (vs) | P-Me (rock) |
| 747 (m)<br>733 (m) | $PMe_2$ (stretch) |
| 588 (m) | $GaMe_2$ $(stretch)_{as}$ |
| 538 (m) | $GaMe_2$ $(stretch)_{sym}$ |
| 483 (m)<br>439 (m) | $GaO_2$ (stretch) |
| 299 (w)<br>283 (w) | $PMe_2$ (d) |

## Table 6.

Infrared spectrum in carbon disulphide and benzene.

| $(Me_2InO_2PMe_2)_2$ | Assignments |
|---|---|
| 1418 (s,sh) | P-$CH_3$ $(d)_{as}$ |
| 1299 (m)<br>1292 (m) | P-$CH_3$ $(d)_{sym}$ |
| 1171 (vs)<br>1057 (vs) | $PO_2$ (stretch) |
| 1151 (s) | In-$CH_3$ $(d)_{sym}$ |
| 1121 (w) | |
| 920 (vw)<br>866 (s) | PMe (rock) |
| 742 (m)<br>713 (m) | $PMe_2$ (stretch) |
| 528 (m) | $InMe_2$ $(stretch)_{as}$ |
| 484 (m) | $InMe_2$ $(stretch)_{sym}$ |
| 466 (ms)<br>438 (s) | $InO_2$ (stretch) |
| 278 (w) | $PMe_2$ (d) |

## Table 7.

Infrared spectrum in carbon disulphide

| $(Me_2AlO_2PPh_2)_2$ | Assignments |
|---|---|
| 1431 (vs) | P-Phenyl(91) |
| 1199 (vs)<br>1188 (s,sh) | Al-$CH_3$ $(d)_{sym}$ |
| 1199 (vs) ?<br>1072 (vs) | $PO_2$ (stretch) |
| 1134 (vs)<br>1027 (m)<br>998 (m) | $C_{ar}$-H (i.p.d.) |
| 922 (vw) | |
| 785 (vw) | Al-Me (rock) |
| 752 (s)<br>730 (s)<br>691 (vs) | $C_{ar}$-H (o.p.d.) |
| 683 (vs) | $AlMe_2$ $(stretch)_{as}$ |
| 620 (vw) | |
| 604 (w)<br>590 (w) | $AlMe_2$ $(stretch)_{sym}$ |
| 548 (m) | P-Phenyl |

## Table 8.

Infrared spectrum in carbon disulphide.

| $(Me_2GaO_2PPh_2)_2$ | Assignments |
|---|---|
| 1431 (vs) | P-Phenyl |
| 1203 (ms) | $Ga-CH_3$ (d)$_{sym}$ |
| 1180 (s) | $PO_2$ (stretch) |
| 1067 (m, sh) | |
| 1048 (s) | |
| 1130 (vs) | $C_{ar}-H$ (i.p.d.) |
| 1024 (ms) | |
| 998 (m) | |
| 751 (ms) | $C_{ar}-H$ (o.p.d.) |
| 727 (s) | |
| 700 (m, sh) | |
| 692 (s) | |
| 594 (m) | $GaMe_2$ (stretch)$_{as}$ |
| 564 (ms) | P-Phenyl |
| 534 (m) | $GaMe_2$ (stretch)$_{sym}$ |

## Table 9,

Infrared spectrum in carbon disulphide and benzene (principal bands only).

| $(Me_2AlOSPPh_2)_2$ | Assignments |
|---|---|
| 1439 (vs) | P-Phenyl |
| 1200 (m)<br>1189 (m,sh) | $Al-CH_3$ $(d)_{sym}$ |
| 1117 (s)<br>1026 (ms)<br>999 (m) | $C_{ar}-H$ (i.p.d.) |
| 1064 (ms)<br>1047 (ms) | PO (stretch) |
| 800 (m)<br>750 (s)<br>746 (s,sh) | Al-Me (rock) |
| 727 (vs)<br>715 (vs)<br>691 (vs) | $C_{ar}-H$ (o.p.d.) |
| 678 (s,sh) | $AlMe_2$ $(stretch)_{as}$ |
| 656 (m,sh) | |
| 629 (ms)<br>612 (ms) | PS (stretch) |
| 568 (m)<br>548 (m) | $AlMe_2$ $(stretch)_{sym}$ |
| 517 (vs) | P-Phenyl |
| 454 (m)<br>403 (m) | AlO (stretch) |
| 355 (s)<br>333 (ms,sh) | AlS (stretch) |

## Table 10.

Infrared spectrum in carbon disulphide and benzene (principal bands only).

| $(Me_2GaOSPPh_2)_2$ | Assignments |
|---|---|
| 1431 (vs) | P-Phenyl |
| 1199 (m) | Ga-$CH_3$ $(d)_{sym}$ |
| 1117 (vs)<br>1027 (ms)<br>999 (m) | $C_{ar}$-H (i.p.d.) |
| 1089 (s)<br>1066 (s) | PO (stretch) |
| 751 (s)<br>745 (s,sh) | Ga-$CH_3$ (rock) |
| 720 (vs)<br>707 (vs)<br>692 (vs) | $C_{ar}$-H (o.p.d.) |
| 676 (m) | |
| 625 (s) | PS (stretch) |
| 604 (vs) | $GaMe_2$ $(stretch)_{as}$ |
| 533 (s,sh) | $GaMe_2$ $(stretch)_{sym}$ |
| 523 (vs)<br>509 (ms,sh) | P-Phenyl |
| 426 (m)<br>389 (m) | GaO (stretch) |
| 300 (vs)<br>274 (w,sh) | GaS (stretch) |

Table 11.

Infrared spectrum in carbon disulphide and benzene (principal bands only).

| $MeAl(S_2PPh_2)_2$ | Assignments |
|---|---|
| 1437 (vs) | P-Phenyl |
| 1307 (w) | |
| 1182 (m) | $Al-CH_3$ $(d)_{sym}$ |
| 1105 (s)<br>1101 (s)<br>1028 (m)<br>1000 (m) | $C_{ar}-H$ (i.p.d.) |
| 813 (w)<br>785 (w) | Al-Me (rock) |
| 744 (s)<br>709 (vs)<br>689 (vs) | $C_{ar}-H$ (o.p.d.) |
| 673 (s) | Al-Me (stretch) |
| 654 (s) | P = S (stretch) |
| 633 (m,sh) | |
| 612 (m) | |
| 566 (vs) | $PS_2$ $(stretch)_{as}$ |
| 529 (w) | P-Phenyl |
| 485 (s) | $PS_2$ $(stretch)_{sym}$ |
| 391 (s)<br>373 (m,sh) | $AlS_2$ (stretch) |
| 329 (m)<br>312 (m,sh) | Al-S (stretch) |
| 230 (m) | |

## Table 12.

Infrared spectrum in carbon disulphide and benzene.

| $Me_2AlS_2PMe_2$ | Assignments |
|---|---|
| 1414 (s) | P-$CH_3$ (d)$_{as}$ |
| 1403 (s) | |
| 1395 (ms) | |
| 1296 (m) | P-$CH_3$ (d)$_{sym}$ |
| 1287 (s) | |
| 1186 (s) | Al-$CH_3$ (d)$_{sym}$ |
| 1174 (w,sh) | |
| 991 (w) | P-Me (rock) |
| 948 (vs) | |
| 912 (vs) | |
| 853 (s) | |
| 762 (s) | Al-Me (rock) |
| 740 (s) | $PMe_2$ (stretch) |
| 729 (s) | |
| 687 (vs) | $AlMe_2$ (stretch)$_{as}$ |
| 646 (ms,sh) | |
| 599 (ms) | $PS_2$ (stretch)$_{as}$ |
| 585 (ms) | |
| 579 (ms) | $AlMe_2$ (stretch)$_{sym}$ |
| 505 (s) | $PS_2$ (stretch)$_{sym}$ |
| 493 (m) | |
| 394 (w) | |
| 348 (vs) | $AlS_2$ (stretch)$_{as}$ |
| 310 (m) | $AlS_2$ (stretch)$_{sym}$? |
| 292 (vw) | |
| 271 (m) | $PMe_2$ (d) |

## Table 13.

Infrared spectrum for Nujol mull and benzene solution.

| $Al(S_2PMe_2)_3$ | Assignments |
|---|---|
| 1290 (vw,sh) | P-$CH_3$ $(d)_{sym}$ |
| 1280 (m) | |
| 1160 (vw) | 847 + 308 = 1155? |
| 956 (s) | P-Me (rock) |
| 944 (s) | |
| 921 (s) | |
| 909 (s) | |
| 858 (w) | |
| 847 (m) | |
| 741 (m,sh) | $PMe_2$ (stretch) |
| 729 (s) | |
| 601 (s) | $PS_2$ $(stretch)_{as}$ |
| 587 (ms) | |
| 501 (m) | $PS_2$ $(stretch)_{sym}$ |
| 328 (vs) | $AlS_2$ (stretch) |
| 308 (s,sh) | |
| 272 (m) | $PMe_2$ (d) |
| 264 (m) | |

## Table 14.

Infrared spectrum in carbon disulphide and benzene.

| $Me_2GaS_2PMe_2$ | Assignments |
|---|---|
| 1418 (s,sh)<br>1406 (s,sh)<br>1397 (ms) | P-$CH_3$ $(d)_{as}$ |
| 1292 (m)<br>1282 (ms) | P-$CH_3$ $(d)_{sym}$ |
| 1190 (ms) | Ga-$CH_3$$(d)_{sym}$ |
| 944 (vs)<br>908 (vs)<br>850 (s) | P-Me (rock) |
| 761 (ms) | Ga-Me (rock) |
| 735 (s,sh)<br>725 (vs) | $PMe_2$ (stretch) |
| 590 (vs) | $GaMe_2$ $(stretch)_{as}$ |
| 590 (vs) ? | $PS_2$ $(stretch)_{as}$ |
| 537 (ms) | $GaMe_2$ $(stretch)_{sym}$ |
| 503 (s) | $PS_2$ $(stretch)_{sym}$ |
| 314 (vs) | $GaS_2$ $(stretch)_{as}$ |
| 277 (m,sh)<br>267 (s) | $PMe_2$ (d) |

## Table 15.

Infrared spectrum in carbon disulphide and benzene

| $Me_2InS_2PMe_2$ | Assignments |
|---|---|
| 1416 (ms,sh)<br>1406 (m,sh)<br>1397 (m) | $P-CH_3$ $(d)_{as}$ |
| 1294 (w)<br>1284 (m) | $P-CH_3$ $(d)_{sym}$ |
| 1147 (vw) | $In-CH_3$ $(d)_{sym}$ |
| 948 (s)<br>911 (s)<br>898 (w,sh)<br>852 (m) | P-Me (rock) |
| 738 (m)<br>724 (ms) | $PMe_2$ (stretch) |
| 596 (s) | $PS_2$ $(stretch)_{as}$ |
| 508 (w) | $InMe_2$ $(stretch)_{as}$ |
| 496 (ms) | $PS_2$ $(stretch)_{sym}$ |
| 323 (ms,sh)<br>313 (s) | $InS_2$ (stretch) |
| 271 (m)<br>256 (m) | $PMe_2$ (d) |

Table 16.

Infrared spectrum in potassium bromide disc and for Nujol mull.

| $Me_2TlS_2PMe_2$ | Assignments |
|---|---|
| 1404 (m) | $P\text{-}CH_3$ $(d)_{as}$ |
| 1290 (vw)<br>1280 (ms) | $P\text{-}CH_3$ $(d)_{sym}$ |
| 1170 (vw) | $Tl\text{-}CH_3$ $(d)_{sym}$ |
| 1087 (vw) | |
| 943 (vs)<br>909 (vs)<br>847 (m) | P-Me (rock) |
| 797 (s) | Tl-Me (rock) |
| 733 (m)<br>710 (s) | $PMe_2$ (stretch) |
| 588 (vs) | $PS_2$ $(\text{stretch})_{as}$ |
| 540 (m) | Me-Tl-Me $(\text{stretch})_{as}$ |
| 496 (ms) | $PS_2$ $(\text{stretch})_{sym}$ |
| 295 (m)<br>287 (w,sh) | $PMe_2$ (d) |
| 233 (ms) | $PS_2$ (d) |

## Table 17.

Infrared spectrum in potassium bromide disc and for Nujol mull.

| $Cs(S_2PMe_2)$ | Assignments |
|---|---|
| 1418 (m)<br>1404 (ms) | $P-CH_3$ $(d)_{as}$ |
| 1290 (m)<br>1279 (s) | $P-CH_3$ $(d)_{sym}$ |
| 1105 (vw) | |
| 952 (s)<br>915 (vs)<br>847 (s) | P-Me (rock) |
| 734 (s)<br>715 (vs) | $PMe_2$ (stretch) |
| 606 (vs) | $PS_2$ $(stretch)_{as}$ |
| 505 (vs) | $PS_2$ $(stretch)_{sym}$ |
| 282 (s) | $PMe_2$ (d) |
| 220 (s) | $PS_2$ (d) |

## Table 18.

Infrared spectrum in potassium bromide disc.

| $Me_2TlBr$ | Assignments |
|---|---|
| 1178 (vw) | $Tl-CH_3(d)_{sym}$ |
| 800 (vs) | Tl-Me (rock) |
| 541 (ms) | Me-Tl-Me $(stretch)_{as}$ |

## Table 19.

Infrared spectrum in carbon disulphide and benzene.

| $(Me_2GaO_2AsMe_2)_2$ | Assignments |
|---|---|
| 1267 (m)<br>1259 (w) | $As{-}CH_3$ (d)$_{sym}$ |
| 1194 (m) | $Ga{-}CH_3$ (d)$_{sym}$ |
| 897 (s)<br>865 (s) | $AsO_2$ (stretch) |
| 884 (vs)<br>818 (m) | As-Me (rock) |
| 738 (ms,sh)<br>725 (ms) | Ga-Me (rock) |
| 675 (vs) | $AsMe_2$ (stretch)$_{as}$ |
| 642 (m) | $AsMe_2$ (stretch)$_{sym}$ |
| 580 (m) | $GaMe_2$ (stretch)$_{as}$ |
| 535 (m) | $GaMe_2$ (stretch)$_{sym}$ |
| 433 (s)<br>408 (s) | $GaO_2$ (stretch) |
| 283 (ms)<br>269 (m) | $AsMe_2$ (d) |

## Table 20.

Infrared spectrum done as liquid.

| $Me_2AsI$ | Assignments |
|---|---|
| 1805 (vw) | 1249 + 565 = 1814 ? |
| 1550 (vw) | |
| 1414 (vs)<br>1404 (vs)<br>1393 (vs) | $As-CH_3$ $(d)_{as}$ |
| 1249 (vs) | $As-CH_3$ $(d)_{sym}$ |
| 1130 (vw) | 897 + 227 = 1124 ? |
| 897 (vs)<br>828 (vs) | As-Me (rock) |
| 794 (vw) | 565 + 227 = 792 ? |
| 748 (vw) | |
| 575-565 (vs, broad band) | $AsMe_2$ (stretch) |
| 227 (vs) | As-I (stretch) |

### Table 21.

Infrared spectrum in potassium bromide disc (principal bands only).

| $Ba(O_2SPh)_2$ | Assignments |
|---|---|
| 1443 (ms) | S-Phenyl |
| 1088 (m) | $C_{ar}$-H (i.p.d.) |
| 1020 (m,sh) | |
| 971 (s) | |
| 986 (vs) | $SO_2$ (stretch) |
| 960 (vs) | |
| 751 (m,sh) | $C_{ar}$-H (o.p.d.) |
| 744 (s) | |
| 704 (ms) | |
| 689 (s) | |
| 581 (s) | S-Phenyl |
| 505 (ms) | $SO_2$ (d) |
| 487 (m) | |

### Table 22.

Infrared spectrum in carbon disulphide (principal bands only).

| $(Me_2AlO_2SPh)_2$ | Assignments |
|---|---|
| 1445 (s,sh) | S-Phenyl |
| 1192 (ms) | Al-$CH_3$ $(d)_{sym}$ |
| 1089 (m) | $C_{ar}$-H (i.p.d.) |
| 1027-1005 (s, broad band) | $SO_2$ (stretch) |
| 980-970 (s, broad band) | |
| 753 (s) | $C_{ar}$-H (o.p.d.) |
| 704 (vs) | |
| 688 (vs) | |
| 620 (m) | $AlMe_2$ $(stretch)_{sym}$? |
| 612 (w) | |
| 588 (w) | S-Phenyl |

## Table 23.

Infrared spectrum in carbon disulphide and benzene (principal bands only).

| $(Me_2GaO_2SPh)_2$ | Assignments |
|---|---|
| 1445 (s) | S-Phenyl |
| 1203 (s) | $Ga-CH_3$ (d) $_{sym}$ |
| 1124 (m) | $C_{ar}-H$ (i.p.d.) |
| 1082 (m) | |
| 1048 (m) | |
| 1005 (vs) | $SO_2$ (stretch) |
| 941 (s) | |
| 735 (s) | $C_{ar}-H$ (o.p.d.)[a] |
| 697 (s) | |
| 683 (s) | |
| 584 (m) | $GaMe_2$ (stretch)$_{as}$ |
| 539 (w) | $GaMe_2$ (stretch)$_{sym}$ |
| 459 (s) | $GaO_2$ (stretch) |
| 420 (s) | |
| 352 (ms) | |
| 329 (m,sh) | |
| 275 (w) | |

[a] These bands were not sharp, unlike all other compounds

## Table 24.

Infrared spectrum measured as Nujol mull and $C_2Cl_4$ solution.

| $(Me_2GaO_2CMe)_2$ | Assignments |
|---|---|
| 1754 (w) | 1203 + 549 = 1752 ? |
| 1534 (vs)<br>1471 (vs) | $CO_2$ (stretch) |
| 1408 (vs) | $C-CH_3$ $(d)_{sym}$ |
| 1203 (s) | $Ga-CH_3$ $(d)_{sym}$ |
| 1053 (m)<br>1030 (ms) | |
| 965 (m) | |
| 761 (ms,sh)<br>740 (s)<br>695 (vs) | Ga-Me (rock) |
| 612 (m) | |
| 601 (s) | $GaMe_2$ $(stretch)_{as}$ |
| 549 (ms) | $GaMe_2$ $(stretch)_{sym}$ |
| 513 (m) | $GaO_2$ (stretch) |
| 329 (m) | |

Table 25.

Infrared spectrum measured as Nujol mull and $C_2Cl_4$ solution.

| $(Me_2GaO_2CCD_3)_2$ | Assignments |
|---|---|
| 1754 (w) | 1203 + 548 = 1751 ? |
| 1515 (vs)<br>1475 (vs) | $CO_2$ (stretch) |
| 1447 (s) | |
| 1203 (s) | $Ga-CH_3$ $(d)_{sym}$ |
| 1092 (w) | |
| 1055 (m)<br>1029 (ms) | |
| 929 (ms)<br>918 (ms) | |
| 841 (s) | |
| 758 (s,sh)<br>735 (vs)<br>696 (ms) | Ga-Me (rock) |
| 661 (vs) | |
| 600 (vs) | $GaMe_2$ $(stretch)_{as}$ |
| 548 (ms) | $GaMe_2$ $(stretch)_{sym}$ |
| 526 (m) | $GaO_2$ (stretch) |
| 471 (w) | |
| 314 (m) | |

## Table 26.

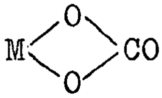
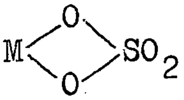
Infrared spectra for Nujol mull and $C_2Cl_4$ solution.

| $(Me_2GaO_2CH)_2$ | Assignments |
|---|---|
| 1616 (vs) | |
| 1587 (vs) | $CO_2$ (stretch) |
| 1555 (vs) | |
| 1377 (vs) | |
| 1353 (vs) | |
| 1206 (ms) | $Ga-CH_3$ $(d)_{sym}$ |
| 1202 (ms) | |
| 1192 (ms) | |
| 823 (s) | |
| 738 (vs) | Ga-Me (rock) |
| 720 (s,sh) | |
| 699 (ms,sh) | |
| 606 (s) | $GaMe_2$ $(stretch)_{as}$ |
| 549 (m) | $GaMe_2$ $(stretch)_{sym}$ |
| 382 (m) | $GaO_2$ (stretch) |

## Phosphinates of Group III Elements.

A ligand with two potentially co-ordinating groups, for example, a diamine $NH_2(CH_2)_nNH_2$ or an amino acid $NH_2(CH_2)_nCOOH$, can function as a chelate group if it is geometrically possible to form a ring of low strain, as in the formation of carbon rings in organic chemistry. As a result of steric strain the energy of bond formation is low for small rings but increases as increasing size of the ring relieves strain. However, the stabilising influence of chelation, which appears in the entropy term, is greatest for small rings. These two terms, working in opposite directions, produce a maximum stability in a five-membered saturated ring. An interesting illustration of this is given by 1,2,3-triaminopropanetetrachloroplatinum (IV). Both five- and six-membered rings are possible for the triamine, which behaves as a bidentate ligand. Mann(93) resolved the complex into optical isomerides, and thus demonstrated the dissymmetric five-membered ring structure.

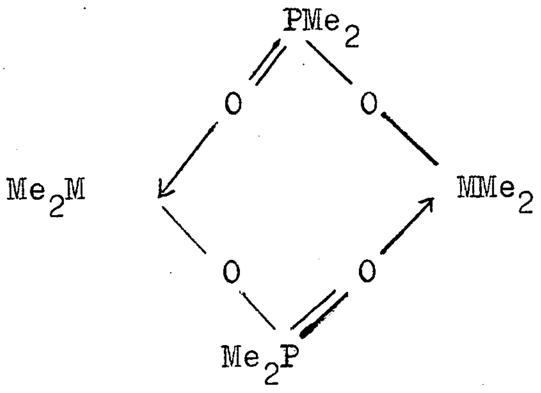
It is of interest that for aromatic ligands or chelates with conjugated linkages, the six-membered rings are more common. This may be due to wider bond angles in these ligands. Therefore, the formation of monomers such as dimethylgallium acetylacetonate(39) and the indium(41) analogue from reactions between acetylacetone and the trimethyl-metal is understandable.

However, the formation of larger or smaller rings is not completely excluded. Compounds have been described containing the succinato(94), sulphonyldiacetic(95) and $NH_2(CH_2)_6NH_2$ ligands(96), in which there are seven-, eight- and nine-membered rings respectively. Carbonato, , and sulphato,  complexes are among the more common four-membered chelates, formed with elements of octahedral stereochemistry. There is hardly any evidence that oxy-acid ligands can form four-membered rings with elements of tetrahedral stereochemistry. This may be due to greater steric strain involved for the necessary deformation of bond angles when the metal is in a tetrahedral rather than an octahedral environment.

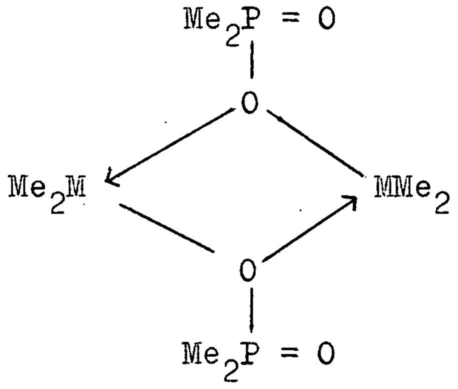
The substitution-addition reactions of excess beryllium(II) and chromium(III) acetylacetonates with diphenylphosphinic acid were investigated in a study of new preparative routes for the synthesis of co-ordination polymers.(97-99) These reactions were carried out in melts from which the dimers $[Be(C_5H_7O_2)(Ph_2PO_2)]_2$ and $[Cr(C_5H_7O_2)_2(Ph_2PO_2)]_2$ were obtained. Some polymers were isolated, for example, $[Be(O_2PPh_2)_2]_x$ when the acid was in excess. The molecular weights were measured by different methods (e.g. ebullioscopically in benzene). For these materials, eight-membered ring structures similar to that mentioned for dimethylgallium acetate dimer (see introduction section, page 31) were postulated but not established because the alternative four-membered ring structures were not taken into consideration. The polymeric dimethyl-, and diphenyl-phosphinates of cobalt have also been described(100).

No information was available on the phosphinates of group III metals. Dimethylaluminium dimethylphosphinate and its analogous gallium and indium compounds were obtained from reactions between a suspension of dimethylphosphinic acid in benzene and a solution of the trimethyl-metal in the same solvent, under an atmosphere of nitrogen. Addition of the acid to the trimethyl-metal caused a lively reaction with gas evolution, and the products of the reaction remained dissolved in the solvent. The solvent was removed under reduced pressure, leaving a white solid. Pure dimethyl-metal phosphinates were obtained from this residue by vacuum sublimation as colourless crystals. The melting points increased on moving from aluminium to indium (43°, 54° and 75-76°C respectively). These compounds were air-sensitive because it was not possible to obtain satisfactory infrared spectra on materials which had been exposed to air. The phosphinates were soluble in organic solvents ether, benzene, carbon disulphide and carbon tetrachloride.

The molecular weights were determined cryoscopically in benzene and the phosphinates were shown to be dimers. Structures III and IV are possible for these dimers in which the metals can attain four-co-ordination (M = Al, Ga or In).



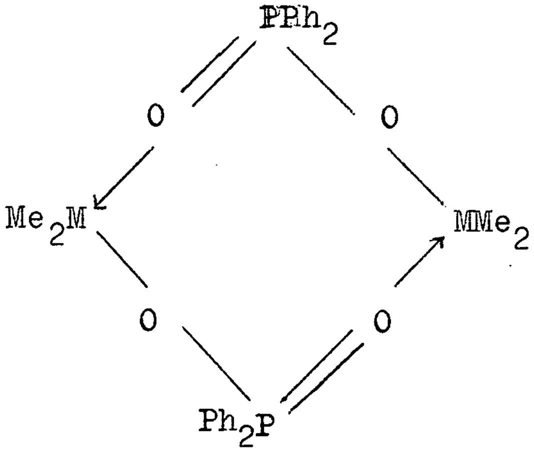
III



IV

For structure III the phosphorus-oxygen bonds are very similar. But for structure IV the phosphorus-oxygen bonds are different, and free P = O is retained, which does not participate in co-ordinate bond formation. Therefore, infrared spectroscopy can be used to choose between these structures. In the ester $Me_2PO_2Me$ where a distinction between two types of phosphorus-oxygen bonds is apparent, bands due to P = O and P - OMe stretching modes are observed at 1230 and 1042 $cm^{-1}$ respectively (Fig. A). These bands which are so wide apart in the ester move closer together in the salts where any distinction between two types of phosphorus-oxygen bonds disappear, and as~~s~~ymmetric and symmetric modes are observed (compare 1168 and 1068 $cm^{-1}$ in $NaO_2PMe_2$). For dimethylgallium dimethylphosphinate and analogous indium and aluminium compounds, bands considered due to phosphorus-oxygen stretching modes are observed at 1164 and 1062, 1171 and 1057, and 1091 and (probably) 1192 $cm^{-1}$ respectively. These bands disappeared in the infrared spectra of the corresponding dithiophosphinates. Therefore, structure III is considered to represent the dimethylphosphinates of aluminium, gallium and indium.

Dimethylaluminium diphenylphosphinate and the corresponding gallium compound were prepared from diphenylphosphinic acid and the trimethyl-metal. Removal of the solvent under reduced pressure left a white residue, from which the phosphinates were obtained by vacuum sublimation at about 160°C. These are less volatile and higher melting than the corresponding dimethylphosphinates. However, like the dimethylphosphinates they are soluble in many organic solvents. The molecular weights were determined cryoscopically in benzene and the compounds were found to be dimers. Bands due to phosphorus-oxygen vibrations were observed in the infrared spectra at 1180 and 1048, and 1072 and probably near 1199 $cm^{-1}$ for the gallium and aluminium compounds respectively. Therefore, structure V is considered to represent these compounds (M = Al or Ga).



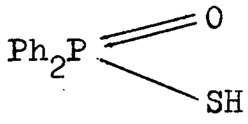
V

Finally it may be mentioned that the infrared spectra of trimethyl- and triphenyl-phosphine oxide and a number of their complexes with various transition metal cations have been described, in a study of the properties of these compounds.(101-106) It was found that complex-formation causes the phosphorus-oxygen stretching frequencies to shift about $50cm^{-1}$ to lower values. Since a simple kinematic effect would raise the frequency, an explanation in terms of a lowering of P-O bond order has been proposed.

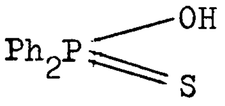
Thiophosphinates of Group III Metals.

No information was available on the thiophosphinates of group III metals. Dimethylaluminium thiophosphinate and the corresponding gallium compound were prepared from diphenylthiophosphinic acid and the trimethyl-metal. Removal of the solvent under reducedpressure left a white residue, from which the thiophosphinates were obtained by vacuum sublimation at 160-80°C. These are slightly less volatile and higher melting than the corresponding diphenylphosphinates. However, like the other phosphinates they are soluble in many organic solvents. The molecular weights were determined cryoscopically in benzene and the compounds shown to be dimers.

Diphenylthiophosphinic acid could have structures represented by IV or V. In the infrared spectrum of the acid

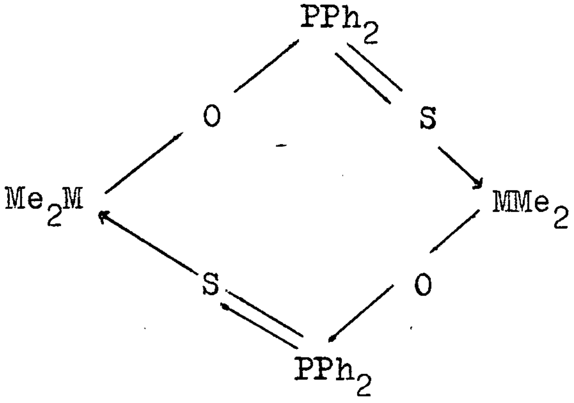


IV

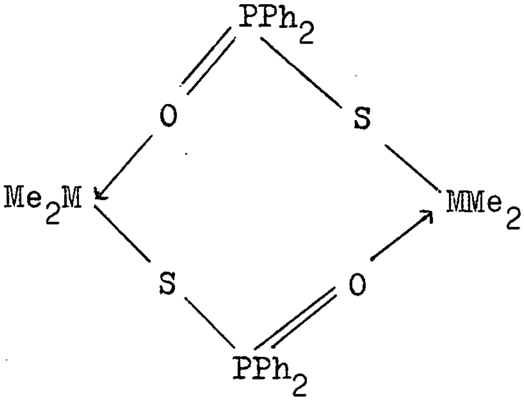


V

(pressed potassium bromide disc), strong bands attributable to P - OH and P = S vibrations were observed at 892 and 633 cm$^{-1}$ respectively. Therefore, the acid is best represented by structure V. The 1100 cm$^{-1}$ region where P = O vibrations required by structure IV may be expected to absorb, was masked by the presence of bands due to aromatic hydrogen in-plane-deformation modes though these are normally not so intense as P = O stretching bands. Hence, available data cannot with certainty decide between structures IV and V, but does fairly strongly indicate the latter. However, this problem is not very relevant to the question of the structures of the aluminium or gallium thiophosphinate dimers. Bands due to phosphorus-oxygen and phosphorus-sulphur vibrations were observed at 1064 and 1047, and 629 $cm^{-1}$ for the aluminium compound. Similar bands were observed at 1089 and 1066, and 625 $cm^{-1}$ for the gallium dimer. Thus, in the infrared spectra of these compounds, bands due to free P = O vibrations were not observed, and partial double bond character of P - S bonds was retained. However, there was a slight shift of phosphorus-sulphur stretching frequencies to lower values. Finally by analogy with the phosphinates a resonance structure may be expected (VIA and VIB; M = Al or Ga).



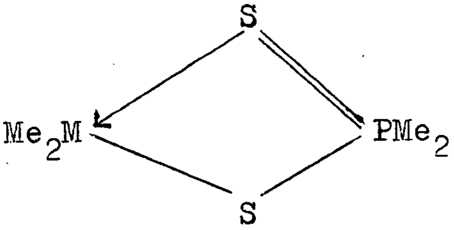
VIA



VIB

Dithiophosphinates of Group III Metals

Dimethylaluminium dimethyldithiophosphinate and the corresponding gallium and indium compounds were prepared by methods analogous to those used for the other dimethylmetal phosphinates described before. All these compounds were sufficiently volatile to be purified by vacuum sublimation as colourless crystals, and their melting points increase on moving from aluminium to indium (103-4, 153-4, and 184-5°C respectively). Further, each compound is higher melting than the corresponding dimethylphosphinate. The aluminium compound is very sensitive to air, and sometimes caught fire when touched with a drop of water (this was similar to the behaviour of dimethylaluminium cyanide tetramer and in contrast to dimethylaluminium dimethylphosphinate and other dimers). The compounds are soluble in many organic solvents. Molecular weights were determined cryoscopically in benzene and the dithiophosphinates were found to be monomers. Therefore, in contrast to phosphinate and thiophosphinate ligands, the dithiophosphinate group can function as a chelating ligand to metals of tetrahedral stereochemistry (VII; M = Al, Ga or In).

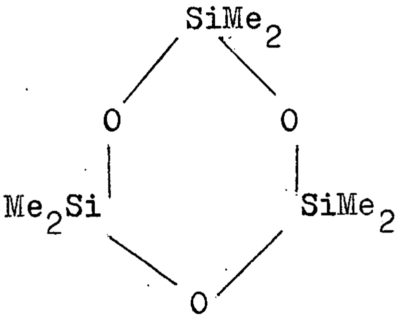


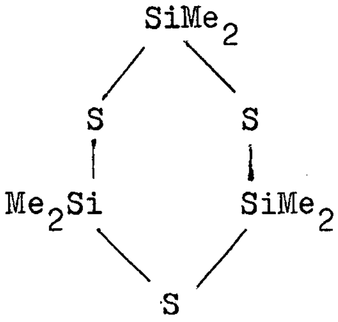
VII

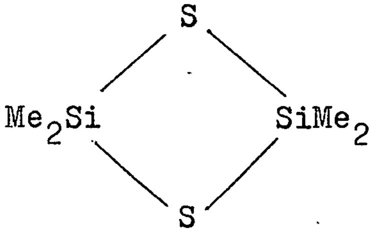
These monomers did not react with trimethylamine.

When oxygen is attached to saturated carbon or nitrogen, the bond angle at oxygen is within a few degrees of the tetrahedral angle in every case (except for small ring compounds, e.g. with carbonato or sulphato ligands which involve "bent" bonds) and is generally slightly smaller than the tetrahedral angle due to lone-pair repulsions being greater than bond-pair repulsions.(53) However, the attachment of oxygen to an aromatic ring (e.g. diphenyl ether) causes the lone-pair electrons partially to delocalise into the aromatic system, the O-C bonds acquire some double-bond character and the bond angle increases to greater values than the tetrahedral angle (compare 108° and 124° in $Et_2O$ and $Ph_2O$ respectively). There is no great tendency for the lone-pair electrons in S, Se and Te to delocalise into an aromatic system. Therefore, the bond angles in diarylsulphides and related compounds are smaller than the tetrahedral angle [compare 109°, 106° and 101° in $(p\text{-}CH_3C_6H_4)_2S$, $(p\text{-}CH_3C_6H_4)_2Se$ and $(p\text{-}CH_3C_6H_4)_2Te$ respectively].

Attachment of oxygen or nitrogen to atoms with incomplete valency shells causes similar delocalisation of lone-pair electrons into the valency shell of these atoms and corresponding increase in the bond angle, as was described for aromatic systems. Thus the Si-O-Si angle is generally found in the range 130-160° in various silicon compounds [e.g. 130° in $(Cl_3Si)_2O$ and 155° in $H_3SiOSiH_3$].(107) Further, the compound $N(SiH_3)_3$ is planar with 120° bond angle, and it has been suggested that these large bond angles are due to $p_\pi - d_\pi$ bonding between nitrogen or oxygen and silicon. When oxygen is replaced by S, Se or Te, it is found that the X-S-X, X-Se-X and X-Te-X bond angles (X is an element from second or higher periods) are consistently smaller than the tetrahedral angle and sometimes approach 90° as in $H_2S$. The possibility of a smaller valency angle at S leads, in several cases, to the structure of a sulphur compound differing from the oxygen analogue. Thus although both the trimeric hexamethylcyclotrisiloxane (A) and hexamethylcyclotrisilthiane (B) are known, of the corresponding dimeric compounds only the sulphur compound, tetramethylcyclodisilthian (C) is known. The structure of this compound requires the Si-S-Si bond angle


A


B

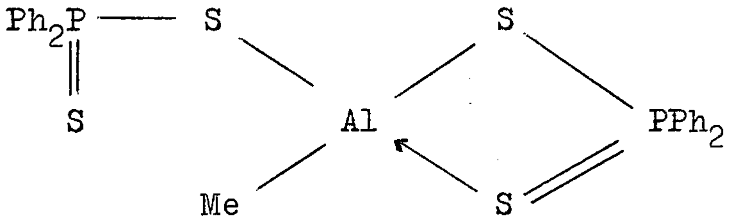

C

to be 90° or less; in fact it is 75° (53). It is evident that oxygen, with its complete valency shell and with its tendency to delocalise its lone-pair electrons into the Si valency shell, does not readily achieve such a small bond angle. Smaller angles are more easily attained by elements of second or higher periods.

The P-O-P bond angles are considerably greater than the tetrahedral angle due to partial double-bond character of P-O-P bonds resulting from delocalisation of oxygen lone-pair electrons (compare 129°, 124° and 132° in $P_4O_6$, $P_4O_{10}$ and the tetrametaphosphate ion $P_4O_{12}^{-4}$ respectively). However, the P-S-P bond-angle in $P_4S_{10}$ is 109° and the compound $P_4S_6$ does not exist. Furthermore, in the compounds $P_4S_3$, $P_4S_5$ and $P_4S_7$, which have no oxygen analogues, the P-S-P bond-angles are 102°, 107° and 106° respectively. Therefore, the ability of thedithiophosphinate group to function as a chelating ligand is understandable.

The greater reactivity of dimethylaluminium dimethyldithiophosphinate (compare the corresponding phosphinates and other dimers which did not catch fire in air when touched with a drop of water), inspired an attempt to prepare the tris-compound. This was obtained from a reaction between trimethylaluminium and three equivalents of the acid in benzene at room temperature. Removal of the solvent under reduced pressure left a white solid, from which pure aluminium tris(dimethyldithiophosphinate) was collected by vacuum sublimation at 190°C, in about 50% yield. No methane was detected when a sample of the compound was hydrolysed in the vacuum line with 2N-sulphuric acid. The compound was reasonably soluble in benzene and was shown to be a monomer in this solvent (exposure to traces of air makes the material at least partly insoluble in benzene). However, the substance was only sparingly soluble in carbon disulphide and the infrared spectrum was recorded for Nujol mull. The potassium bromide disc method (which is usually very satisfactory for air-stable materials) did not give good results and this is a further indication to the air-sensitive character of this compound. No bands attributable to P = S vibrations were observed in the infrared spectrum of the compound. The doublet in the 600 $cm^{-1}$ region (601 and 587 $cm^{-1}$) was considered due to $PS_2$ asymmetrical stretching modes by analogy with a similar doublet (599 and 585 $cm^{-1}$) in $Me_2AlS_2PMe_2$ monomer, where there is no P = S structural unit. It should be added that bands due to $PS_2$ symmetrical stretching vibrations were identified at lower frequencies for both compounds (501, and 505 and 493 $cm^{-1}$ for the tris- and mono-dithiophosphinates respectively). Finally, bands due to $PS_2$ as~~s~~ymmetrical and symmetrical stretching modes were observed at 606 and 505 $cm^{-1}$ in caesium dimethyldithiophosphinate. Therefore, it appears that the aluminium atom in the monomeric tris- compound is in an octahedral environment, and each of the dithiophosphinate ligand acts as a chelating group.

The involatile compound $MeAl(S_2PPh_2)_2$ was obtained from trimethylaluminium and the corresponding acid. It was shown to be a monomer in benzene. A strong band attributable to P = S vibration was observed at 654 $cm^{-1}$ (compare 656 $cm^{-1}$ for P = S stretching mode in $Ph_2PS_2H$). Further, bands due to $PS_2$ asymmetrical and symmetrical stretching modes were observed at 566 and 485 $cm^{-1}$ respectively. Therefore, structure VII is suggested for the monomer.



VII

The compound was soluble in many organic solvents.

Dimethylthallium dimethyldithiophosphinate was obtained from the reaction between dimethylthallium cyanide and dimethyldithiophosphinic acid in a mixture of water and alcohol. It was purified by recrystallisation from hot ethanol as a white glistening solid. The compound was non-volatile, insoluble in benzene and decomposed at 185°C. It was slightly soluble in water, and in this medium the conductance measurements were carried out at 25°C. The results are given in the experimental section and the plot of equivalent conductance against the square-root of concentration in moles/litre is shown in graph 4 .

For a 1:1 electrolyte the Debye-Huckel-Onsager conductance equation, assuming complete dissociation, may be written in the form

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{C}$$

where A and B are 60.20 and 0.229 respectively for water at 25°C, and the concentration given in moles/litre. Therefore from graph 4, an expression can be written, as given below:

$$55.0 = \Lambda_0 - (60.20 + 0.229\Lambda_0)\ (0.104)$$

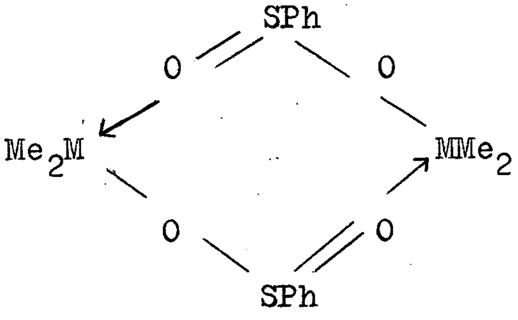
Therefore, $\Lambda_0 = 62.7$ and the slope of the line $A + B\Lambda_0 = 74.6$. The observed(108) Onsager slopes for LiCl, $NaNO_3$, KBr, KCNS and CsCl are 81.1, 82.4, 87.9, 76.5 and 76.0 respectively. The calculated slopes being 72.7, 74.3, 80.2, 77.8 and 80.5 respectively. Hence it is concluded that the thallium compound behaves as a strong uni-univalent electrolyte in water at 25°C, $[Me_2Tl]^+ [S_2PMe_2]^-$.

The interesting question arises about the possibility of this compound being present as four-membered rings in the solid state, similar to the analogous aluminium, gallium and indium dithiophosphinates, which were shown to be monomeric in benzene. The lack of volatility and solubility in benzene is an indication that the thallium compound is a salt in the solid state. Furthermore, the bands assigned to different structural features of the dithiophosphinate group, in the infrared spectrum of the thallium compound were very similar to those in caesium dimethyldithiophosphinate (prepared from caesium carbonate and the acid) which is doubtless a salt. Bands due to the $Me_2Tl$ group were similar to those in dimethylthallium bromide (See Fig. C) which is a salt, and the $Me_2Tl$ group is linear. These spectra were recorded for pressed potassium bromide discs, and the presence of four-membered rings in dimethylthallium dimethyldithiophosphinate in the solid state would have involved non-linear $Me_2Tl$ groups, hence, the spectrum should have been different from that observed for the linear group in dimethylthallium bromide. It is of interest that no strong bands due to the symmetrical deformation of the methyl groups were observed, this being forbidden in the infrared for the linear $Me_2Tl$ group. It seems, then, that $Me_2Tl[S_2PMe_2]$ is also a salt in the solid state as in solution in water.

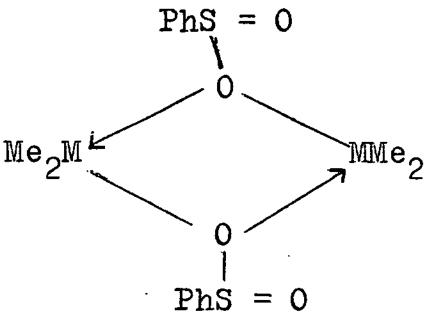
## Sulphinates of Group III Metals

The compound aluminium tris(ethylsulphinate) obtained from the reaction between sulphur dioxide and triethylaluminium has been described(109). But the molecular weight of this substance was not measured. Furthermore, no other information was available about any sulphinates of group III metals. In the present work, dimethylaluminium benzenesulphinate and its analogous gallium compound were obtained from reactions between benzene sulphinic acid and the trimethyl-metal in ether or benzene, under an atmosphere of nitrogen. Addition of the acid to the trimethyl-metal caused a lively reaction with gas evolution, and the products of the reaction remained dissolved in the solvent. The solvent was removed under reduced pressure, leaving a white solid. Pure dimethyl-metal sulphinates were obtained from this residue by vacuum sublimation at about 120°C. The compounds are soluble in many organic solvents.

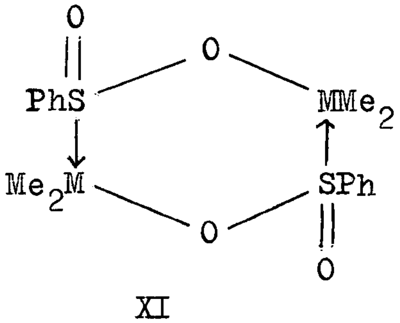
The molecular weights were determined cryoscopically in benzene and the sulphinates were shown to be dimers. Structures IX, X and XI are possible for these dimers in which the metals can attain four- co-ordination (M = Al or Ga).



IX



X



XI

For structure IX the sulphur-oxygen bonds are very similar, but for structures X and XI the sulphur-oxygen bonds are different, and free S = 0 is retained, which does not participate in co-ordinate bond formation. Therefore, infrared spectroscopy can be used to distinguish between structures IX and the others. In the ester $PhSO_2Me$ where a distinction between two types of sulphur-oxygen bonds is apparent, bands due to S = 0 and S - OMe stretching modes are observed at 1136-1126 and 960 $cm^{-1}$ respectively(88). These bands which are so wide apart in the ester move closer together in the salts where any distinction between two types of sulphur-oxygen bonds disappear, andasymmetric and symmetric modes are observed (compare(88) 1020 and 980 $cm^{-1}$ in $KO_2SPh$). For dimethylaluminium benzenesulphinate and the analogous gallium compound, bands considered due to sulphur-oxygen stretching modes were observed at 1027-1005 and 980-970, and 1005 and 941 $cm^{-1}$ respectively. Therefore, structure IX is considered to represent the sulphinates of aluminium and gallium. Previous observations on the methyl- and phenyl-phosphinates of these metals reinforced this conclusion.

A large number of complexes of sulphoxides have been(110-112) described (e.g. $Me_2SO,BF_3$; $2Me_2SO,PdCl_2$ etc.). The structures of many of these have been established on the basis of infrared and visible spectra, magnetic measurements and steric considerations. Sulphoxides are pyramidal molecules with unshared electron pairs on both sulphur and oxygen, therefore, the identification of the donor atom in consideration of their structures was of interest. It was found that in most cases examined oxygen was the donor atom. Only for $PdCl_2$, $2Me_2SO$ and the corresponding platinum complexes, Pd ⟵ S and Pt ⟵ S bonds were considered probable. It may be mentioned that these metals form some of their most well-known complexes (e.g. $PdCl_2$, $2Et_2S$) with donor atoms which have vacant d orbitals; such atoms include sulphur but not oxygen.

A brief description follows of the arguments used to decide between the alternate structures for these sulphoxide complexes on the basis of their infrared spectra. The S-O bond in the sulphoxides has partial double-bond character, resulting from $p_\pi - d_\pi$ back bonding from O to S superimposed upon the S ⟶ O sigma bond. Therefore, the attachment of the oxygen atom to an acceptor, and subsequent draining of electrons from oxygen should reduce the $p_\pi - d_\pi$ back bonding and hence lower the S-O bond order and stretching frequency. On the other hand, attachment of sulphur to an acceptor atom would be expected to increase the $p_\pi - d_\pi$ back bonding and thus raise the S - O stretching frequency (compare 938, 952 and 1116 $cm^{-1}$ for

$Me_2SO,BF_3$; $2Me_2SO,ZnCl_2$ and $2Me_2SO,PdCl_2$ respectively; the spectra of $Me_2SO$ in $CHCl_3$ and $CS_2$ has a very strong broad band at 1055 $cm^{-1}$ due to S - O stretching modes, this band shifts to 1100 $cm^{-1}$ region for spectra examined in vapour phase).

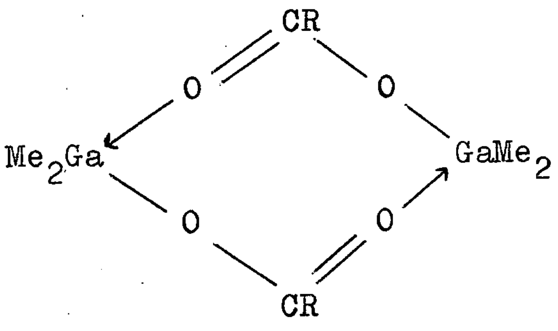
## Sulphonates of Group III Metals

A number of alkyl sulphonates of aluminium have been described(113) e.g., diethylaluminium benzenesulphonate, dioctylaluminium p-toluenesulphonate, diethylaluminium p-toluenesulphonate, divinylaluminium methanesulphonate, diphenylaluminium benzenesulphonate etc. These were prepared from reactions between alkyl aluminium halides and an ester of the acid. The molecular weights were not revealed, nor was any information available on dimethylaluminium methanesulphonate or any gallium sulphonate. This sulphonate of aluminium and the corresponding gallium compound were prepared from methane sulphonic acid and the trimethyl-metal in benzene, under an atmosphere of nitrogen. Addition of the acid to the trimethyl-metal caused a lively reaction with gas evolution, andthe products of the reaction remained dissolved in the solvent. The solvent was removed under reduced pressure, leaving a white solid. Pure dimethyl-metal sulphonates were obtained from this residue by vacuum sublimation at about 100°C. These were air-sensitive. Examination of infrared spectra was restricted by the difficulty of finding suitable solvents, for example, the sulphonates were sparingly soluble in carbon disulphide. However, they were soluble in benzene, in which the molecular weights were cryoscopically determined and the compounds were found to be trimers (compare the sulphinates which were dimers). Absence of infrared data makes it impossible to suggest any structures for these compounds.

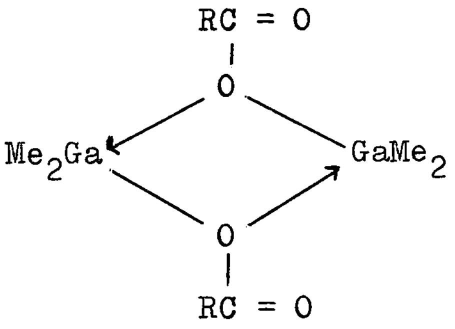
## Carboxylates of Group III Elements.

It was mentioned in the introductory section that dimethylgallium acetate(39) was found to be a dimer, but its structure was not established. This investigation was taken up in the present work, and the new compounds dimethylgallium ($d^3$) acetate and the formate were also examined to help interpret the spectra. These compounds were obtained from reactions between trimethylgallium and the corresponding acid in ether. The deutro-acetate was similar in volatility to the acetate, but the formate was slightly more volatile. Thus it was convenient to purify these materials by vacuum sublimation.

The molecular weight of the formate was determined cryoscopically in benzene and it was shown to be a dimer. Structures XII and XIII are possible for the carboxylates under consideration, in which the metal can attain four-co-ordination (R = $CH_3$, $CD_3$ or H).



XII



XIII

For structure XII the carbon-oxygen bonds are very similar, but for structure XIII the carbon-oxygen bonds are different, and free C = O is retained, which does not participate in co-ordinate bond formation. Therefore, infrared spectroscopy can be used to distinguish between these structures. In normal saturated esters(114) where a distinction between two types of carbon-oxygen bonds is apparent, bands due to C = O stretching modes are observed in the region 1750-1735cm$^{-1}$. Similarly bands due to C - O - stretching vibrations are observed in the regions 1200-1180 cm$^{-1}$ and 1250 - 1230 cm$^{-1}$ in the formates and acetates respectively(114). These bands which are so wide apart in the ester move closer together in the salts where any distinction between two types of carbon-oxygen bonds disappears, and asymmetric and symmetric modes are observed (compare(115) 1578 and 1408 cm$^{-1}$ in NaOAc). For dimethylgallium acetate and the corresponding ($d^3$) acetate and formate, bands considereddue to carbon-oxygen stretching vibrations were observed at 1534 and 1471, 1515 and 1475, and 1587 and 1555 cm$^{-1}$ respectively (the origin of a band at 1616 cm$^{-1}$ in the spectrum of the formate is difficult to interpret). Therefore, structure XII must represent the carboxylates of gallium.

The compounds $Bu^i{}_2AlO_2CEt$, $Et_2AlO_2CMe = CH_2$, $Bu^i{}_2AlOAc$ etc. obtained from the trialkylaluminium and the corresponding acid have been described(116), but molecular weights were not revealed. Action of $CO_2$ on triethylaluminium in an inert solvent gives diethylaluminium propionate, which reacts further with triethylaluminium as shown by the following equations(117)

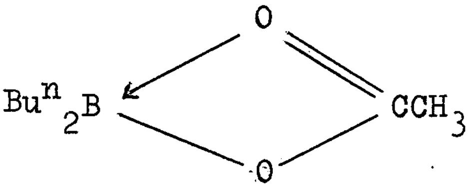
$$Et_3Al \xrightarrow{CO_2} Et_2Al.O.CO.Et \xrightarrow{2AlEt_3}$$

$$Et_2Al.O.AlEt_2 + Et_3COAlEt_2 \xrightarrow{H_2O} Et_3COH$$

A number of derivatives of boron containing the carboxylate ligand have been described(118,119) The compound $Bu^n{}_2B.OAc$ is more similar to the materials investigated in the present work. This was prepared by the reaction between acetic acid and $Bu^n{}_2BCl$ in n-pentane. It was examined spectroscopically and bands at 1825 and 1757 $cm^{-1}$ were observed due to some acetic anhydride. Therefore, the following equilibrium has been suggested

$$2\ Bu^n{}_2B.OAc \rightleftharpoons Bu^n{}_2BOBBu^n{}_2 + Ac_2O$$

The carbonyl stretching frequency was rather low (1603 $cm^{-1}$) and a chelating monomeric structure has been proposed for the compound.



No measurements on molecular weights were described. It is of interest to note that the tri-acetates of La(III) have been recently described. These were ebullioscopically found to be monomeric in benzene,(120) but the metal would be octahedrally co-ordinated.

It was considered of interest to measure the molecular weight of a compound of the type $R_2BOAc$. Diethylboron acetate was prepared by the reaction between triethylborane and acetic acid in ether, as described by Meerwein and Sonke(47). The molecular weight was determined cryoscopically in benzene and found to be 175, and it did not change significantly with alteration in the concentration of the benzene solution (calculated for $Et_2BOAc$, 128). Bands observed in the infrared spectrum are given in the experimental section. It appears to be difficult to make any interpretation of the nature of this compound on the basis of molecular weight and infrared spectrum.

### Dimethylgallium Dimethylarsinate

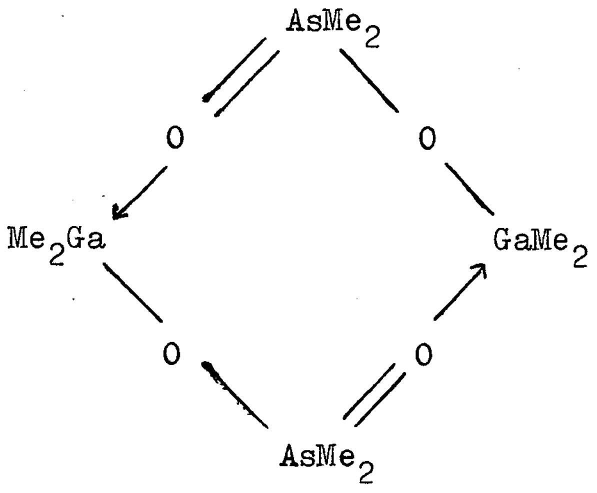
No information was available on the arsinates of group III metals. Dimethylgallium dimethylarsinate was prepared from trimethylgallium and the corresponding acid in benzene. Removal of the solvent under reduced pressure left a white solid, from which the pure compound was obtained by vacuum sublimation as colourless crystals.

The near infrared spectrum and far-infrared spectrum were recorded in carbon disulphide and benzene respectively.

Bands at 1267 and 1259 cm$^{-1}$ were assigned to the symmetrical deformation modes of the methyl groups attached to arsenic (compare 1263 and 1248 cm$^{-1}$ in $CsO_2AsMe_2$ and 1242 and 1263 in $Me_3As$(69)). Very little information is available on infrared absorption due to arsenic-oxygen bonds. A band at 811 cm$^{-1}$ observed by Mitra(121) in the infrared spectrum of $AsOF_3$ was assigned to the As = O stretching mode. In triphenylarsine oxide and its co-ordination compounds the absorption due to the arsenic-oxygen linkage occurs in the 880 cm$^{-1}$ region(122). This region was complicated in the spectrum of dimethylgallium dimethylarsinate by the presence of bands due to As-Me rocking vibrations. These rocking vibrations were identified from the spectrum of iododimethylarsine (Table 20). It appears that in the infrared spectrum of the gallium compound (Table 19) bands at 897(s), 884(vs), 865(s) and 818(m) cm$^{-1}$ must be due to As-O stretching or As-Me rocking vibrations (compare 909, 885, 862, 839 and 809 cm$^{-1}$ in $CsO_2AsMe_2$). In the analogous phosphorus compound, $(Me_2GaO_2PMe_2)_2$, bands due to phosphorus-oxygen stretching modes were of comparable intensity (Table 5). On this basis, the bands at 897 and 865 cm$^{-1}$ may be assigned to arsenic-oxygen stretching vibrations.

The molecular weight was determined cryoscopically in benzene and the compound was shown to be a dimer.

Therefore, by analogy with the phosphinates, an eight-membered ring structure is suggested for this compound (XIV)



XIV

# EXPERIMENTAL

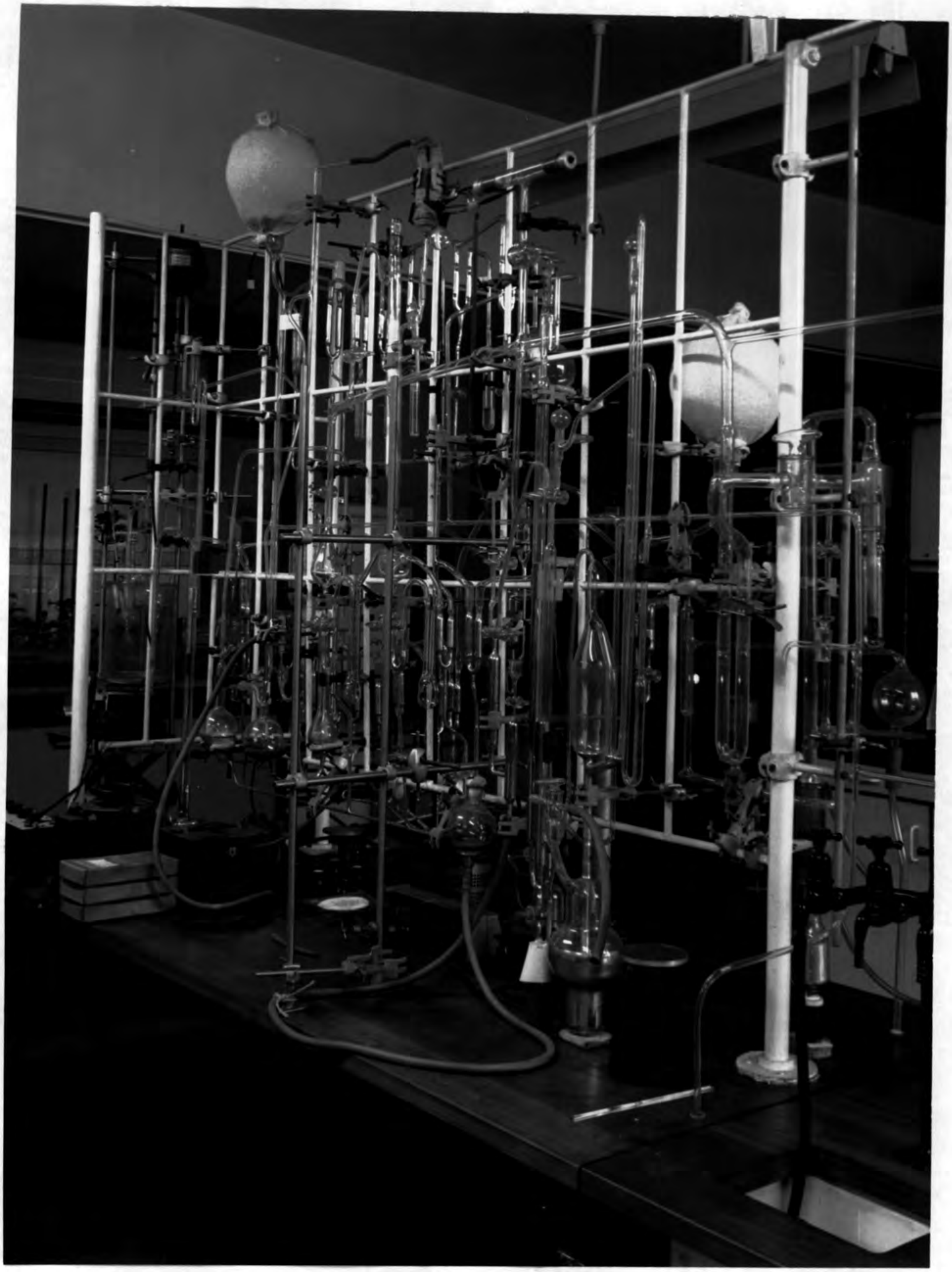


Fig. 1

## EXPERIMENTAL

### General Apparatus and Techniques

A vacuum system with mercury float valves was constructed for the manipulation of volatile materials and for gas analysis; it was largely made from pieces derived from a similar apparatus which had previously been used in another laboratory. The general features and utility of this apparatus are described below:

(a) The storage section was used for keeping volatile materials as solid, liquid or vapour. For example, trimethylindium, trimethylgallium and hydrogen cyanide respectively.

(b) The distillation section was used for the separation of the components of a mixture by fractional distillation. For example, a mixture of trimethylindium and dimethylmercury was separated by fractional distillation from a trap kept at 0°C, through a fractionating column filled with Fenske helices, a cold finger condenser at -22°C, a trap at -35°C and finally a liquid air trap to condense the pure dimethylmercury.

(c) The measuring bulb section was used for the determination of the quantity of a condensable gas (e.g. trimethylamine) or a suitable vapour (e.g. trimethylgallium). It consisted of a small bulb and a cold finger (about

300 ml.) connected to a larger bulb and a cold finger (about 3.5 litre) through a mercury float valve. A single limb manometer made of precision bore tubing was attached to the small bulb. Thus, for the measurement of the volume of a suitable volatile material at room temperature, the small bulb was either used separately or in combination with the larger bulb. These bulbs were accurately calibrated in the usual way by means of known quantities of carbon dioxide. Two graphs showing the volume in normal milli-litre against the observed depression in pressure were plotted for the two bulbs.

(d) For the measurement of a non-condensable gas like methane or hydrogen, a Topler pump with a gas burette was used, rather as described by Sanderson.(123)

(e) There was also a high temperature bulb for the measurement of molecular weights.

(f) An ordinary manometer was attached to the apparatus.

(g) When necessary, the vacuum was always let down with oxygen-free nitrogen. For this, commercial white spot nitrogen drawn from taps was purified by passage over heated copper (about 400°C) and then over phosphorus pentoxide. The copper was regenerated with hydrogen from time to time and the phosphorus pentoxide tube was replaced when necessary.

(h) An inlet or outlet for the introduction or withdrawal of materials.

(i) The evacuation was done with an Edwards High Vacuum mechanical pump and a mercury diffusion pump. Suitable traps were used to prevent any volatile material getting into these pumps.

(j) The mercury float valves were operated by a separate mechanical pump.

## Molecular Weight Measurements

Molecular weights were determined cryoscopically in benzene. 'Analar' benzene was dried over sodium wire and calibrated with biphenyl before use. The molecular weight measurements were done in an atmosphere of nitrogen, and precautions were taken to prevent changes of solution composition due to evaporation of benzene in the nitrogen.

## Purification of Nitrogen

Commercial white spot nitrogen drawn from a tap or a cylinder was unsuitable to use for preparative work or molecular weight measurements of many of the extremely air sensitive materials described later. Therefore, the nitrogen was purified by passing over heated copper (about 400°C) and molecular sieve. The copper was regenerated with hydrogen from time to time and the molecular sieve was activated by heating to 300°C with pumping.

## Infrared Spectra

Infrared spectra were recorded with a Grubb-Parsons

GS2A prism-grating spectrometer (wavelength below 23 microns) and a Grubb-Parsons DB3/DM2 200-line per cm. grating instrument (wavelength below 50 microns). Spectra of solid materials at shorter wavelengths were taken on specimens pressed in alkali halide discs, as mulls in Nujol and hexachlorobutadiene or as solutions in a suitable solvent like carbon disulphide and carbon tetrachloride. The spectra of liquids or solutions were recorded in a liquid cell which was dismantled and cleaned after use. It was reassembled with a suitable spacer depending on the solubility or spectroscopic properties of the material whose spectrum was to be recorded. In general, liquid or solution spectra were taken with a motor speed of 1 R.P.M. while the other spectra (mulls and alkali halide discs) were recorded with a motor speed of 4 R.P.M. For spectra at longer wavelengths, caesium iodide optics were used. All manipulations involving air sensitive materials were carried out in a dry box.

### Dry Box

A (Lintott) dry box of a conventional type was used. It was purged with nitrogen and then the nitrogen was recycled through a nitrogen purification system. This nitrogen purification system was similar to the one described before. Some phosphorus pentoxide was also placed inside the box to keep the atmosphere dry.

### Vapour Pressure Measurements

The vapour pressure or dissociation pressure measurements

Fig. 2

were done in an apparatus (Fig. 2) which was attached to the vacuum line when necessary. The arm A was detached and weighed together with a $B_{24}$ Cap (lightly lubricated with high-vacuum silicone stopcock grease). A small amount of the compound (e.g. dimethylaluminium cyanide tetramer) was placed in it in an atmosphere of nitrogen, the $B_{24}$ Cap was fixed, and weighed again. The apparatus was reassembled in the dry box, using a small amount of silicone grease for the $B_{24}$ cone of arm A; a suitable amount of mercury was placed in the manometer and the taps B and C, which had been lubricated with 'Apiezon L' grease were closed. The apparatus was taken out of the dry box, attached to the vacuum line at point D, evacuated with tap B closed and then with it being open. The calculated amount of the volatile component (e.g. trimethylamine) was condensed on the compound in arm A. The tap B was closed and the adduct was allowed to warm to room temperature. Any unreacted volatile material was removed. The tap C was opened and the equilibrium dissociation pressures were measured at different temperatures.

## Quantitative Analysis

### Micro-analysis

Micro-analysis (C and H) were by Miss V. Conway, Mr. T. Cagill or Mr. A. Wiper of this department.

## Estimation of Beryllium

Materials containing about 0.1 gm. of beryllium were decomposed with 5 ml. water, and 5 ml. of dilute nitric acid were added to dissolve the precipitate. Precautions were taken to prevent any loss of the metal in decompositions involving gas evolution (e.g. methylberyllium cyanide). The solution was transferred to a 250 ml. beaker, diluted to 150 ml, and almost neutralised by adding 1:1 ammonia solution drop-wise. It was heated to boiling, and 1:4 ammonia solution was slowly added with stirring until present in very slight excess. It was boiled for 2 minutes more and filtered through a No. 541 filter paper. The bulk of the precipitate was transferred to the filter. A small quantity of the precipitate adhering to the walls of the beaker was dissolved in the minimum volume of hot very dilute nitric acid, heated to boiling and precipitated as before. It was also filtered through the same paper and washed with 1:4 ammonia solution. The filter paper was placed on a weighed silica crucible, dried, heated at a low temperature until the carbon had been destroyed, and finally ignited with a Mecker burner (1000°C) to constant weight.

Estimation of Cyanide.

Samples containing 0.05-0.10 gm. of cyanide were decomposed with 5 ml. water, and dilute nitric acid was slowly added until the precipitate dissolved (e.g. beryllium cyanide). Precautions were taken to prevent any loss of volatile hydrogen cyanide. This was achieved by doing most of the operations at low temperature. The cyanide was precipitated with excess of aqueous silver nitrate solution, collected on a weighed filter crucible, and dried (110°C) to constant weight.

Estimation of Aluminium, Gallium and Indium

The metals aluminium, gallium and indium were gravimetrically estimated by precipitation with 8-hydroxyquinoline, as described in standard books on quantitative analysis(125) or in the literature.(126)

In a typical analysis, a sample (e.g. dimethylaluminium cyanide) containing about 0.02 gm. of aluminium was decomposed with 5 ml. water (the corresponding gallium compound was refluxed 10 hours with concentrated hydrochloric acid in a 250 ml. round-bottomed flask fitted with an air condenser, for the complete removal of methyl groups) and dilute hydrochloric acid was slowly added until the precipitate dissolved. The hydrogen cyanide was boiled off, and the solution was diluted to 150 ml. after being transferred to a 300 ml. conical flask. The pH of this solution was checked with B.D.H. Universal Indicator paper and found to be 6. It was warmed to 50-60°C and the oxine solution (2% solution in acetic acid prepared in the usual way) was slowly added with stirring (20% excess). This was followed by the addition of a solution of 40 gm. of ammonium acetate dissolved in the minimum amount of water. The precipitate was allowed to settle, collected on a weighed filter crucible, washed with hot water, and dried (110°C) to constant weight.

## Starting Materials and Reagents

### Trimethylaluminium

Trimethylaluminium was available in a cylinder on loan from Ethyl Corporation. It was withdrawn from the cylinder in an atmosphere of nitrogen and purified by vacuum distillation.

### Dimethylmercury

The dimethylmercury was prepared by a modification of the method described by Gilman and Brown.(124) Methyl bromide (200 gm.), magnesium metal (50 gm.) and mercuric chloride (210 gm.) reacted in two stages to give dimethylmercury (150 gm. 83% yield). A 5 litre bulb with a flanged neck was used. It was fitted with an efficient stirrer, a cold finger condenser, a dropping funnel which was kept cold, an inlet for nitrogen and an outlet for volatile materials. The magnesium was placed in the bottom of the flask and the apparatus was purged with nitrogen. Then the metal was covered with ether (500 ml.) and a solution of methyl bromide in ether (1500 ml.) was added slowly with appropriate cooling after the reaction had been initiated with ethylene dibromide. The reaction vessel was surrounded with cold water, the cold finger condenser was maintained at -30°C with carbon dioxide in acetone and the dropping funnel was kept cold by surrounding it with a few pieces of solid carbon dioxide. After the addition of methyl bromide was complete, the Grignard reagent was stirred for one hour at room temperature. Then the dropping funnel was removed. The cold finger condenser was replaced by a Soxhlet extractor and an efficient water condenser. The mercuric chloride was introduced in two batches and extracted in about six hours. Now, the Soxhlet was removed and replaced by a condenser. Then the reaction mixture was refluxed for eight hours more. It was cooled and slowly hydrolysed with 500 ml. water. The ether layer was separated and dried over freshly ignited magnesium sulphate . The dimethylmercury was separated from ether by fractional distillation.

Trimethylgallium.

For the preparation of trimethylgallium a method described by Coates(19) was followed. Dimethylmercury (140 gm.) reacted with gallium metal (23 gm.) to give trimethylgallium in nearly quantitative yield. The apparatus used was an all glass system without any greased joints. It consisted of a glass bulb (250 ml.) and a fractionating column 4 cm. in diameter and 30 cm. long filled with Fenske helices. On top of the column, there was a thermometer pocket, a condenser and a mercury cut-off to withdraw trimethylgallium from time to time. There was also a side-arm attached to the bulb which was sealed off after the gallium metal and a trace of mercuric chloride had been introduced. The dimethylmercury was introduced by vacuum distillation. The vacuum was released with nitrogen and the reaction mixture was heated so that the dimethylmercury started to reflux gently with the thermometer registering almost its boiling point. Gradually the temperature at the top of the fractionating column dropped to the boiling point of trimethylgallium when a small quantity of it was withdrawn by lowering the mercury cut-off. This was done at suitable intervals until the reaction was complete.

### Trimethylindium

A concentrated indium amalgam containing 20 gm. of the metal reacted with excess of dimethylmercury (120 gm.) to give 6 gm. of trimethylindium. The amalgam was prepared by the action of 2 ml. of mercury on the weighed quantity of the metal cut into small pieces with a pair of strong scissors. It dissolved in mercury to give a liquid at room temperature. The excess of mercury was distilled off under vacuum leaving behind a solid metal amalgam. Just before use, it was divided into small pieces, hammered into thin sheets and cut into thin strips.

The apparatus used was an all-glass system and it consisted of a glass bulb (200 ml.) filled with a water condenser (6" long), the stem of which went up 3 inches more and ended in a ⊣ fork. The vertical arm was kept open and the side arm connected to the vacuum line through a $B_{18-9}$ ball and socket joint (using apiezon grease). Thus connected the apparatus became provided with a mercury blow-off type of manometer which could be used to indicate pressures up to about 80 cm. The apparatus was briefly evacuated (using a rubber bung to close the open end) and then the vacuum was released with oxygen-free nitrogen. The rubber bung was removed and indium amalgam cut as thin strips was introduced against a counter-current of nitrogen and then the open end was sealed. The apparatus was then evacuated and the dimethylmercury introduced by vacuum distillation with the bulb cooled to -60°C. The vacuum was released with nitrogen and the reaction mixture was electrically heated in an oil bath at 100°C for three days and then at 120°C for five days. The reaction was slow to start with but towards the end the entire amalgam had dissolved in a big globule of mercury formed in the reaction. The trimethylindium formed remained dissolved in the excess of dimethylmercury as a colourless liquid without any brown tinge which was observed in a previous experiment in which the dimethylmercury was mechanically introduced from outside instead of by vacuum distillation. At the end of the reaction the volatile materials were withdrawn into the vacuum line and the trimethylindium was separated from dimethylmercury by fractional condensation from 0°C to -22°C, to -35°C and to liquid air.

### Trimethylthallium

A suspension of dimethylthallium bromide (8 gm.) in ether (30 ml.) reacted with methyl lithium (15 ml. of 2.1 M solution in ether) to give trimethylthallium (4.5 gm; 75% yield). A three neck round bottomed flask (250 ml.) fitted with a stirrer, a dropping funnel (100 ml.), an inlet for nitrogen and an outlet for volatile materials was used. The experiment was done in diffused light. Dimethylthallium bromide was placed in the reaction vessel and the apparatus was then purged with nitrogen. Then ether was added. The apparatus was covered with a dark cloth and methyl lithium solution was slowly added with stirring. Gradually the dimethylthallium bromide passed into solution and a very small amount of finely divided thallium was formed. The product was distilled under vacuum to give a solution of trimethylthallium in ether.

### Beryllium Reagents

A solution of dimethylberyllium in ether and its trimethylamine complex in the pure state were available, having been prepared by Dr. S. I. E. Green in connection with his own work.

### Hydrogen Cyanide

A concentrated solution of potassium cyanide (6 moles) in water (1000 ml.) reacted with 1:3 sulphuric acid (10 moles of $H_2SO_4$) to give hydrogen cyanide in good yield (5 moles). The apparatus consisted of a three-neck round bottomed flask (3 litre) fitted with a stirrer, a dropping funnel and a fractionating column (4 cm. in diameter and 25 cm. long) filled with glass helices. The top of the column had a thermometer and an arm suitably leading to a cold finger condenser, a receiver and a bubbler. The sulphuric acid was placed in the flask and maintained at 50°C by heating with an isomantle. Then the aqueous solution of potassium cyanide was slowly added with stirring. The hydrogen cyanide distilled and collected in the receiver over phosphorus pentoxide. The cold finger condenser and the receiver were maintained at -10°C with ice and salt. After the completion of the reaction the apparatus was allowed to cool and then it was purged with air to drive all the hydrogen cyanide into the receiver. The receiver was detached and shaken with more phosphorus pentoxide. The hydrogen cyanide was purified by redistillation and stored over a small amount of phosphorus pentoxide.

## Phosphinic Acids

An aqueous solution of dimethylphosphinic acid was available. It was pumped dry and the acid was purified by vacuum sublimation (0.01 mm/Hg; 70°C) as a white glistening crystalline solid.

Diphenylphosphinic acid, diphenylthiophosphinic acid, and dimethyldithiophosphinic acid were also available, since they were needed for other work in progress.

### Cacodylic Acid

The cacodylic acid used was a commercial sample. It was pumped dry before use.

### Benzene Sulphinic Acid

Benzene sulphinic acid was obtained by precipitation with hydrochloric acid from an aqueous solution of sodium benzene sulphinate. The preparation was done in an atmosphere of nitrogen. The acid was collected by filtration, washed with water, and pumped dry.

### Methane Sulphonic Acid

A commercial sample of methane sulphonic acid was used without further purification.

### Acetic Acid

Glacial acetic acid was dried by cooling it to its freezing point and discarding any liquid left. The fractional freezing was repeated four times.

### Heavy Acetic Acid

Heavy malonic acid made by the action of carbon suboxide on heavy water was available. Heavy acetic acid was prepared by the pyrolysis of heavy malonic acid. The malonic acid contained in a 250 ml. round bottomed flask was attached to the vacuum line against a counter-current of nitrogen. Then it was given a prolonged pumping to drive off any heavy water present. The vacuum was released to a pressure of about half an atmosphere and the heavy malonic acid was heated to a temperature of 150-60°C in an oil bath. It decomposed into heavy acetic acid and carbon dioxide. The heavy acetic acid distilled over and collected in a trap kept cold by surrounding with solid carbon dioxide. Most of the carbon dioxide formed in the pyrolysis together with some heavy acetic acid passed on to a second trap kept immersed in liquid air. After the completion of the pyrolysis the carbon dioxide was separated from heavy acetic acid by pumping through a trap kept at -78°C. The pure heavy acetic acid was withdrawn under vacuum into a glass storage tube provided with a greased tap. The vacuum was released to about half-atmosphere to protect the grease from attack by acetic acid vapour (m.p.12.0-13.0°C).

Formic Acid

'Analar' formic acid was dried over boric anhydride. It was decanted and purified by vacuum distillation.

Acetamide

A commercial sample of acetamide was purified by vacuum sublimation (0.01 mm./Hg; 60°C)as a white glistening crystalline solid.

Trimethylamine

A commercial sample of trimethylamine was shaken with phosphorus pentoxide. It was distilled and stored over a small amount of phosphorus pentoxide in a glass container provided with a Teflon tap capable of withstanding pressures more than an atmosphere.

Dimethylaluminium, Cyanide Tetramer, $[Me_2Al.CN]_4$.

Preparation.

(a) Hydrogen cyanide (42.9 ml. at S.T.P., 0.0019 mole) reacted with trimethylaluminium (0.1439 gm., 0.0020 mole) in a sealed tube at room temperature without a solvent to give white dimethylaluminium cyanide (m.p. 90°C) and methane (42.5 ml. at S.T.P.).

(b) On a larger scale, hydrogen cyanide (3 gm., 0.11 mole) in benzene (35 ml.) reacted with a solution of trimethylaluminium (8 gm., 0.11 mole) in benzene (40 ml.) to produce white crystalline dimethylaluminium cyanide (60%), some brown non-volatile impurity and methane. The preparation was done in a flask (1 litre) fitted with two dropping funnels (50 ml.), a stirrer, an inlet for nitrogen and an outlet for volatile materials through a paraffin oil bubbler. The apparatus was purged with nitrogen and the flask was surrounded with water to dissipate the heat of the exothermic reaction. The reactants contained in the two dropping funnels were simultaneously added to benzene (10 ml.) previously placed in the flask. Efficient stirring was maintained and care was taken to prevent vigorous evolution of methane and possible loss of the volatile reactants. The products of the reaction remained dissolved, and the reaction mixture acquired a slightly brown colour. At the end of the preparation, the solvent was removed under reduced pressure. Dimethylaluminium cyanide was purified by vacuum sublimation (0.01 mm.; 100°C) as a white crystalline solid (Found: Al, 32.2; $Me_2Al.CN$ requires Al, 32.5%). The sublimation started at 85°C. A brown non-volatile impurity was left behind.

Dimethylaluminium cyanide (m.p. 89°C) was very sensitive to air. It decomposed slowly in the atmosphere with evolution of hydrogen cyanide and inflamed in contact with a drop of water. It dissolved in ether, carbon tetrachloride without decomposition, but reacted with carbon disulphide, forming a yellow substance. The brown impurity was also sensitive to air and was decomposed exothermically by water with evolution of hydrogen cyanide, leaving a white residue.

Hydrolysis.

Dimethylaluminium cyanide (0.1015 gm.) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. The methane was measured (54.2 ml. at S.T.P.). Calculated for 0.1015 gm. dimethylaluminium cyanide, 54.8 ml. at S.T.P.

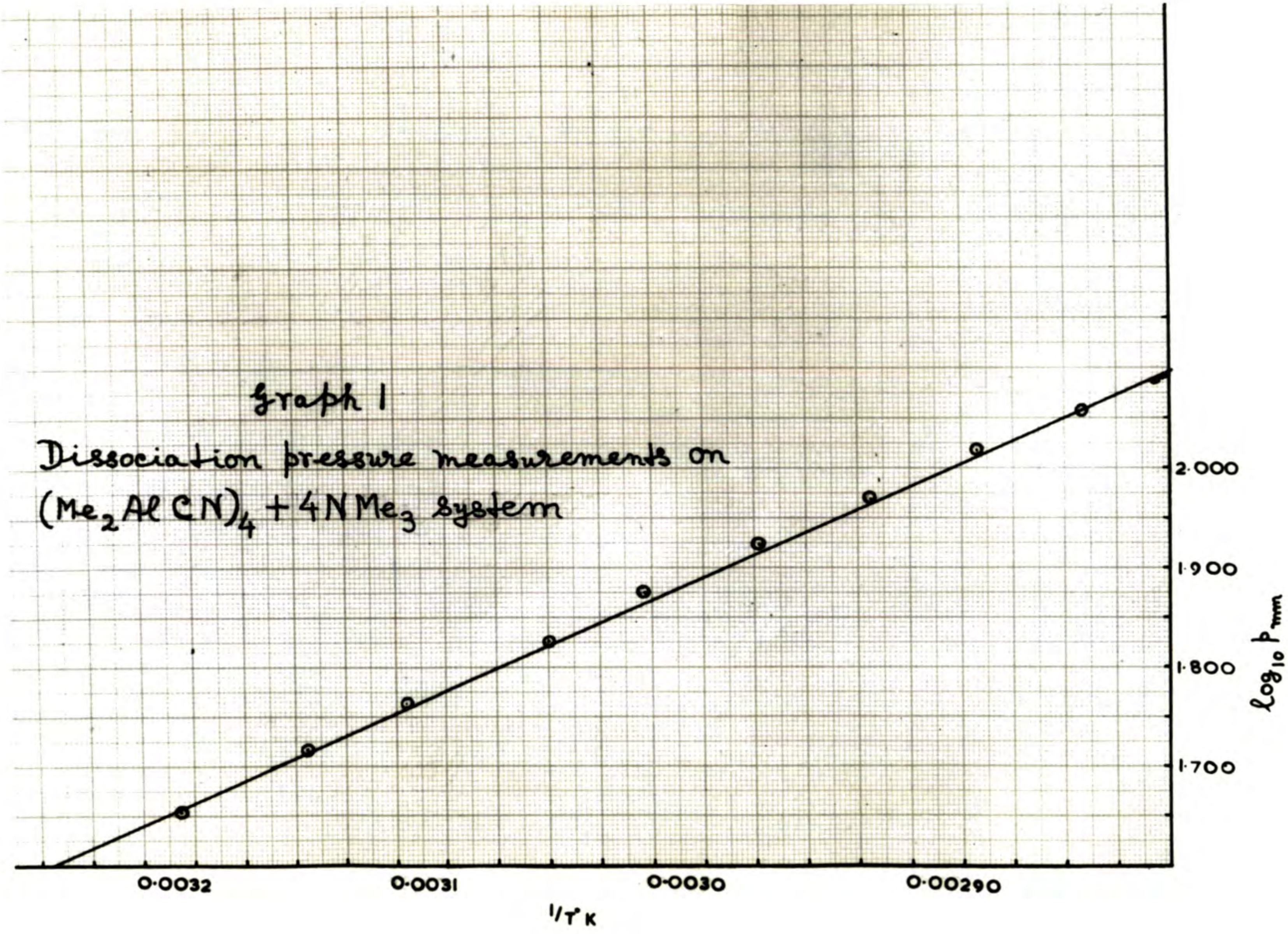
## Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.69, 1.16 and 1.31 gm. of dimethylaluminium cyanide in 100 gm. of benzene gave respectively 330, 331.5 and 326 for molecular weights. The tetramer $[Me_2Al.CN]_4$ requires 332.

## Action of Hydrogen Cyanide on Dimethylaluminium Cyanide Tetramer.

It was observed that dimethylaluminium cyanide reacts very slowly with liquid hydrogen cyanide at room temperature with evolution of methane. There was no solid-gas reaction at room temperature. Pure dimethylaluminium cyanide reacted with hydrogen cyanide gas at 100°C to give a deep brown product evidently containing some hydrogen cyanide polymer and a mixture of presumably higher cyanides together with a small amount of the unreacted starting material. The starting material was recovered and identified by its melting point. It was not possible to purify any of the higher cyanides.

A direct reaction between trimethylaluminium in benzene and excess of hydrogen cyanide in benzene gave an insoluble non-volatile product contaminated with hydrogen cyanide polymer. No further purification was achieved.



Graph 1

Dissociation pressure measurements on $(Me_2AlCN)_4 + 4NMe_3$ system

## Action of Trimethylamine on Dimethylaluminium Cyanide Tetramer.

Trimethylamine (76.8 ml. at S.T.P.; 0.0034 mole) was condensed on dimethylaluminium cyanide tetramer (0.3204 gm.; 0.0038 mole) in the vapour pressure apparatus. The reactants were allowed to warm to room temperature and any unreacted trimethylamine (16.2 ml. at S.T.P.) was removed. The dissociation pressures of the adduct measured at different temperatures are given below:

| Temperature | Pressure |
|---|---|
| 41°C | 45 mm. |
| 46 | 52 |
| 50 | 58 |
| 56 | 67 |
| 60 | 75 |
| 65 | 84 |
| 70 | 93 |
| 75 | 104 |
| 80 | 114 |

## Infrared Spectrum of Dimethylaluminium Cyanide Tetramer.

Examination of the infrared spectrum of dimethylaluminium cyanide tetramer at lower frequencies was restricted by the difficulty of finding suitable solvents. The tetramer reacts with, for example, carbon disulphide, forming a yellow substance. The bands which were identified are given below:

(a) Hexachlorobutadiene mull

2224 (s)

(b) Carbon tetrachloride solution

2213 (s), 1195 (s), 1047 (s)

## Dimethylgallium Cyanide Tetramer, $[Me_2Ga.CN]_4$

Preparation.

(a) Hydrogen cyanide (42.1 ml. at S.T.P., 0.0019 mole) reacted with trimethylgallium (42.9 ml. at S.T.P., 0.0019 mole) in a glass bulb (100 ml.) connected to the vacuum line through a 4 mm. tap, at room temperature without a solvent to produce white dimethylgallium cyanide (m.p. 79°C) and methane (41.2 ml. at S.T.P.). Hydrogen cyanide (0.0012 mole) also reacted with trimethylgallium (0.0006 mole) under similar conditions to produce dimethylgallium cyanide and methane (0.0006 mole). The excess of hydrogen cyanide was recovered quantitatively.

(b) On a larger scale, hydrogen cyanide (1.2 gm., 0.044 mole) in benzene (30 ml.) reacted with trimethylgallium (5.0 gm., 0.043 mole) in benzene (30 ml.) to produce white crystalline dimethylgallium cyanide (73%) some brown non-volatile impurity, and methane. The experimental procedure was similar to that described for the preparation of dimethylaliuminium cyanide. At the end of the reaction, the solvent was removed under reduced pressure and dimethylgallium cyanide was purified by vacuum sublimation (0.01 mm.; 90°C) as a white crystalline solid (Found: Ga, 55.0; $Me_2Ga.CN$ requires Ga, 55.3%). The sublimation started at 60°C. A brown non-volatile impurity was left behind.

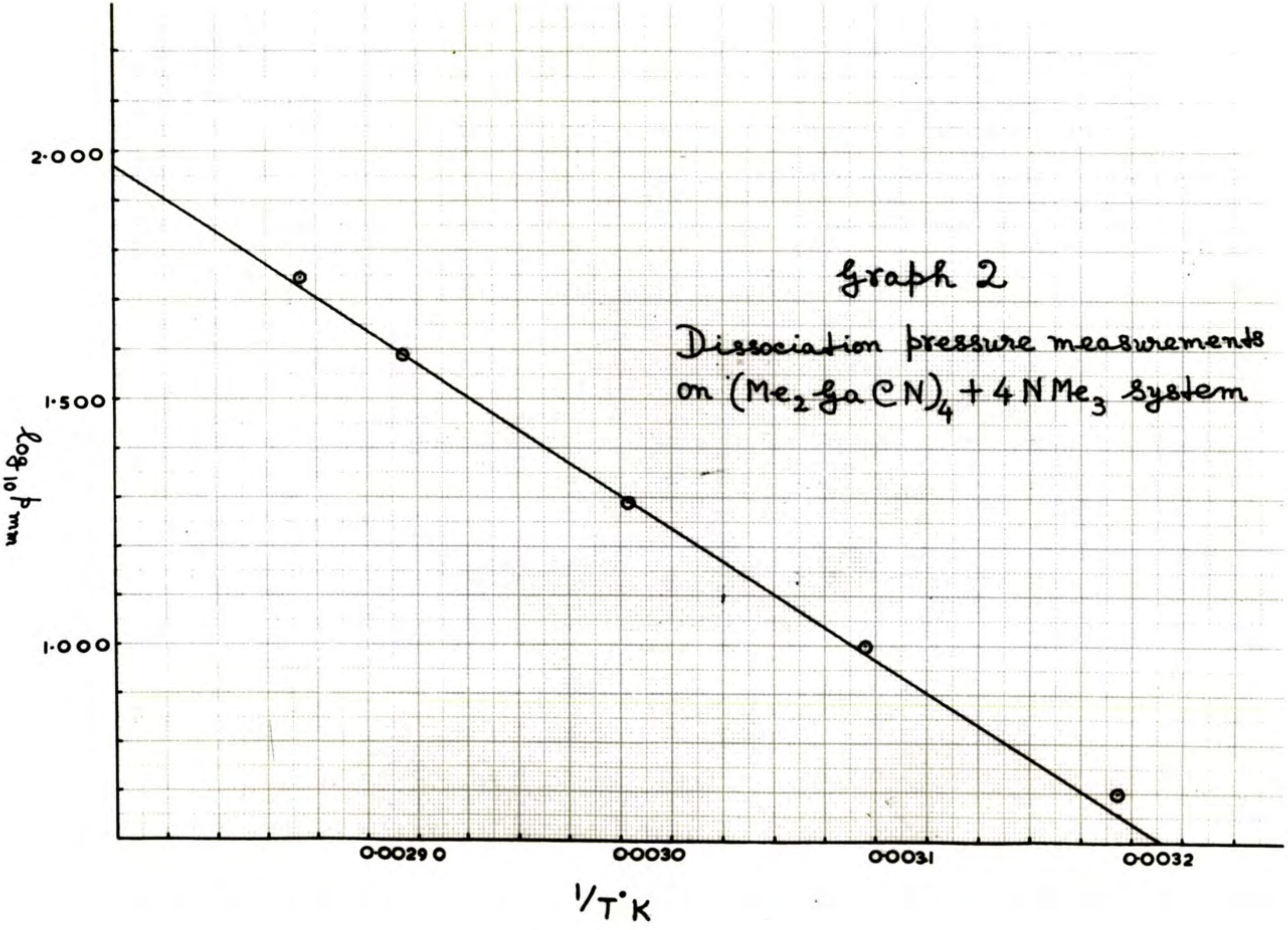
Dimethylgallium cyanide (m.p. 79°C) decomposed slowly in the atmosphere with evolution of hydrogen cyanide. It passed through a liquid phase which solidified in a short time. This solid was spectroscopically identified as dimethylgallium hydroxide.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.38, 1.12 and 1.68 gm. of dimethylgallium cyanide in 100 gm. of benzene gave respectively 536, 541 and 496 for molecular weights. The tetramer $[Me_2Ga.CN]_4$ requires 503.

Action of Trimethylamine on Dimethylgallium Cyanide Tetramer.

Trimethylamine (46.4 ml. at S.T.P.; 0.0021 mole) was condensed on dimethylgallium cyanide tetramer (0.2650 gm.; 0.0021 mole) in the vapour pressure apparatus. The reactants were allowed to warm to room temperature and then heated (55°C) for one hour. The apparatus was


Graph 2

Dissociation pressure measurements on $(Me_2GaCN)_4 + 4NMe_3$ system allowed to cool and any unreacted trimethylamine (3.2 ml. at S.T.P.) was removed. The dissociation pressures of the adduct measured at different temperatures are given below:

| Temperature | Pressure |
|---|---|
| 40°C | 5 mm. |
| 50 | 10 |
| 60 | 19.5 |
| 70 | 39 |
| 75 | 56 |

Infrared Spectrum of Dimethylgallium Cyanide Tetramer.

The infrared spectrum of dimethylgallium cyanide was recorded in different solvents. The bands which were identified for the compound are given below:

(a) Hexachlorobutadiene mull.

2216 (s)

(b) Carbon tetrachloride solution

2202 (s)

(c) Carbon disulphide solution

1207(ms), 1134(vw), 766(s,sh), 746(vs), 705(ms), 607(ms,sh), 598(s), 591(ms,sh), 548(m).

## Dimethylindium Cyanide Tetramer $[Me_2In.CN]_4$

Preparation.

Hydrogen cyanide (0.4 gm.; 0.015 mole) in benzene

(10 ml.) reacted with trimethylindium (2.4 gm.; 0.015 mole) in ether (20 ml.) to give dimethylindium cyanide (75%), some white non-volatile impurity and methane. The experimental procedure was similar to that described for the preparation of dimethylaluminium cyanide. At the end of the reaction the products remained dissolved in the solvent. The solvent was removed under reduced pressure, leaving a white solid (this was in contrast to the strongly or faintly coloured materials obtained respectively from the corresponding aluminium or gallium reactions after the removal of the solvent). Dimethylindium cyanide was purified by vacuum sublimation (120-40°C./0.05 mm.) as a white crystalline solid (Found: In,67.1; $Me_2In.CN$ requires In, 67.2%).

Dimethylindium cyanide (m.p. 147°C) decomposed very slowly in the atmosphere with evolution of hydrogen cyanide. In this respect its stability was comparable to dimethylgallium cyanide and in sharp contrast to the highly sensitive and inflammable dimethylaluminium cyanide.

Hydrolysis

Dimethylindium cyanide (0.0806 gm.) was treated with 2-methoxyethanol in the vacuum line. It dissolved without gas evolution. Addition of 2N-sulphuric acid caused slow evolution of methane at room temperature, and for measurement of methyl content the reaction mixture had to be heated to 60°C (20.8 ml. at S.T.P.). Calculated for 0.080 gm. dimethylindium cyanide 21.1 ml. at S.T.P.

Molecular Weight.

The molecular weights were determined cryoscopically in benzene. In this solvent, it was less soluble than the corresponding aluminium or gallium tetramer. Solutions containing 0,28 and 0.43 gm. of dimethylindium cyanide in 100 gm. of benzene gave respectively 663 and 688 for molecular weights. The tetramer $[Me_2In.CN]_4$ requires 683.

Infrared Spectrum of Dimethylindium Cyanide.

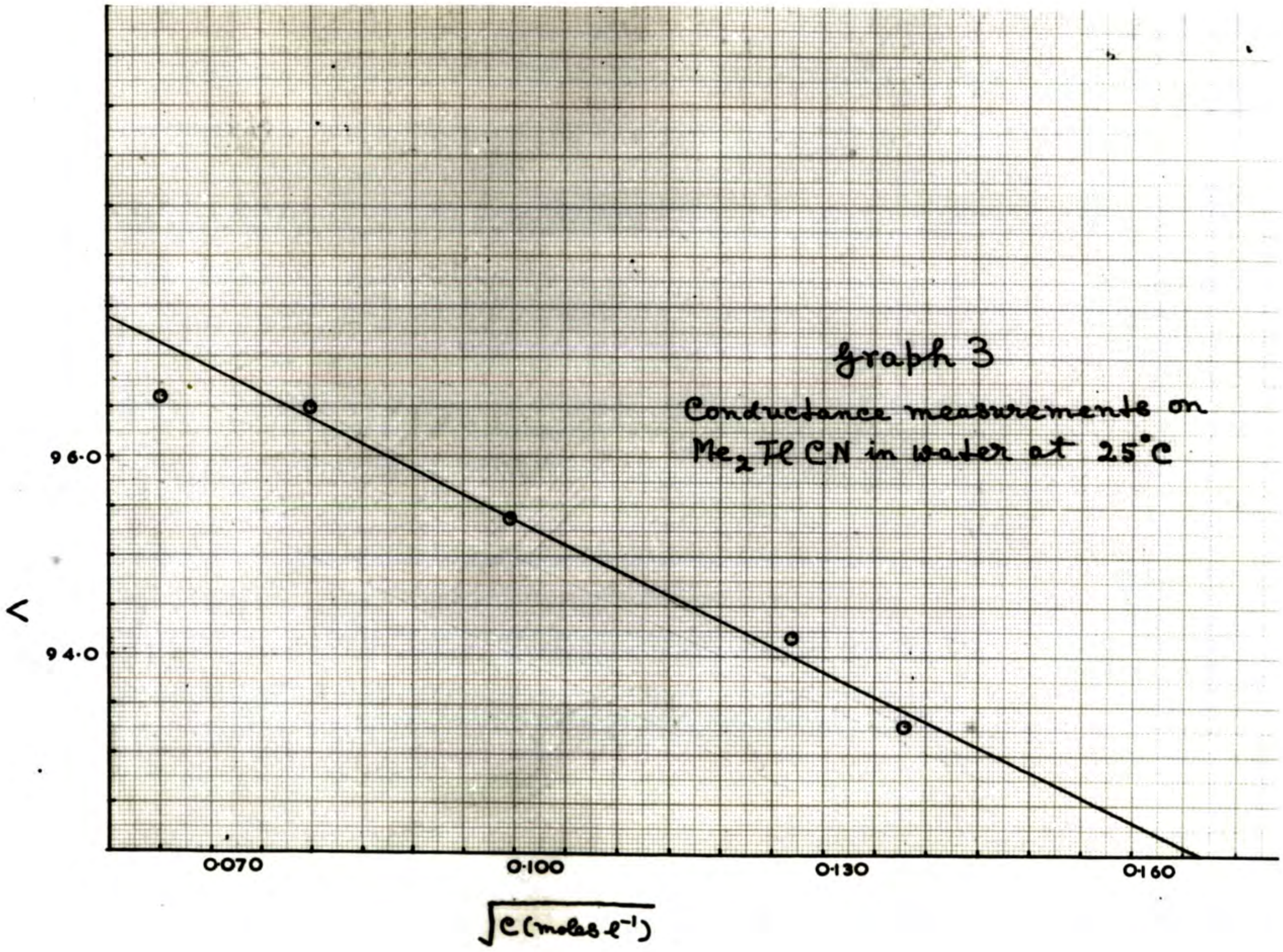
The infrared spectrum of dimethylindium cyanide was measured as solution in carbon tetrachloride, in a liquid cell with potassium bromide windows. The only band which could be identified for the compound is given below:

2178 (m)

## Dimethylthallium Cyanide

Preparation.

Hydrogen cyanide (0.5 gm.) in excess in benzene (10 ml.) was added to trimethylthallium (3.2 gm) in ether (40 ml.), giving methane and an immediate quantitative precipitate of dimethylthallium cyanide, which was washed with ether and pumped dry; it decomposed to a black mass at 275°C (Found: C, 13.8; H, 2.4; CN, 10.0. $C_3H_6NTl$ requires C, 13.8; H, 2.3; CN, 10.0%). The same compound was also prepared



Graph 3

Conductance measurements on $Me_2TlCN$ in water at 25°C by adding potassium cyanide (0.5 gm.) in water (10 ml.) to dimethylthallium fluoride (2.0 gm) in water (20 ml.); the resulting crystalline precipitate was washed with a little cold water and pumped dry. Dimethylthallium cyanide was soluble in water (2.7 gm. in 100 gm. of water at 25°C).

Conductance Measurements

The conductance measurements for dimethylthallium cyanide were done at 25°C in aqueous medium. The results are given in Table A .

Table A .

| $\sqrt{C}$ (mole $l^{-1}$) | $\Lambda$ |
|---|---|
| 0.0653 | 96.6 |
| 0.0800 | 96.5 |
| 0.0998 | 95.4 |
| 0.1271 | 94.2 |
| 0.1379 | 93.3 |

Infrared Spectrum of Dimethylthallium Cyanide.

Strong bands at 2101 and 790 cm$^{-1}$ were observed in the infrared spectrum of dimethylthallium cyanide measured for Nujol mull.

## Methylberyllium Cyanide, $[MeBe.CN]_n$

Preparation.

Dimethylberyllium (0.014 mole in 5 ml. of ether) and hydrogen cyanide (0.016 mole in 5 ml. of benzene) were simultaneously added, drop by drop and with stirring to ether (4 ml). After the reaction, in which gas was evolved, ether (10 ml.) was added, and white insoluble matter separated by filtration through a sintered disc under nitrogen. Evaporation of the colourless filtrate gave a solid product which lost ether slowly when pumped at room temperature. The solid lost more ether when pumped at 70°C, and a very small amount of colourless material sublimed. The white, involatile and insoluble residue appeared to have been impure polymeric methylberyllium cyanide (Found: Be, 17.5; MeBe.CN requires Be, 18.0%).

Methylberyllium cyanide was sensitive to air, and decomposed with evolution of hydrogen cyanide. Addition of 2,2'-bipyridyl to an ether solution of methylberyllium cyanide gave an orange-yellow solution.

Hydrolysis.

Methylberyllium cyanide (0.0474 gm) was hydrolysed in the vacuum line with 2N-sulphuric acid. The methane was measured (20.6 ml. at S.T.P.). Calculated for 0.0474 gm. methylberyllium cyanide 21.3 ml. at S.T.P.

Infrared Spectrum of Methylberyllium Cyanide.

A strong band was observed at 2222 cm.$^{-1}$ in the infrared spectrum of methylberyllium cyanide measured for

Nujol mull.

## Beryllium Cyanide

Preparation.

Dimethylberyllium (0.014 mole in 5 ml. of ether) was added dropwise to an excess of hydrogen cyanide (0.066 mole in 8 ml. of benzene). Methane was evolved and the white precipitate of beryllium cyanide was collected and pumped dry (Found: Be, 15.0; CN 84.1. Calculated for $C_2BeN_2$:Be, 14.75; CN, 85.2%). No residue remained when the filtrate was evaporated. No methane was detected when the beryllium cyanide was hydrolysed with dilute sulphuric acid. The compound was sensitive to air, and decomposed with evolution of hydrogen cyanide. It did not absorb trimethylamine at room temperature or at 70°C.

## Cyanomethyl(trimethylamine)beryllium, $[(Me_3N)MeBe.CN]_n$.

Preparation.

Dimethyl(trimethylamine)beryllium, $Me_2(Me_3N)Be$ (2.7gm,; 0.027 mole), in benzene (25 ml.), and hydrogen cyanide (0.8 gm,; 0.029 mole) in benzene (15 ml.), were slowly and simultaneously addedto stirred benzene (10 ml.). Gas was evolved and after the reaction the clear supernatant liquid was decanted from a small amount of white insoluble matter, and solvent was removed by pumping first at room temperature and then for 15 minutes at 80°C. The colourless involatile amorphous product did not melt or decompose below 300°C. (Found: CN, 23.7; $C_5H_{12}BeN_2$ requires CN, 23.85%). It was sensitive to air.

Hydrolysis.

Cyanomethyl(trimethylamine)beryllium (0.0270 gm.) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. The methane was measured (5.3 ml. at S.T.P.). Calculated for 0.0270 gm. $(Me_3N)MeBe.CN$ 5.5 ml. at S.T.P.

Infrared Spectrum.

A strong band at 2200 $cm^{-1}$ was observed in the infrared spectrum of cyanomethyl(trimethylamine)beryllium measured for Nujol mull. Satisfactory resolution was not achieved in other regions of the spectrum.

## Dimethylaluminium Dimethylphosphinate.

Preparation.

Trimethylaluminium (2.9 gm.; 0.040 mole) in benzene (15 ml.) reacted with a suspension of dimethylphosphinic acid (3.5 gm.; 0.037 mole) in benzene (100 ml.) to give white crystalline dimethylaluminium dimethylphosphinate and methane. The preparation was done in a flask (250 ml.) fitted with a dropping funnel (100 ml.), a stirrer, an inlet for nitrogen and an outlet for volatile materials through a paraffin oil bubbler. When the apparatus had been purged with nitrogen, the trimethylaluminium solution was introduced with a syringe, and the suspension of dimethylphosphinic acid was then slowly added. An exothermic reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent. The solvent was removed under reduced pressure, leaving a white residue. Pure dimethylaluminium dimethylphosphinate was obtained from this residue by vacuum sublimation (0.01 mm/100°C) as a white crystalline solid. It had m.p. 43°C (Found: Al, 18.0; $Me_2AlO_2PMe_2$ requires Al, 18.0%). The compound was soluble in solvents like ether, benzene, carbon tetrachloride and carbon disulphide. It was sensitive to air. It did not react with trimethylamine at room temperature.

Hydrolysis

Dimethylaluminium dimethylphosphinate (0.1520 gm) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. It dissolved in 2-methoxyethanol at about 0°C without gas evolution. Gas evolution started as the solution warmed to room temperature. The hydrolysis was completed with 2N-sulphuric acid. The methane was measured (44.8 ml. at S.T.P.). Calculated for 0.1520 gm. dimethylaluminium dimethylphosphinate 45.4 ml. at S.T.P.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.90, 1.36 and 1.47 gm. of dimethylaluminium dimethylphosphinate in 100 gm. of benzene gave respectively 313, 333 and 332 for molecular weights. The dimer $[Me_2AlO_2PMe_2]_2$ requires 300.

Infrared Spectrum

The infrared spectrum of dimethylaluminium dimethylphosphinate (below 2000 $cm^{-1}$) was measured for solutions in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1428(s,sh), 1316(s), 1307(s), 1192(vs), 1091(vs), 935(w), 878(s), 757(m), 728(m), 682(vs), 581(m).

Dimethylgallium Dimethylphosphinate

Preparation.

Trimethylgallium (2.6 gm.; 0.022 mole) in benzene (25 ml.) reacted with a suspension of dimethylphosphinic acid (2.1 gm.; 0.022 mole) in benzene (50 ml.) to give white crystalline dimethylgallium dimethylphosphinate and methane. The experimental procedure was similar to that described for the preparation of dimethylaluminium dimethylphosphinate. The trimethylgallium solution was placed in the flask and the suspension of dimethylphosphinic acid was slowly added. An exothermic reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent. The solvent was removed under reduced pressure, leaving a white residue. Pure dimethylgallium dimethylphosphinate was obtained from this residue by vacuum sublimation (0.01 mm/ 80°C) as a white glistening crystalline solid. It had m.p. 54°C (Found: Ga, 36.1; $Me_2GaO_2PMe_2$ requires Ga, 36.2%)

Molecular Weight.

The molecular weights were determined cryoscopically in benzene. Solutions containing 1.32, 1.98 and 2.16 gm. of dimethylgallium dimethylphosphinate in 100 gm. of benzene gave respectively 389, 375 and 370 for molecular weights. The dimer $[Me_2GaO_2PMe_2]_2$ requires 385.

Infrared Spectrum

The infrared spectrum of dimethylgallium dimethylphosphinate (below 2000 $cm^{-1}$) was recorded as solution in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1300(m), 1294(m), 1200(m), 1164(vs), 1112(w), 1062(vs), 923(vw), 870(vs), 747(m), 733(m), 588(m), 538(m), 483(m), 439(m).

The far-infrared spectrum recorded as solution in benzene is given below:

439(m), 299(w), 283(w).

## Dimethylindium Dimethylphosphinate

### Preparation

Trimethylindium (1.6 gm; 0.0100 mole) in ether (15 ml.) reacted with a suspension of dimethylphosphinic acid (0.8 gm; 0.0085 mole) in ether (15 ml) to give dimethylindium dimethylphosphinate (80%) and methane. The experimental procedure was similar to that described for the previous compound., The trimethylindium solution was placed in the flask and the suspension of dimethylphosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylindium dimethylphosphinate was obtained from this residue by vacuum sublimation (0.01 mm./60-5°C) as a white glistening crystalline solid. It had m.p. 75-6°C (Found: In, 48.2; $Me_2InO_2PMe_2$ requires In, 48.3%). The compound was soluble in organic solvents like ether, benzene, carbon tetrachloride and carbon disulphide.

### Hydrolysis

Dimethylindium dimethylphosphinate (0.1772 gm.) was treated with 2-methoxyethanol in the vacuum line. It dissolved without gas evolution. Addition of 2N-sulphuric acid caused slow evolution of methane at room temperature, and for measurement of methyl content the reaction mixture had to be heated to 80°C (33.1 ml. at S.T.P.). Calculated for 0.1772 gm. dimethylindium dimethylphosphinate 33.4 ml. at S.T.P.

Molecular Weight

The molecular weights were determined cryoscopically in benzene. Solutions containing 1.13 and 1.69 gm. of dimethylindium dimethylphosphinate in 100 gm. of benzene gave respectively 474 and 480 for molecular weights. The dimer $[Me_2InO_2PMe_2]_2$ requires 475.5.

Infrared Spectrum.

The infrared spectrum of dimethylindium dimethylphosphinate (below 2000 $cm^{-1}$) was recorded as solution in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1418(s,sh), 1299(m), 1292(m), 1171(vs), 1151(s), 1121(w), 1057(vs), 920(vw), 866(s), 742(m), 713(m), 528(m), 484(m).

## Dimethylaluminium Diphenylphosphinate

Preparation

Trimethylaluminium (0.7 gm; 0.0098 mole) in benzene

(10 ml.) reacted with a suspension of diphenylphosphinic acid (2.0 gm; 0.0091 mole) in benzene (20 ml.) to give white crystalline dimethylaluminium diphenylphosphinate (75%) and methane. The experimental procedure was similar to that described for the previous compound. The trimethylaluminium solution was placed in the flask and the suspension of diphenylphosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylaluminium diphenylphosphinate was obtained from this residue by vacuum sublimation (0.01 mm./160°C) as a white crystalline solid. It had m.p. 153-6°C. (Found: Al, 9.8; $Me_2AlO_2PPh_2$ requires Al, 9.85%). The compound was soluble in organic solvents like ether, benzene, carbon tetrachloride and carbon disulphide.

Hydrolysis

Dimethylaluminium diphenylphosphinate (0.2056 gm) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. It dissolved in 2-methoxyethanol giving a colourless solution at room temperature with almost complete evolution of methane. The hydrolysis was completed with 2N-sulphuric acid and the methane was measured (33.4 ml. at S.T.P.). Calculated for 0.2056 gm.

dimethylaluminium diphenylphosphinate 33.6 ml. at S.T.P. Addition of 2N-sulphuric acid to the solution of the product of hydrolysis of dimethylaluminium diphenylphosphinate in 2-methoxyethanol caused an immediate precipitation of diphenylphosphinic acid. This was gravimetrically estimated after the removal of 2-methoxyethanol and proper dilution (Found: $Ph_2PO_2$ as $Ph_2PO_2H$, 79.7; $Me_2AlO_2PPh_2$ requires $Ph_2PO_2$ as $Ph_2PO_2H$, 79.6%).

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.59 and 0.89 gm. of dimethylaluminium diphenylphosphinate in 100 gm. of benzene gave in each case 527 for molecular weight. The dimer $[Me_2AlO_2PPh_2]_2$ requires 548.

Infrared Spectrum

The infrared spectrum of dimethylaluminium diphenylphosphinate (below 2000 cm.$^{-1}$) was recorded for solutions in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1431(vs), 1199(vs), 1188(s,sh), 1134(vs), 1072(vs), 1027(m), 998(m), 922(vw), 785(vw), 752(s), 730(s), 691(vs) 683(vs), 620(vw), 604(w), 590(w), 548(m).

## Dimethylgallium Diphenylphosphinate

Preparation.

Trimethylgallium (1.3 gm; 0.011 mole) in benzene (25 ml.) reacted with a suspension of diphenylphosphinic acid (2.1 gm; 0.009 mole) in benzene (15 ml.) to give white crystalline dimethylgallium diphenylphosphinate and methane. The experimental procedure was similar to that described for the previous compound. The trimethylgallium solution was placed in the flask and the suspension of diphenylphosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylgallium diphenylphosphinate was obtained from this residue by vacuum sublimation (0.01 mm./160°C) as a white crystalline solid. It had m.p. 164°C. (Found: Ga, 21.9, $Ph_2PO_2$ as $Ph_2PO_2H$, 68.3; $Me_2GaO_2PPh_2$ requires Ga, 22.0, $Ph_2PO_2$ as $Ph_2PO_2H$, 68.8%). In contrast to the corresponding aluminium compound, it was necessary to heat dimethylgallium diphenylphosphinate with strong hydrochloric acid for complete decomposition, and quantitative precipitation of diphenylphosphinic acid, on diluting with water afterwards. The compound was soluble in organic solvents like ether, benzene, carbon tetrachloride and carbon disulphide.

### Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 1.25, 1.89 and 2.06 gm. of dimethylgallium diphenylphosphinate in 100 gm. of benzene gave respectively 667, 646 and 642 for molecular weight. The dimer $[Me_2GaO_2PPh_2]_2$ requires 633.5.

### Infrared Spectrum.

The infrared spectrum of dimethylgallium diphenylphosphinate (below 2000 $cm^{-1}$) was recorded for solution in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1431(vs), 1203(ms), 1180(s), 1130(vs), 1067(m,sh), 1048(s), 1024(ms) 998(m), 751(ms), 727(s), 700(m,sh), 692(s), 594(m), 564(ms), 534(m).

## Dimethylaluminium Diphenyl-thiophosphinate

### Preparation.

Trimethylaluminium (0.7 gm.; 0.0098 mole) in benzene (15 ml.) reacted with a suspension of diphenylthiophosphinic acid (2.0 gm.; 0.0085 mole) in benzene (20 ml.) to give white crystalline dimethylaluminium diphenyl-thiophosphinate (75%) and methane. The experimental procedure was similar to that described for the preparation of the previous compound. The trimethylaluminium solution was placed in the flask and the suspension of diphenylthiophosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylaluminium diphenylthiophosphinate was obtained from this residue by vacuum sublimation (0.01 mm./160-80°C) as a white crystalline solid. It had m.p. 227-8°C (Found: Al, 9.2; $Me_2AlOSPPh_2$ requires Al, 9.3%). The compound was soluble in organic solvents like ether, benzene and carbon disulphide.

Hydrolysis.

Dimethylaluminium diphenyl-thiophosphinate (0.1456gm) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. The methane was measured (22.2 ml. at S.T.P.). Calculated for 0.1456 gm. dimethylaluminium diphenyl-thiophosphinate 22.5 ml. at S.T.P.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.90 and 1.40 gm. of dimethylaluminium diphenyl-thiophosphinate in 100 gm. of benzene gave respectively 597 and 564 for molecular weights. The dimer $[Me_2AlOSPPh_2]_2$ requires 580.

Infrared Spectrum.

The infrared spectrum of dimethylaluminium diphenyl-thiophosphinate (below 2000 $cm^{-1}$) was recorded for solution in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1439(vs), 1200(m), 1189(m,sh), 1117(s), 1064(ms), 1047(ms), 1026(ms), 999(m), 800(m), 750(s), 746(s,sh), 727(vs), 715(vs), 691(vs), 678(s,sh), 656(m,sh), 629(ms), 612(ms), 568(m), 548(m), 517(vs).

The far-infrared spectrum recorded as solution in benzene is given below:

454(m), 403(m), 355(s), 333(ms,sh).

## Dimethylgallium Diphenyl-thiophosphinate

Preparation.

Trimethylgallium (1.1 gm; 0.0095 mole) in benzene (15 ml.) reacted with a suspension of diphenylthiophosphinic acid (2.0 gm; 0.0085 mole) in benzene (20 ml.) to give white crystalline dimethylgallium diphenyl-thiophosphinate (75%) and methane. The experimental procedure was similar to that described for the preparation of the previous compound. The trimethylgallium solution was placed in the flask and the suspension of diphenylthiophosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white solid. Pure dimethylgallium diphenyl-thiophosphinate was obtained from this

this residue by vacuum sublimation (0.01 mm./160-80°C) as a white crystalline solid. It had m.p. 203-4°C. (Found: Ga, 20.9; $Me_2GaOSPPh_2$ requires Ga, 20.9%). The compound was soluble in organic solvents like ether, benzene and carbon disulphide.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 1.20 and 1.70 gm. of dimethylgallium diphenyl-thiophosphinate in 100 gm. of benzene gave respectively 664 and 676 for molecular weights. The dimer $[Me_2GaOSPPh_2]_2$ requires 666.

Infrared Spectrum

The infrared spectrum of dimethylgallium diphenylthiophosphinate (below 2000 $cm^{-1}$) was recorded for solutions in carbon disulphide in a liquid cell with potassium bromide windows and a 0.1 mm. spacer. The bands observed (excluding the solvent bands) are given below:

1431(vs), 1199(m), 1117(vs), 1089(s), 1066(s), 1027(ms), 999(m), 751(s), 745(s,sh), 720(vs), 707(vs), 692(vs), 676(m), 625(s), 604(vs), 533(s,sh), 523(vs), 509(ms,sh).

The far-infrared spectrum recorded as solution in benzene is given below:

426(m), 389(m), 300(vs), 274(w,sh).

## Dimethylaluminium Dimethyl-dithiophosphinate

Preparation.

Trimethylaluminium (1.6 gm.; 0.0222 mole) in benzene (15 ml.) reacted with a solution of dimethyldithiophosphinic acid (2.5 gm.; 0.0206 mole) in benzene (20 ml.) to give white crystalline dimethylaluminium dimethyl-dithiophosphinate and methane. The trimethylaluminium solution was placed in the flask and the solution of dimethyldithiophosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylaluminium dimethyl-dithiophosphinate was obtained from this residue by vacuum sublimation (0.01 mm./40-5°C) as a colourless rhombic (angles almost equal to 90°) crystalline solid. It had m.p. 103-4°C (Found: Al, 14.5; $Me_2AlS_2PMe_2$ requires Al, 14.8%). The compound was very sensitive to air and inflamed when touched with a drop of water. It did not react with trimethylamine at room temperature. It was soluble in organic solvents like ether, benzene, carbon tetrachloride and carbon disulphide.

Hydrolysis.

Dimethylaluminium dimethyl-dithiophosphinate (0.1450gm) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. It dissolved in 2-methoxyethanol at room temperature giving a colourless solution with almost complete evolution of methane. The hydrolysis was completed with 2N-sulphuric acid and the methane was measured (35.4 ml. at S.T.P.) Calculated for 0.1450gm dimethylaluminium dimethyl-dithiophosphinate 35.7 ml. at S.T.P.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.98 and 1.47 gm. of dimethylaluminium dimethyl-dithiophosphinate in 100 gm. of benzene gave respectively 218 and 206 for molecular weights. The monomer $Me_2AlS_2PMe_2$ requires 182.

Infrared Spectrum.

The infrared spectrum (solution in carbon disulphide) is given below:

1414(s), 1403(s), 1395(ms), 1296(m), 1287(s), 1186(s), 1174(w,sh), 991(w), 948(vs), 912(vs), 853(s), 762(s), 740(s), 729(s), 687(vs), 646(ms,sh), 599(ms), 585(ms), 579(ms), 505(s), 493(m).

The far infrared spectrum (solution in benzene) is given below:

394(w), 348(vs), 310(m), 292(vw), 271(m).

## Methylaluminium Bis(diphenyl-dithiophosphinate).

Preparation.

This compound was obtained in an attempt to prepare dimethylaluminium diphenyl-dithiophosphinate. Trimethylaluminium (0.6gm; 0.008 mole) in benzene (15 ml.) reacted with a solution of diphenyldithiophosphinic acid (2.0gm; 0.008 mole) in benzene (25 ml.) to give white methylaluminium bis(diphenyl-dithiophosphinate), methane and some unreacted trimethylaluminium. The trimethylaluminium solution was placed in the flask and the solution of diphenyldithiophosphinic acid was rapidly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a colourless viscous liquid. More volatile materials were lost on further pumping at 200°C, and a white solid was left behind. The compoundbecame soft at 180°C and melted completely at 260°C.(Found: Al, 4.6; $MeAl(S_2PPh_2)_2$ requires Al, 5.0%).

Hydrolysis.

Methylaluminium bis(diphenyl-dithiophosphinate) was hydrolysed (0.1390) in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. The methane was measured (5.7 ml. at S.T.P.). Calculated for 0.1390 gm.

methylaluminium bis(diphenyl-dithiophosphinate) 5.7 ml. at S.T.P.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 1.0 and 1.5 gm. of methylaluminium bis(diphenyl-dithiophosphinate) in 100 gm . of benzene gave respectively 560 and 541 for molecular weights. The monomer $MeAl(S_2PPh_2)_2$ requires 540.5.

Infrared Spectrum.

The infrared spectrum (solution in carbon disulphide) is given below:

1437(s), 1385(vw), 1337(vw), 1325(vw), 1307(w), 1182(m), 1160(vw), 1105(s), 1101(s), 1068(vw), 1028(m), 1000(m), 985(vw), 969(vw), 920(vw), 813(w), 785(w), 744(s), 709(vs), 689(vs), 673(s), 654(s), 633(m,sh), 612(m), 566(vs), 529(w) 485(s).

The far infrared spectrum (solution in benzene) is given below:

391(s), 373(m,sh), 329(m), 312(m,sh), 230(m).

Aluminium Tris(dimethyl-dithiophosphinate)

Preparation.

Trimethylaluminium (0.4 gm; 0.0055 mole) in benzene (5 ml.) reacted with a solution of dimethyldithiophosphinic acid (2.0gm; 0.0158 mole) in benzene (20 ml.) to give aluminium tris(dimethyl-dithiophosphinate) and methane. The dimethyldithiophosphinic acid solution was placed in the flask and the solution of trimethylaluminium was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white solid. It was heated at 100°C with pumping to drive out any volatile impurities. Pure aluminium tris(dimethyl-dithiophosphinate) was obtained by vacuum sublimation (0.01mm/190°C) as a white crystalline solid (50% yield). It had m.p. 186-8°C. (Found: Al, 6.6; $Al[S_2PMe_2]_3$ requires Al, 6.7%). No methane was detected when a sample of the compound was hydrolysed in the vacuum line with 2N-sulphuric acid.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.97 and 1.40 gm. of aluminium tris(dimethyl-dithiophosphinate) in 100 gm. of benzene gave respectively 429 and 441 for molecular weights. The monomer $Al[S_2PMe_2]_3$ requires 402.5.

Infrared Spectrum.

The infrared spectrum (Nujol mull) is given below: 1290(vw,sh), 1280(m), 1160(vw), 956(s), 944(s), 921(s), 909(s), 858(w), 847(m), 741(m,sh), 729(s), 601(s), 587(ms), 501(m).

The far infrared spectrum (solution in benzene) is given below:

328(vs), 308(s,sh), 272(m), 264(m).

## Dimethylgallium Dimethyl-dithiophosphinate

### Preparation.

Trimethylgallium (1.9 gm.; 0.0165 mole) in benzene (15 ml.) reacted with a solution of dimethyldithiophosphinic acid (2.0 gm; 0.0158 mole) in benzene (20 ml.) to give white crystalline dimethylgallium dimethyl-dithiophosphinate and methane. The trimethylgallium solution was placed in the flask and the solution of dimethyldithiophosphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylgallium dimethyl-dithiophosphinate was obtained from this residue by vacuum sublimation (0.01 mm/100°C) as a white rhombic (angles almost equal to 90°) crystalline solid. It had m.p. 153-4°C (Found: Ga, 30.9; $Me_2GaS_2PMe_2$ requires Ga, 31.0%). The compound was soluble in ether, benzene and carbon disulphide. It did not react with trimethylamine at room temperature.

### Molecular Weight.

This was determined cryoscopically in benzene. Solutions containing 0.93 and 1.39 gm. of dimethylgallium dimethyl-dithiophosphinate in 100 gm. of benzene gave in each case 247 as molecular weight. The monomer $Me_2GaS_2PMe_2$ requires 225.

Infrared Spectrum

The infrared spectrum (solution in carbon disulphide) is given below:

1418(s,sh), 1406(s,sh), 1397(ms), 1292(m), 1282(ms), 1190(ms), 944(vs), 908(vs), 850(s), 761(ms), 735(s,sh), 725(vs), 590(vs), 537(ms), 503(s).

The far infrared spectrum (solution in benzene) is given below:

314(vs), 277(m,sh), 267(s).

## Dimethylindium Dimethyl-dithiophosphinate

Preparation.

Trimethylindium (1.2gm; 0.0075 mole) in ether (·15ml.) reacted with a solution of dimethyldithiophosphinic acid (0.8 gm; 0.0063 mole) in ether (20 ml.) to give white crystalline dimethylindium dimethyl-dithiophosphinate and methane. The trimethylindium solution was placed in the flask and the solution of dimethyldithiophosphinic acid was slowly added. There was a lively reaction with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylindium dimethyl-dithiophosphinate was obtained from this residue by vacuum sublimation (0.01 mm./110-20°C) as a white crystalline solid. It had m.p. 184-5°C. (Found: In, 42.5; $Me_2InS_2PMe_2$ requires In, 42.5%). The compound was soluble in ether, benzene and carbon disulphide.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.49 and 0.74 gm. of dimethylindium dimethyl-dithiophosphinate in 100 gm. of benzene gave respectively 291 and 293 for molecular weights. The monomer $Me_2InS_2PMe_2$ requires 270.

Infrared Spectrum.

The infrared spectrum (solution in carbon disulphide) is given below:

1416(ms,sh), 1406(m,sh), 1397(m), 1294(w), 1284(m), 1147(vw), 948(s), 911(s), 898(w,sh), 852(m), 738(m), 724(ms), 596(s), 508(w), 496(ms).

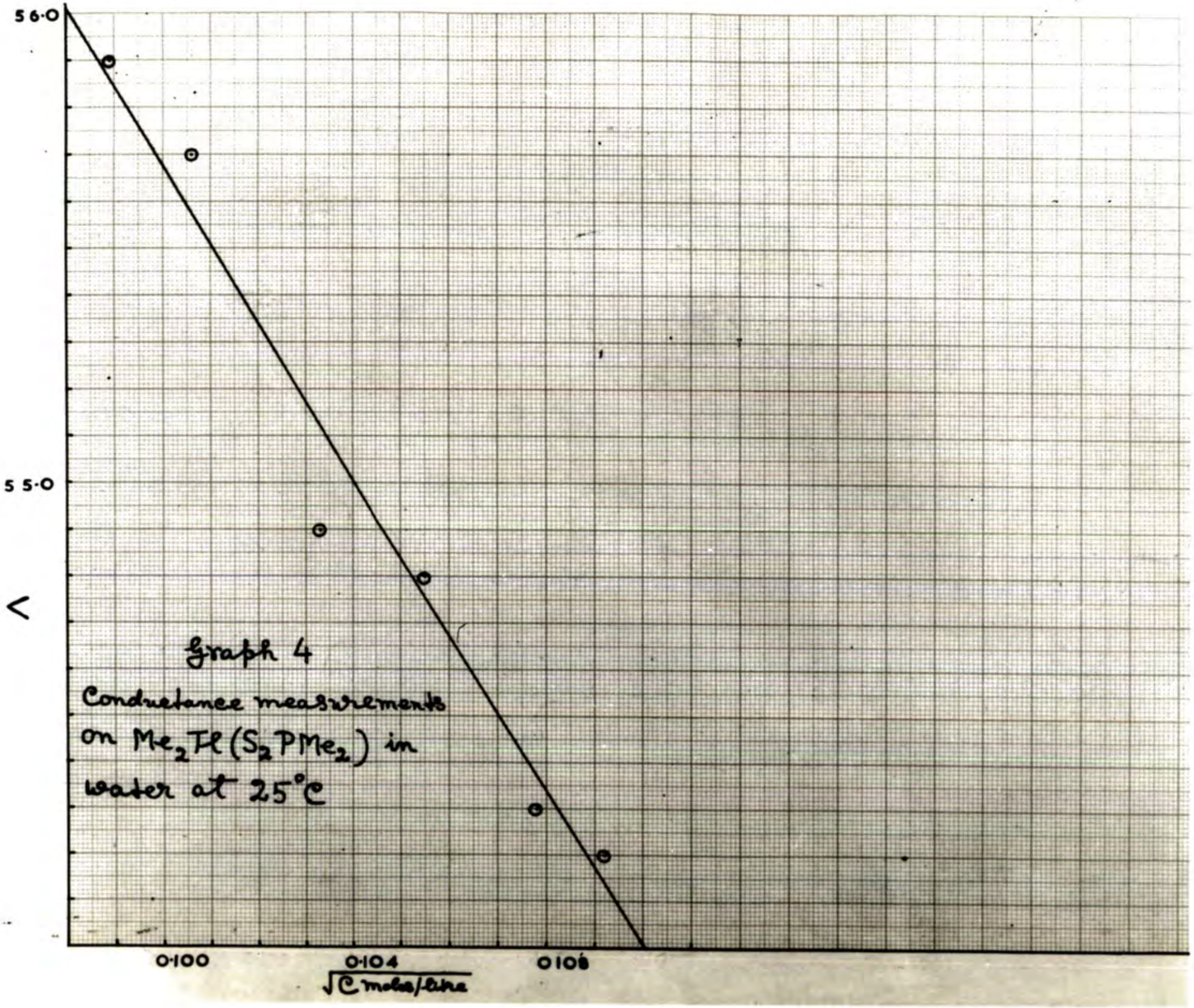
The far infrared spectrum (solution in benzene) is given below:

323(m,sh), 313(s), 271(m), 256(m).

Dimethylthallium Dimethyl-dithiophosphinate.

Preparation.

A solution of dimethylthallium cyanide (1.0 gm.; 0.0038 mole) in water (50 ml.) reacted with a solution



Graph 4

Conductance measurements on $Me_2Tl(S_2PMe_2)$ in water at 25°C of dimethyldithiophosphinic acid (0.5 gm.; 0.0038 mole) in ethanol (15 ml.) to give a white precipitate of dimethylthallium dimethyl-dithiophosphinate in about 60% yield. It was filtered and purified by recrystallisation from hot ethanol as a white glistening solid. The compound started to decompose slowly at 185°C and rapidly turned into a black mass at 200°C (Found: H, 3.4; C, 13.3; $Me_2TlS_2PMe_2$ requires H, 3.3; C, 13.4%). It was slightly soluble in water but insoluble in benzene.

Conductance Measurements.

The conductance measurements were done at 25°C in water. The results are given below:

| $\sqrt{C(\text{mole } l^{-1})}$ | $\Lambda$ |
|---|---|
| 0.0989 | 55.9 |
| 0.1006 | 55.7 |
| 0.1033 | 54.9 |
| 0.1055 | 54.8 |
| 0.1078 | 54.3 |
| 0.1092 | 54.2 |

Infrared Spectrum.

The infrared spectrum (pressed potassium bromide disc) is given below:

1404(m), 1290(vw), 1280(ms), 1170(vw), 1087(vw), 943(vs), 909(vs), 847(m), 797(s), 733(m), 710(s), 588(vs), 540(m), 496(ms).

The far infrared spectrum (nujol mull) is given below:

295(m), 287(w,sh), 233(ms).

### Caesium Dimethyl-dithiophosphinate

Preparation.

A solution of caesium carbonate (2.6 gm.; 0.008 mole) in water (15 ml.) was slowly added to a solution of dimethyl dithiophosphinic acid (2.0 gm.; 0.016 mole) in ethanol (15 ml.). A lively reaction took place with gas evolution. The solvent was removed under reduced pressure, leaving a white crystalline solid. It was purified by recrystallisation from a mixture of water and alcohol (Found: H, 2.5; C, 9.3; $Cs[S_2PMe_2]$ requires H, 2.3; C, 9.3%).

Infrared Spectrum.

The infrared spectrum (pressed potassium bromide disc) is given below:

1418(m), 1404(ms), 1290(m), 1279(s), 1105(vw), 952(s), 915(vs), 847(s), 734(s), 715(vs), 606(vs), 505(vs).

The far infrared spectrum (nujol mull) is given below:

282(s), 220(s).

## Dimethylaluminium Benzenesulphinate

Preparation.

Trimethylaluminium (1.2 gm.; 0.0166 mole) in benzene (15 ml.) reacted with a solution of benzene sulphinic acid (2.1 gm.; 0.0147 mole) in the same solvent (100 ml.) to give white crystalline dimethylaluminium benzenesulphinate and methane. The trimethylaluminium solution was placed in the flask and the solution of benzene sulphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylaluminium benzene-sulphinate was obtained from this residue by vacuum sublimation (0.01 mm./120-30°C) as a white crystalline solid. It had m.p. 61-2°C. (Found: Al, 13.4; $Me_2AlO_2SPh$ requires Al, 13.6%). The compound was soluble in ether, benzene, and carbon disulphide.

Hydrolysis.

Dimethylaluminium benzene-sulphinate (0.1828 gm.) was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. The methane was measured (40.9 ml. at S.T.P.). Calculatedfor 0.1828 gm. dimethylaluminium benzene-sulphinate 41.3 ml. at S.T.P.

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.74 and 1.09 gm. of dimethylaluminium benzene-sulphinate in 100 gm. of benzene gave in each case 429 for molecular weight. The dimer $[Me_2AlO_2SPh]_2$ requires 396.

Infrared Spectrum.

The infrared spectrum (solution in carbon disulphide) is given below:

1445(s,sh), 1192(ms), 1089(m), 1027-1005(s,broad band), 980-970(s, broad band), 753(s), 704(vs), 688(vs), 620(m), 612(w), 588(w).

## Dimethylgallium Benzene-sulphinate

Preparation.

Trimethylgallium (1.5 gm.; 0.0130 mole) in ether (15 ml.) reacted with a solution of benzene sulphinic acid (1.7 gm.; 0.0119 mole) in ether (50 ml.) to give white crystalline dimethylgallium benzene-sulphinate and methane. The trimethylgallium solution was placed in the flask and the solution of benzene sulphinic acid was slowly added. A lively reaction took place with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylgallium benzene-sulphinate was obtained from this residue by vacuum sublimation (0.01 mm./120°C) as a white crystalline solid. It had m.p. 56-7°C. (Found: Ga, 28.8; $Me_2GaO_2SPh$ requires

Ga, 28.9%).

Molecular Weight.

The molecular weights were determined cryoscopically in benzene. Solutions containing 0.77 and 1.13 gm. of dimethylgallium benzene-sulphinate in 100 gm. of benzene gave respectively 495 and 477 for molecular weights. The dimer $[Me_2GaO_2SPh]_2$ requires 482.

Infrared Spectrum.

The infrared spectrum (solution in carbon disulphide and benzene) is given below:

1445(s), 1203(s), 1124(m), 1082(m), 1048(m), 1005(vs), 941(s), 735(s), 697(s), 683(s), 584(s), 539(s), 459(s).

The far infrared spectrum (benzene solution) is given below:

420(s), 352(s), 329(ms,sh), 275(w).

<u>Barium Benzene-sulphinate</u>

Preparation.

Benzene sulphinic acid (2.1 gm.) dissolved in about 50 ml. water was shaken with excess of barium carbonate, in an atmosphere of nitrogen. There was a lively reaction with gas evolution. The reaction mixture was slightly heated towards the end. It was diluted to 200 ml. and the unreacted barium carbonate was removed by filtration. The barium benzene-sulphinate was purified by recrystallisation from water [Found: H, 2.5; C, 34.2; $Ba(O_2SPh)_2$ requires H, 2.4;

C, 34.35%].

Infrared Spectrum.

The infrared spectrum (pressed potassium bromide disc) is given below:

1443(ms), 1088(m), 1020(m,sh), 986(vs), 971(s), 960(vs), 751(m,sh), 744(s), 704(ms), 689(s), 581(s), 505(ms), 487(m).

Dimethylaluminium Methane-sulphonate

Preparation.

Trimethylaluminium (1.3 gm.; 0.0180 mole) in benzene (15 ml.) reacted with a well-shaken emulsion of methane sulphonic acid (1.7 gm.; 0.0177 mole) in benzene (30 ml.) to give white crystalline dimethylaluminium methane-sulphonate and methane. The trimethylaluminium solution was placed in the flask and the emulsion of methane-sulphonic acid was slowly added. There was a lively reaction with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylaluminium methane-sulphonate was obtained from this residue by vacuum sublimation (0.01 mm./100°C) as a white crystalline solid. It had m.p. 65-6°C. (Found: Al, 17.7; $Me_2AlO_3SMe$ requires Al 17.7%).

Hydrolysis.

Dimethylaluminium methane-sulphonate (0.1042 gm.)

was hydrolysed in the vacuum line with 2-methoxyethanol and 2N-sulphuric acid. The methane was measured (30.4 ml. at S.T.P.). Calculated for 0.1042 gm. dimethylaluminium methane-sulphonate 30.7 ml. at S.T.P.

Molecular Weight.

The molecular weights were determined cryoscopically in benzene. Solutions containing 0.74 and 1.11 gm. of dimethylaluminium methane-sulphonate in 100 gm. of benzene gave respectively 432 and 467 for molecular weights. The trimer $[Me_2AlO_3SMe]_3$ requires 456.

Infrared Spectrum.

Examination of the infrared spectrum of dimethylaluminium methane-sulphonate was restricted by the difficulty of finding a suitable solvent, for example, the substance was sparingly soluble in carbon disulphide. It was also sensitive to air.

## Dimethylgallium Methane-sulphonate

Preparation.

Trimethylgallium (1.7 gm.; 0.0147 mole) in benzene (20 ml.) reacted with a well-shaken emulsion of methane sulphonic acid (1.4 gm.; 0.0145 mole) in benzene (30 ml.) to give white crystalline dimethylgallium methane-sulphonate and methane. The trimethylgallium solution was placed in the flask and the emulsion of methane-sulphonic acid was slowly added. There was a lively reaction with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylgallium methane-sulphonate was obtained from this residue by vacuum sublimation (0.01 mm/100°C) as a white crystalline solid. It had m.p. 79-80°C. (Found: Ga, 35.7; $Me_2GaO_3SMe$ requires Ga, 35.8%).

Molecular Weight.

This was determined cryoscopically in benzene. Solutions containing 0.67 and 1.01 gm. of dimethylgallium methane-sulphonate in 100 gm. of benzene gave in each case 587 for molecular weight. The trimer $[Me_2GaO_3SMe]_3$ requires 584.

## Dimethylgallium Dimethylarsinate

Preparation.

Crystals of dimethylarsinic acid (1.4 gm.; 0.0101 mole) were slowly added to a solution of trimethylgallium (1.3 gm. in 20 ml. benzene; 0.0113 mole) in an atmosphere of nitrogen. There was a slow reaction with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylgallium dimethylarsinate was obtained from this residue by vacuum sublimation (0.01 mm./110°C) as a white glistening crystalline solid, nearly quantitative yield. It had m.p. 144-5°C. (Found: Ga, 29.8; $Me_2GaO_2AsMe_2$ requires Ga, 29.9%).

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 1.08 and 1.60 gm. of dimethylgallium dimethylarsinate in 100 gm. of benzene gave respectively 475 and 502 for molecular weights. The dimer $[Me_2GaO_2AsMe_2]_2$ requires 473.

Infrared Spectrum.

The infrared spectrum (solution in carbon disulphide) is given below:

1267(m), 1259(w), 1194(m), 897(s), 884(vs), 865(s), 818(m), 738(ms,sh), 725(ms), 675(vs), 642(m), 580(m), 535(m).

The far infrared spectrum (benzene solution) is given below:

433(s), 408(s), 283(ms), 269(m).

## Dimethylgallium Formate.

Preparation.

Trimethylgallium (2.3 gm.; 0.020 mole) in ether (25 ml.) reacted with a solution of formic acid (0.90 gm.; 0.0195 mole) in ether 25 ml.) to give white crystalline dimethylgallium formate and methane. The trimethylgallium solution was placed in the flask and the solution of formic acid was slowly added. There was a lively reaction with gas evolution. The products of the reaction remained dissolved in the solvent, which was removed under reduced pressure, leaving a white residue. Pure dimethylgallium formate was obtained from this residue by vacuum sublimation (0.01 mm/60°C)as colourless crystals. It had m.p. 97-8°C (Found: Ga, 48.1 $Me_2GaO_2CH$ requires Ga, 48.2%).

Molecular Weight.

This was determined cryoscopically in benzene. Solutions containing 0.2 and 0.3 gm. of dimethylgallium formate in 100 gm. of benzene gave in each case 312 for molecular weight. The dimer $[Me_2GaO_2CH]_2$ requires 290.

Infrared Spectrum.

The infrared spectrum from 300 to 2000 $cm^{-1}$ (Nujol mull and $C_2Cl_4$ solution) is given below:

1616(vs), 1587(vs), 1555(vs), 1377(vs), 1353(vs), 1206(ms), 1202(ms), 1192(ms), 823(s), 738(vs), 720(s,sh), 699(ms,sh), 606(s), 549(m), 382(m).

Dimethylgallium Acetate

Preparation.

Dimethylgallium acetate was prepared from the reaction between trimethylgallium (1.70 gm.; 0.0148 mole) and acetic acid (0.80gm; 0.0133 mole) in benzene. It was purified by vacuum sublimation (0.01 mm/90-5°C) as a white crystalline solid (m.p. 162-3°C).

Infrared Spectrum.

The infrared spectrum from 300 to 2000 $cm^{-1}$ (Nujol mull and $C_2Cl_4$ solution) is given below:

1754(w), 1534(vs), 1471(vs), 1408(vs), 1203(s), 1053(m), 1030(ms), 965(m), 761(ms,sh), 740(s), 695(vs), 612(m), 601(s), 549(ms), 513(m), 329(m).

## Diethylboron Acetate

Preparation.

Diethylboron acetate was prepared from the reaction between triethylborane (2.6 gm; 0.0265 mole) and acetic acid (1.5 gm.; 0.0250 mole) in ether, as described by Meerwein and Sönke.(47)

Molecular Weight.

Molecular weights were determined cryoscopically in benzene. Solutions containing 0.6, 0.9 and 1.0 gm. of diethylboron acetate in 100 gm. of benzene gave respectively 170, 180 and 171 for molecular weights.

Infrared Spectrum.

The infrared spectrum from 500 to 2000 $cm^{-1}$ (Nujol mull and $C_2Cl_4$ solution) is given below (principal bands only).

1709(s), 1610(s), 1587(ms), 1488(m,sh), 1468(s), 1418(m), 1300(m), 1289(m), 1247(w), 1064(s), 1031(s), 769(s), 735(s).

## Dimethylgallium ($d^3$) Acetate

Preparation.

Dimethylgallium ($d^3$) acetate was prepared from the reaction between trimethylgallium (1.5 gm; 0.0130 mole) and ($d^4$) acetic acid (0.7 gm; 0.0109 mole) in benzene. It was purified by vacuum sublimation (0.01 mm/100-10°C) as a white crystalline solid (m.p. 164-5°C).

Infrared Spectrum.

The infrared spectrum from 300 to 2000 cm$^{-1}$ (Nujol mull and $C_2Cl_4$ solution) is given below:

1754(w), 1515(vs), 1475(vs), 1447(s), 1203(s), 1092(w), 1055(m), 1029(ms), 929(ms), 918(ms), 841(s), 758(s,sh), 735(vs), 696(ms), 661(vs), 600((vs), 548(ms), 526(m), 471(w), 314(m).

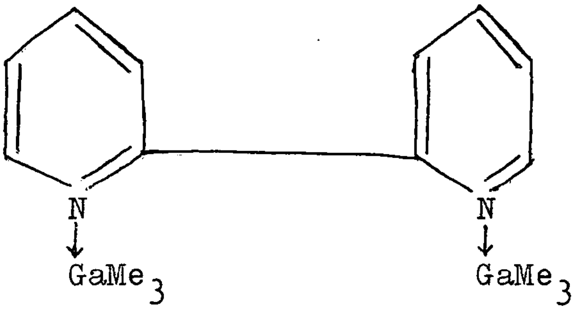
# APPENDIX I

## Co-ordination Compounds of Bipyridyl with Alkyls and Hydrides of Group III Elements.

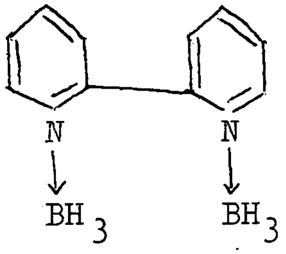
Addition compounds of 2,2'-bipyridyl with the alkyls and halides of beryllium have been described.(57) The compounds $BipyBeCl_2$, $BipyBeBr_2$, $BipyBeI_2$, $BipyBePh_2$, $BipyBeMe_2$ and $BipyBeEt_2$ were found to be white, pale cream, yellow, yellow, yellow and red respectively. Ultraviolet spectra of these compounds were measured, and it was suggested that the transition causing these colours is an electron transfer from one of the Be-X bonds (X = Cl, Br, $CH_3$ etc.) to the lowest unoccupied π-orbital of bipyridyl or, in the case of halides, from lone pairs on the halogen atom.

Therefore, it was considered of interest to investigate the interaction of bipyridyl with the alkyls and hydrides of group III elements. The compounds $BipyAlH_3$, $BipyAlMe_3$, $BipyAlEt_3$ and $BipyGaMe_3$ were found to be violet, yellow, red and blue-green respectively in colour. However, the $AlH_3$ and $AlEt_3$ adducts were fairly unstable and decomposed readily on standing. The blue-green crystals of the gallium compound appeared to loose colour on standing. The alkyl adducts were prepared from the components in ether, and $Me_3NAlH_3$(127) was used as the source of aluminium hydride for the complex $BipyAlH_3$. Satisfactory analyses were obtained for $BipyAlMe_3$, which was insoluble in organic solvents. Molecular weight determinations or ultraviolet spectroscopic measurements were restricted by the insolubility or instability of these materials (compare$^{(57)}$ $BipyBeEt_2$ which was found to be monomeric in benzene). The structures of these compounds have not yet been established. After this work was completed, it has been claimed that the adducts of the type $BipyAlR_3$, are monomeric in benzene$^{(128)}$.

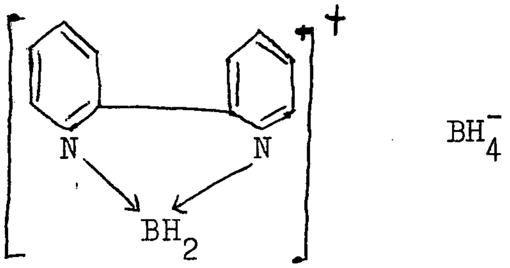
Bipyridyl was dissolved in excess of trimethylgallium to give a colourless solution. Removal of the unreacted trimethylgallium under reduced pressure, left a white solid which had the composition $Bipy(GaMe_3)_2$. The following structure is suggested for this compound.



The compound $Bipy(BH_3)_2$ was prepared from diborane and bipyridyl in ether. This was insoluble in organic solvents, and it was not possible to distinguish between structures I and II.



I.



II.

## EXPERIMENTAL

### Bipyridyl Trimethylalane.

Bipyridyl (1.60 gm; 0.010 mole) was placed in a two-neck round-bottomed flask (100 ml.) attached to the vacuum line, ether (15 ml.) was condensed on it and allowed to warm to dissolve the bipyridyl. The trimethylaluminium (0.77 gm; 0.010 mole) was then condensed on it, and the reactants were warmed from liquid air temperature. A yellow insoluble precipitate was obtained, which was purified by washing with ether (Found: Al, 11.75; $BipyAlMe_3$ requires Al, 11.8%). It was sensitive to air, and decomposed at 140°C without melting. The compound was insoluble in benzene at room temperature. An attempt was made to extract and crystallise it from hot benzene, using a soxhlet fitted with a sintered disc. The compound was easily extracted with hot benzene giving a red solution which did not deposit crystalson cooling to room temperature, evidently it had decomposed.

Bipyridyl trimethylalane (0.0920 gm.) on hydrolysis with 2-methoxyethanol and 2N-sulphuric acid gave 25.9 ml. of methane at S.T.P. Calculated for 0.0920 gm. $BipyAlMe_3$ 27.0 ml. at S.T.P.

### Bipyridyl Bis(trimethylgalane)

Bipyridyl (0.2066 gm; 0.00132 mole) was placed in a two-neck round-bottomed flask (100 ml.) attached to the vacuum line through a 4 mm. tap. A measured amount of trimethylgallium (441.6 ml. at S.T.P.) was condensed on it. The tap was closed and the reactants allowed to reach room temperature. The bipyridyl dissolved in liquid trimethylgallium giving a colourless solution. The excess of trimethylgallium was condensed back and measured (381.2 ml. at S.T.P.) Hence, 60.4 ml. of trimethylgallium had reacted with the bipyridyl. Thus, 0.00132 mole of bipyridyl reacted with 0.00269 mole of trimethylgallium to give white bipyridyl bis(trimethylgalane), Bipy$(GaMe_3)_2$.

### Bipyridyl Diborane

Diborane (from $NaBH_4$ and $BF_3.OEt_2$ in diglyme) was passed through a solution of bipyridyl (2 gm.) in ether (75 ml.). A white insoluble precipitate of bipyridyl diborane was obtained, which was purified by washing with ether (Found: C, 65.4, H, 3.6; Bipy$B_2H_6$ requires C, 65.4, H, 3.3%). It was stable to air, and decomposed at 130°C without melting.

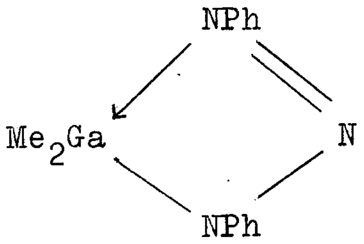
The infrared spectrum from 400 to 2775 $cm^{-1}$ (pressed potassium iodide disc) is given below (principal bands only). 2398(vs), 2358(vs), 2339(vs,sh), 2294(s,sh), 1616(ms), 1582(m), 1475(s), 1443(ms), 1295(m), 1256(w), 1181(vs), 1163(s,sh), 1136(m), 1119(m), 1096(s), 1071(m), 1030(m), 938(m,sh), 941(ms), 793(vs), 752(m), 559(w,sh), 552(w).

## APPENDIX II

### A Gallium Derivative of Diazoaminobenzene

The compound, $Me_2GaNPh.N:NPh$ was prepared by the reaction between trimethylgallium (1.8 gm.; 0.0156 mole) and diazoaminobenzene (3.0 gm.; 0.0152 mole recrystallized from ethanol shortly before use) in benzene, under an atmosphere of nitrogen. It was purified by vacuum sublimation (0.01 mm/100°C) as a yellow crystalline solid (2.3 gm; 50% yield). The compound was soluble in organic solvents. It had m.p. 53-55°C (Found: Ga, 23.3; $Me_2GaNPh.N:NPh$ requires Ga, 23.6%).

The molecular weight was determined cryoscopically in benzene. Solutions containing 1.6 and 2.5 gm. of the compound in 100 gm. of benzene gave in each case 332 for molecular weight. The monomer $Me_2GaNPh.N:NPh$ requires 296. Therefore, the following structure is suggested for this compound.



Bands at 595 and 545 $cm^{-1}$ were observed due to $GaMe_2$ asymmetrical and symmetrical stretching modes respectively in the infrared spectrum of the compound

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