

COORDINATION COMPOUNDS OF ALKYL GALLIUM HYDRIDES

by

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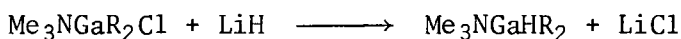
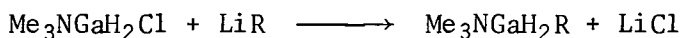
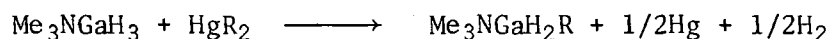
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### Abstract

Although the organo hydride derivatives of boron and aluminum are well characterized, little work has been reported on the corresponding gallium systems. The present study was initiated to determine the relative stabilities and reactivity of organo gallium hydride derivatives as compared with the stabilities and reactions of the corresponding compounds of boron and aluminum.

Various preparative routes to this new class of gallium compounds have been investigated. These include the use of organo-mercury, organo-lithium and lithium hydride derivatives in reactions with gallium hydride and gallium alkyl compounds and their halogen substituted derivatives:



A fourth preparative method involves disproportionation reactions between gallium hydride compounds and organo gallium compounds to yield the mixed organo hydride derivatives. Alkyl-hydride disproportionation reactions were also examined using organo and hydride derivatives of different Group IIIB elements in order to obtain a better understanding of the exchange process.

Both infrared and proton NMR spectroscopy have been used extensively in following the progress of these reactions and in the characterization of the products.

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## VII. Introduction

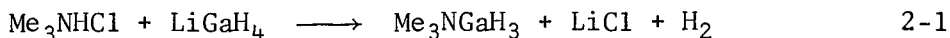
Since the discovery of gallium in 1875 (1) the knowledge of its chemistry has increased steadily but only modestly in comparison to its congeners, boron and aluminum. Quite recently, though, with the use of gallium in the electronics industry, renewed emphasis is being placed on the study of gallium. Reviews of gallium chemistry have appeared in 1936 in Gmelin (2), in 1937 by Einecke (3), in 1955 by P. de le Breteque (4) and more recently in 1963 by N. N. Greenwood (5) and J. C. Hutter (6) and in 1966 by Sheka et al (7).

In naming gallium hydride coordination compounds the  $\text{GaH}_3$  entity is termed gallane and is treated as the parent compound. Derivatives in which the formal coordination number of gallium is three, are named accordingly; e.g.  $\text{GaHCl}_2$  dichlorogallane,  $\text{GaH}_2\text{NMe}_2$  dimethylaminogallane,  $\text{GaMe}_3$ , trimethylgallane. Addition compounds in which the coordination of gallium is four or greater are named thus;  $\text{Et}_3\text{PGaH}_3$  triethylphosphine gallane,  $\text{Me}_3\text{NGaHCl}_2$  trimethylamine dichlorogallane. Similar nomenclature is applied to the analogous boron and aluminum compounds. The only exceptions to this nomenclature are the well established names, such as lithium gallium hydride for the compound  $\text{LiGaH}_4$ .

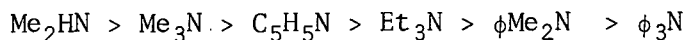
One important characteristic of Group IIIB compounds is their electron deficiency, that is, in the trivalent state one of the four orbitals ( $n_s$ ,  $n^p_x$ ,  $n^p_y$ ,  $n^p_z$ ) available for bonding is empty. This characteristic is

exemplified by the dimeric and polymeric nature of a great many of these compounds, and by their ability to form dative bonds with strong electron donors. The energy change is small in going from planar  $sp^2$  to tetrahedral  $sp^3$  configurations if electrons can be supplied to the vacant orbitals. This can be achieved by forming either multi-centred bridged bonds as in the boron hydrides or donor-acceptor bonds such as the  $N \rightarrow Al$  dative bond in  $Me_3NAlH_3$ .

Coordination compounds of gallane,  $GaH_3$  and halogenogallanes,  $GaH_{3-n}X_n$ , with amines and phosphines have been investigated extensively over the past few years (8-12). The first adduct prepared and the most stable is trimethylamine gallane,  $Me_3NGaH_3$ , which is prepared at room temperature in ether solution by the reaction:

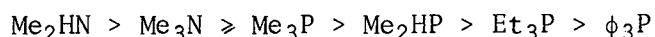


A 2:1 adduct can also be prepared by adding more amine gas to the compound, but this 2:1 adduct decomposes at  $-21^\circ C$ . Though dimethylamine is a stronger donor to gallane than trimethylamine, the adduct  $Me_2HNGaH_3$  slowly loses one mole of hydrogen to form the dimer  $[Me_2NGaH_2]_2$ . Other amine ligands have been used with gallane but their adduct strengths are considerably weaker and their ability to coordinate decreases in the sequence;



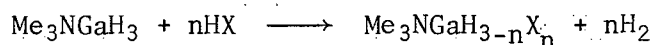
Trimethylphosphine,  $Me_3P$ , has also been used as a ligand and its adduct strength is almost equal to that of trimethylamine. This is in contrast to

the great instability (10) of the aluminum analogue  $\text{Me}_3\text{PAlH}_3$  which can not be isolated. Other phosphine ligands form much less stable adducts with the gallane moiety,  $\text{GaH}_3$ , and a 2:1 adduct with trimethylphosphine is not observed, even at low temperatures (10). The sequence of ligand strengths is;

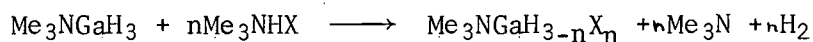


Arsine ligands form adducts with gallane but these are too unstable to isolate as are those formed with oxygen and sulphur ligands.

Halogenogallane adducts with trimethylamine have been prepared by the following reactions;

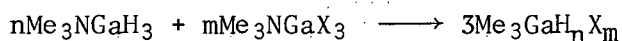


where "n" = 1 or 2 and "X" = Cl or Br



where "n" = 1 and "X" = Cl or Br; "n" = 2 and "X" = Cl.

or by the reaction;



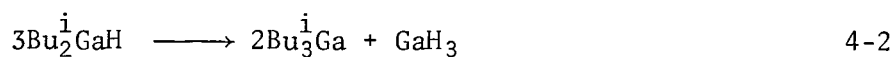
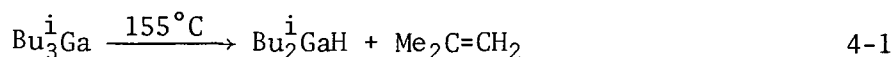
where "n" + "m" = 3, "X" = Cl, Br or I and "n" = 1, or 2 with Cl.

The coordination chemistry of some of the simpler alkyl gallanes have also been thoroughly studied (13,14). Coordination compounds of trimethylgallane with all the trimethyl derivatives of Group VB and dimethyl derivatives of Group VIB elements have been prepared by mixing trimethylgallane with the appropriate ligand. The strength of the donor-acceptor bond in compounds

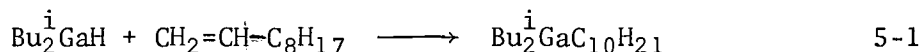
formed with Group VB ligands decreases in the sequence  $N > P > As > Sb$ . For Group VIB an irregular sequence is observed  $O > Se > S = Te$ . This sequence differs from Group VIB ligand strengths with trimethylalane where a regular decrease in ligand strength down the Group is observed. The irregularity in the trimethylgallane series is thought to be influenced by d-orbital participation in bonding. The chemical shift of Ga-Me in the trimethylgallane adducts can be related to the strength of the donor-acceptor bond (17); those of greatest bond strength i.e. greatest dissociation energy, have largest  $\tau$  values.

Little work has been carried out on the chemistry of organogallanes and none has been reported on coordination compounds of the type  $DGaH_{3-n}R_n$  where "D" represents a Lewis base, i.e.  $Me_3N$ , and "R" represents a simple alkyl group e.g. Me, or Et. The earliest report of an organogallane was by Wiberg (15) who reported the isolation of  $(Me_2GaH)_2$  from the products obtained by cooling a mixture of  $Me_3Ga$  and  $H_2$  after it had been subjected to a gas discharge at low pressure. Doubt (16) has been cast on this result by a later investigation and it now appears that  $(Me_2GaH)_2$  is not prepared in this manner.

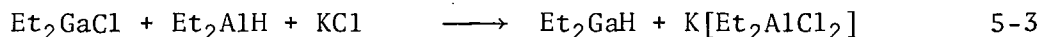
A hydride species is postulated by Eisch (18) as an intermediate in the thermal decomposition of triisobutylgallane



In the presence of olefins such as 1-decene, the diisobutylgallane formed as in equation 4-1 adds rapidly to the olefin.



Eisch was also able to prepare (19) the uncoordinated hydride, diethylgallane,  $\text{Et}_2\text{GaH}$ , by the successful exchange reaction between a gallium halide and an aluminum hydride. The yield of the desired product was low, but by the reaction he was able to prepare considerable quantities of the hydride.

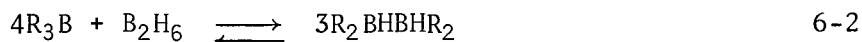
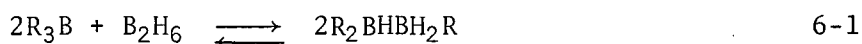


Diethylgallane was found to add very readily to olefins to form unsymmetrical organogallanes but these readily disproportionated to form symmetrical organo-gallium compounds.

The only other significant preparations of uncoordinated gallanes have been the preparations of a few compounds of the form  $\text{GaH}_2\text{R}$  and  $\text{GaHR}_2$  as well as the preparation of an unstable polymeric  $(\text{GaH}_3)_x$  (20). The compounds of the form  $\text{GaH}_2\text{R}$  prepared are  $\text{GaH}_2\text{Cl}$  (11) and  $\text{GaH}_2\text{NMe}_2$ ,  $\text{GaH}_2\text{PMe}_2$  (12) and these are dimeric as expected. Compounds of the form  $\text{GaHR}_2$  have been prepared by Schmidbaur et al (21,22) who were able to prepare  $\text{GaHCl}_2$  and  $\text{GaHBr}_2$ , dimers, in good yield from trimethylsilane and the appropriate halide. The Ga-H bond of these compounds is found to readily hydrogallate a great many unsaturated organic groups (23). Almost all the uncoordinated

gallanes are difficult to prepare pure and are found to be much less stable than the corresponding alanes.

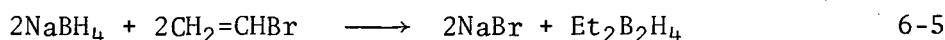
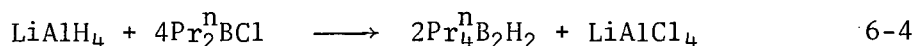
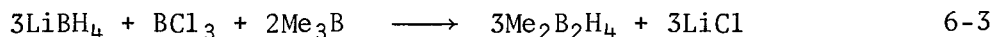
In contrast to the sparsely known organogallanes, the organohydride derivatives of the preceding members of Group IIIB are well characterized. Uncoordinated alkyl boranes have been known since 1935 when Schlesinger and coworkers investigated the reaction of boron trialkyls with diborane (24-27).



"R" = Me, Et, Pr

All five of the possible mono to tetra alkyl boranes have been prepared by this manner.

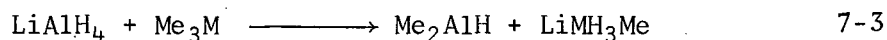
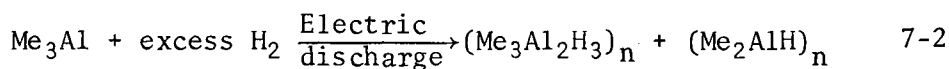
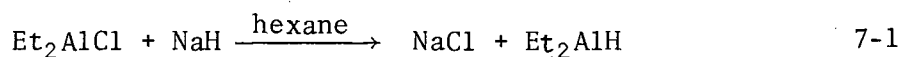
More modern preparative methods to this type of compound utilize the complex metal hydrides as starting materials (28-31).



Uncoordinated organoboranes are usually dimers with hydrogen bridges preferred over alkyl or aryl bridges. They are readily oxidized and very readily add under mild conditions to all types of aliphatic and aromatic olefins and with dienes and acetylene hydrocarbons.



Uncoordinated alkyl aluminum hydrides have also been synthesized by a variety of methods (32-34).

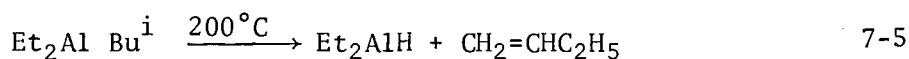


where "M" = B, Al, Ga

A more general method involves the direct olefin and hydrogen reaction with aluminum metal.



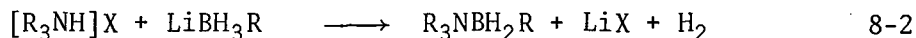
Thermal decomposition of higher trialkyls has also produced hydride species (35).



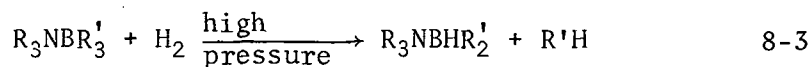
Organo alanes readily add across the double bond of 1-olefins but with much greater difficulty across 2- or higher olefins. Mixed organoalanes tend to disproportionate to form symmetric organoalanes. Exchange of alkyl groups of organoalanes occurs very rapidly in non-polar solvents but exchange is slowed down in polar solvents (36).

Coordination compounds of organo boron hydrides and organo aluminum hydrides are well characterized. Thus organo-boron hydrides of the form  $\text{BR}_{3-n}\text{H}_n$  (where "n" = 0, 1, 2, 3) react with amines to form 1:1 amine boranes.

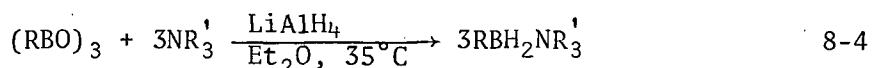
A large number of these 1:1 addition compounds with cyclic and acyclic, primary, secondary and tertiary amines have been reported (37).



where "X" = halogen.

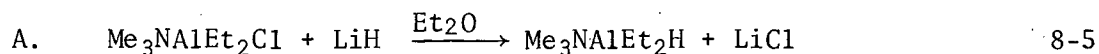


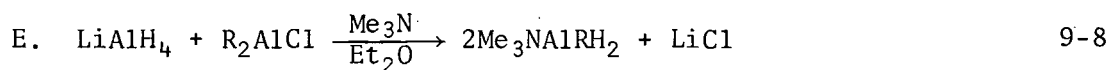
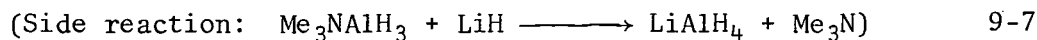
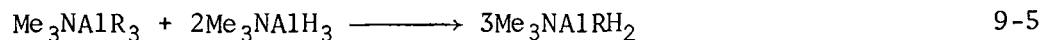
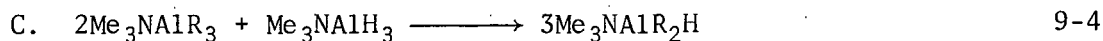
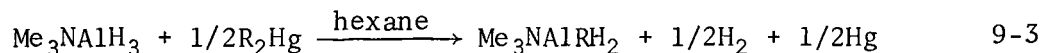
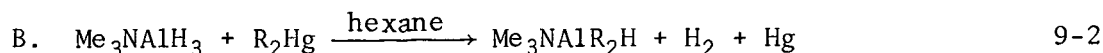
Amine organoboranes have also been synthesized by other procedures. Hawthorne (38,39) demonstrated that amine monoalkylboranes could be obtained in good yield by the reaction of B-trialkyl boroxines  $(-\text{BR}-\text{O}-)_3$  with  $\text{LiAlH}_4$  in the presence of amines.



Highly pure amine-organoboranes are thermally and hydrolytically more stable than the uncoordinated species. They have found use as reagents in some specific reactions because of their reactivity towards some carbonyls in aldehydes and ketones and towards mercaptans (44).

Alkyl aluminum hydride amine complexes have been investigated and characterized by several groups of workers in recent years (40-42). The synthetic methods employed are listed below:





The reactivity of the Al-C and Al-H bonds is greatly reduced in forming 1:1 adducts and this may be utilized in preparing hitherto unpreparable highly labile organo aluminum compounds (43).

The  $\text{R}_3\text{Al}$  moiety is a stronger acceptor than the  $\text{R}_3\text{B}$  moiety, and the organo aluminum forms 1:1 donor-adduct complexes with most Group VB and VIB ligands. The strength of the ligand-Al bond decreases regularly down a group and with Group VB ligand forming stronger bonds than Group VIB ligands.

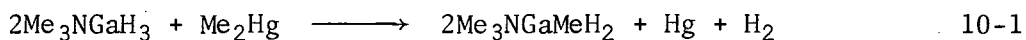
The present investigation was initiated to determine the relative stabilities of organogallane derivatives as compared with the stabilities of the corresponding well known boron and aluminum compounds. In addition it was hoped that the study would further expand our knowledge of the coordination chemistry of gallium compounds, and in particular, would demonstrate the effect of having an organo group attached to the gallium on the acceptor properties of the gallane moiety,  $\text{GaH}_3$ .

## VIII. Discussion and Results

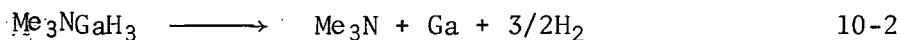
### A. Trimethylamine Adducts of Organogallanes

The low thermal stability of the known uncoordinated alkylgallanes (19) suggested that the most profitable line of approach to the desired compounds would be via substitution reactions involving introduction of organo groups into coordinated gallium compounds. Several methods of synthesis were attempted.

The first synthetic route involved the reaction of trimethylamine gallane with organomercury compounds, both ether and benzene being used as solvents.

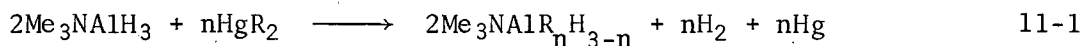


At room temperature or below, no product was formed, even after one day. The only reaction occurring was the decomposition of the starting material, trimethylamine gallane.



At higher temperatures a definite product according to equation 10-1 did result. It was found that this reaction occurs more favorably under

refluxing conditions when the hydrogen generated was allowed to escape, rather than in a sealed Carius tube where the excess pressure would tend to stop or even reverse the reaction. A higher temperature, such as in refluxing benzene rather than diethyl ether, gave a higher yield, though even under these conditions the yield of product was low due to the thermal instability of both the  $\text{Me}_3\text{NGaH}_3$  starting material and the trimethylamine monomethylgallane,  $\text{Me}_3\text{NGaMeH}_2$ , product. The presence of finely divided gallium metal, from the decomposition of  $\text{Me}_3\text{NGaH}_3$ , see equation 10-2, in the reaction system probably catalyses further decomposition of the product into hydrogen, methane and trimethylamine gases and gallium metal. This type of autocatalytic decomposition has been noted in a number of gallium systems (18,45). The analogous reaction in aluminum chemistry gave quite high yields of trimethylamine organoalanes (40,41,46).



where  $n = 1, 2, 3$  and  $R = \text{alkyl or aryl}$ .

The mechanism proposed for this reaction (40) is electrophilic attack of the aluminum on to the alkyl with the aluminum now being five-coordinate. This is then followed by cleavage of the mercury alkyl bond and elimination of a hydride ion which is picked up by the mercury to form an alkyl mercury hydride which subsequently decomposes to mercury metal and hydrogen gas.

Gallium compounds, on the other hand, exhibit far less ability to form five-coordinate configurations. The only established molecule of this type is  $(\text{Me}_3\text{N})_2\text{GaH}_3$  which dissociates to the tetra-coordinated compound above  $-21^\circ\text{C}$  (9). The aluminum analogue of this compound  $(\text{Me}_3\text{N})_2\text{AlH}_3$  is a monomeric

solid with a melting point of 90°C (46). Thus, since gallium is unable to penta-coordinate at room temperature and because  $\text{Me}_3\text{NGaH}_3$  is slightly unstable at this temperature, decomposition occurred. At lower temperatures where  $\text{Me}_3\text{NGaH}_3$  is stable and there is a possibility of gallium penta-coordinating no reaction was observed, possibly because the Hg-alkyl bond is then thermo-chemically stable to electrophilic attack. This is indicated in the aluminum reaction, (see equation 11-1), where elevated temperatures and refluxing solvents, usually cyclohexane, were needed to ensure complete reaction. At higher temperatures  $\text{Me}_3\text{NGaH}_3$  could possibly dissociate, and the  $\text{GaH}_3$  moiety then react.

Another important consideration is the difference in electronegativity between gallium and aluminum. Aluminum has an electronegativity, (Allred-Rochow), of 1.47 and since the electronegativity of hydrogen is 2.1, the Al-H bond is considerably polarized with the hydrogen more strongly attracting the bond-forming electrons giving it a  $\delta^-$  charge and giving the aluminum atom a substantial  $\delta^+$  charge. Thus, the aluminum is provided with a strong driving force for the electrophilic attack and for easy loss of hydride ion. Gallium, on the other hand, has an electronegativity, Allred-Rochow, of 1.82, rendering the Ga-H bond far less polar and thus decreasing both, the driving force for electrophilic attack and the ability to lose a hydride ion.

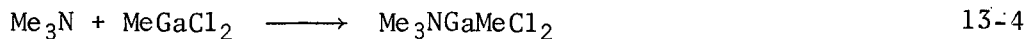
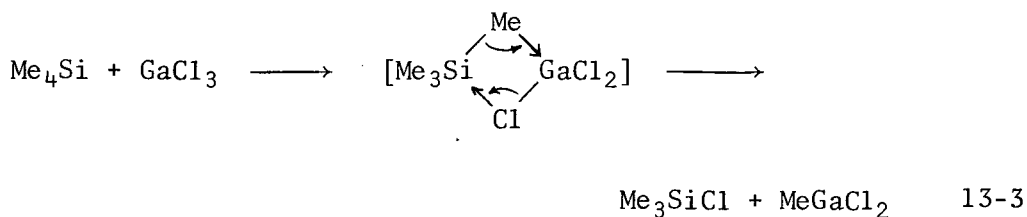
That a definite reaction takes place, as indicated by the equation 10-1, rather than mere decomposition of the starting material was evidenced by the proton NMR spectrum of the product which showed three peaks at  $\tau = 10.12$ , 10.21, 10.28 ( $\tau_{\text{C}_6\text{H}_6} = 2.84$  p.p.m.), closely resembling the Ga-Me absorption peaks observed in products obtained by alternate routes. In addition the

infrared spectrum of the product in benzene solution showed two bands at 1840, 1780  $\text{cm}^{-1}$  in the Ga-H stretching frequency region indicating the presence of several species. Small droplets of mercury metal were observed in the residue in the reaction flask giving further evidence of reaction. However, the low yields of organogallane products obtained by this method turned our attention to alternative routes.

The second synthetic route involved the lithium hydride reduction of trimethylamine adducts of organogallium halides;



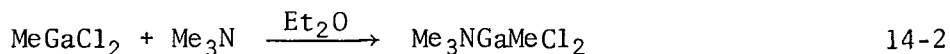
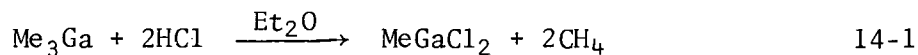
The trimethylamine monomethyldichlorogallane can readily be prepared by the following routes.



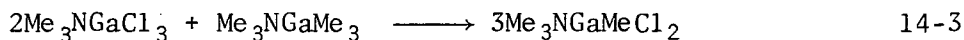
The reaction 13-3, reported by Schmidbaur and coworkers (21,22,47) proceeds smoothly without solvent at 40°C to yield trimethylchlorosilane,  $\text{Me}_3\text{SiCl}$ , boiling point 57.9°C (48) and monomethyldichlorogallane,  $\text{MeGaCl}_2$ , melting point 75-76°C, in high yield. The volatile components  $\text{Me}_3\text{SiCl}$  and excess  $\text{Me}_4\text{Si}$  were pumped off at 0°C to leave the desired product,  $\text{MeGaCl}_2$ , a

white solid which analysed for Cl = 46.2% and Ga = 42.6%; theoretical Cl = 46.6% and Ga = 44.8%. The methyl group on the gallium atom could not be removed by hydrolysing with water, although presumably it could be removed by boiling  $\text{MeGaCl}_2$  in concentrated acid (69). The gallium was analysed as the precipitate  $\text{GaMe}[\text{C}_9\text{H}_6\text{NO}]_2$ . An excess of trimethylamine was then added to the solid monomethyldichlorogallane and the mixture held at  $0^\circ\text{C}$  for some hours after which the excess amine was removed to leave a white solid  $\text{Me}_3\text{NGaMeCl}_2$  in the flask.

Alternative routes to this latter compound involve reaction of hydrogen chloride with trimethylgallane in ether followed by amine addition,



or equilibrium reaction between trimethylamine trichlorogallane and trimethylamine trimethylgallane.

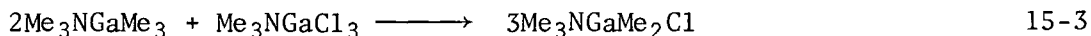
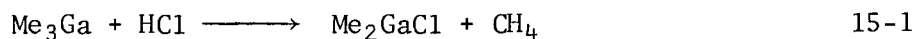


All the above reactions proceed in high yield. An NMR spectrum of the compound  $\text{Me}_3\text{NGaMeCl}_2$  showed two peaks, one at  $\tau = 8.36$  corresponding to Me-N resonance and a second peak of one-third the integrated intensity at  $\tau = 9.92$  for the Ga-Me resonance.

The preparation of trimethylamine dimethylmonochlorogallane (49,50),  $\text{Me}_3\text{NGaMe}_2\text{Cl}$ , involved the reaction of stoichiometric amounts of hydrogen



chloride and trimethylgallane in ether, followed by amine addition, or the utilization of the equilibrium reaction



The final reduction of these trimethylamine adducts of chloromethylgallane was carried out by adding the LiH in ether at  $-20^\circ\text{C}$ , followed by a period of two hours at room temperature. The reaction mixture was filtered and the ether removed at low temperature to leave a white solid which was then purified by sublimation.

The product in benzene, from the reaction of trimethylamine monomethyldichlorogallane with two moles of lithium hydride, gave an NMR spectrum with two peaks, attributed to Ga-Me at  $\tau = 9.99, 10.14$ . The latter corresponds to Ga-Me in  $\text{Me}_3\text{NGaMeH}_2$  and the former may be either due to Ga-Me in the partly reduced species  $\text{Me}_3\text{NGaMeClH}$  or to Ga-Me in  $\text{LiGaMeX}_2\text{H}$ , this latter species being formed by the reaction



where  $\text{X} = \text{H}$  or  $\text{Cl}$ .

The former possibility seems most likely as the material could be readily sublimed. The area under the peaks suggests that only about 25% of the product exists as  $\text{Me}_3\text{NGaMeH}_2$ . The infrared spectrum of the reduced species showed

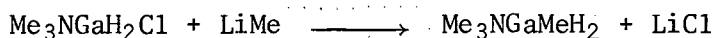
two bands in the Ga-H stretching frequency range at  $1880\text{ cm}^{-1}$  and  $1830\text{ cm}^{-1}$ .

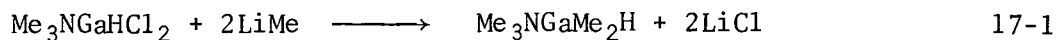
The reduction of trimethylamine dimethylmonochlorogallane with lithium hydride produced a product which in benzene solution showed a Ga-Me NMR resonance peak at  $\tau = 10.20$  corresponding to the position obtained for  $\text{Me}_3\text{NGaMe}_2\text{H}$  prepared by other methods and significantly higher than the Ga-Me resonance in  $\text{Me}_3\text{NGaMe}_2\text{Cl}$  which appeared at  $\tau = 10.11$ . In both of the above reductions, that is using the mono- and dichloro-gallanes, the yield of trimethylamine methyl gallanes was very low and the products were always contaminated with chloride which was difficult or impossible to remove. Reactions at higher temperatures or for longer periods of time only resulted in the decomposition of the products. Reactions using excess LiH gave none of the expected product, possibly only the lithium compounds,  $\text{LiGaMe}_2\text{XH}$  and  $\text{LiGaMeX}_2\text{H}$ , where X is Cl or H, (see equation 15-4), would be formed.

Analogous aluminum reactions gave similar results (41). Thus reacting  $\text{Me}_3\text{NAlEt}_2\text{Cl}$  with LiH for nine hours in refluxing ether resulted in only one-half of the chloride being reduced to the hydride  $\text{Me}_3\text{NAlEt}_2\text{H}$ . Times of up to 24 hours were used in attempting the LiH reduction of  $\text{Me}_3\text{NAlEtCl}_2$  to  $\text{Me}_3\text{NAlEtH}_2$ , but only partial conversion was observed. The  $\text{Me}_3\text{NAlMe}_2\text{Cl}$  compound in contrast to the ethyl compound did not react at all with LiH in refluxing ether, and neither did  $\text{Me}_3\text{NAlMeCl}_2$ .

Although this second method of preparation was superior to the dimethyl mercury route, subsequent methods led to higher yields.

Thus a more advantageous synthesis involved the reaction of lithium methyl with halogenogallanes (11).

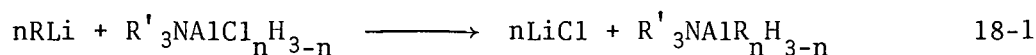




When stoichiometric amounts of trimethylamine monochlorogallane and lithium methyl were mixed in ether, lithium chloride was precipitated. After filtration and removal of solvent at low temperature, the product  $\text{Me}_3\text{NGaMe}_2\text{H}$  could be sublimed to give a high yield of a chloride-free material. The infrared and NMR spectra of this compound, with other physical data were collected and are discussed later. The NMR spectrum showed a peak at  $\tau = 8.18$  assigned to Me-N resonance, and also three peaks corresponding to Ga-Me resonance at  $\tau = 10.09, 10.18, 10.24$  which compare favorably to the spectra of  $\text{Me}_3\text{NGaH}_2\text{Me}$  samples prepared by other routes. Similarly when two molar equivalents of lithium methyl were reacted with one molar equivalent of trimethylamine dichloromonomethylgallane in like manner, the compound  $\text{Me}_3\text{NGaMe}_2\text{H}$  was produced, which could be sublimed as a nearly pure product, though a trace of chloride was always present. The infrared and NMR spectra of this compound were also recorded. The NMR spectrum contained a peak at  $\tau = 8.20$  assigned to Me-N resonance, and also for Ga-Me resonance indicated three peaks at  $\tau = 10.10, 10.18, 10.25$  which compare favorably to the spectra of  $\text{Me}_3\text{NGaMe}_2\text{H}$  samples prepared by other methods. In addition there was a very small peak at  $\tau = 10.04$  which was probably due to the Ga-Me of the  $\text{Me}_3\text{NGaMeHCl}$  species. This same chloro species was postulated as a side product from the preparations using  $\text{Me}_3\text{NGaMeCl}_2$  and  $\text{LiH}$ , giving a peak at  $\tau = 10.02$  and was similarly difficult to remove by sublimation.

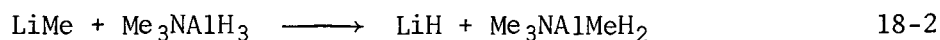
These chlorogallane compounds react very similarly to their aluminum analogues (40,51) where at room temperature, in either benzene or ether solvent, lithium methyl reacted very rapidly with trialkylamine

chloroalkylalanes, as indicated below, in equation 18-1, to produce trialkyl-

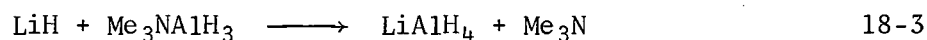


where  $n = 1, 2, 3$ ,  $\text{R} = \text{alkyl or aryl}$ , and  $\text{R}' = \text{Me or Et}$ .

amine organoalanes. Lithium alkyl also reacts with trimethylamine alane to produce an alkylated alane adduct,

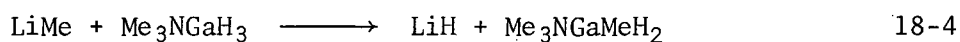


but a side reaction



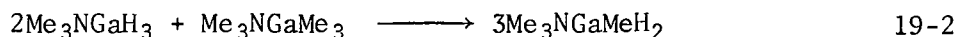
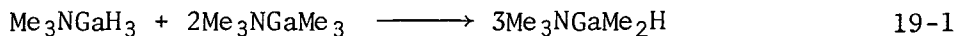
made it difficult to control the stoichiometry of the desired reaction and the yield of  $\text{Me}_3\text{NAlMeH}_2$  was low. This side reaction seems to be a standard reaction with Group IIIB alkyls (52) where a stronger nucleophile such as  $\text{LiH}$ ,  $\text{Me}_2\text{NH}$ , or  $\text{CaH}_2$  replaces a weaker nucleophile such as  $\text{Me}_3\text{N}$ .

When a similar reaction was attempted, using lithium methyl with trimethylamine gallane, none of the desired product  $\text{Me}_3\text{NGaMeH}_2$  was produced. The reaction probably proceeded first by alkylation of the gallane followed by lithium hydride replacement of trimethylamine.



The ether solvent was removed at low temperature and the NMR spectrum of the white solid dissolved in benzene was recorded. This gave several peaks, a singlet at  $\tau = 9.92$  assigned to Ga-Me in  $\text{LiGaMeH}_3$  and a triplet and quartet centred at  $\tau = 9.2$  and  $6.9$  respectively which are assigned to ether coordinated to the  $\text{LiGaMeH}_3$  molecule. On prolonged pumping of the white solid,  $\text{LiGaMeH}_3$ , at room temperature all the ether could be removed and  $\text{LiGaMeH}_3$  now seemed to be only partly soluble in benzene. Possibly the  $\text{LiGaMeH}_3$  had polymerized, some graying was also observed indicating that the lithium compound was decomposing. Lithium gallium hydride,  $\text{LiGaH}_4$ , is also postulated to have ether coordinated to it (55) and decomposes at room temperature in ether solution or when the ether solvent is removed. No Me-N resonance was observed in the NMR spectra. This system was not investigated further, because it seemed not to lead to the desired organogallane amine adducts.

The final method employed for synthesising trimethylamine adducts of organogallanes was the highly successful route involving the equilibrium reaction between trimethylamine gallane and trimethylamine trimethylgallane.



Again the products can be purified by sublimation, but in this method the starting materials are both extremely pure and there are no side products. Infrared and NMR spectra were collected on the products and compared favourably to those obtained from compounds prepared by alternative routes.

The aluminum analogues were prepared in the very same manner by mixing stoichiometric quantities of  $\text{Me}_3\text{NAlMe}_3$  and  $\text{Me}_3\text{NAlH}_3$  and distilling or subliming off, in quantitative yield, the alkylalane amine complex.

B. Properties and Reactions of Trimethylamine Adducts of Organogallanes

(a) Physical Properties

The trimethylamine organogallanes appear at very low temperatures to be nice white solids but at room temperatures they appear as waxes or oils.  $\text{Me}_3\text{NGaMe}_2\text{H}$  was placed in a sublimator and sublimed onto the cold finger cooled to  $-78^\circ\text{C}$ . Then this cold finger was allowed to slowly warm up and its temperature noted. At about  $-6^\circ\text{C}$  some of the material on the cold finger began to melt but the melting point was not sharp continuing until about  $20^\circ\text{C}$  at which temperature all the compound was liquid.  $\text{Me}_3\text{NGaMeH}_2$  was likewise sublimed onto the cold finger and warmed up. At  $4^\circ\text{C}$  some of the  $\text{Me}_3\text{NGaMeH}_2$  began to melt and at about  $25^\circ\text{C}$  all of the compound had melted into a very viscous oil. When some  $\text{Me}_3\text{NGaMeH}_2$  was placed in a capillary tube and sealed off under nitrogen, the compound again showed a melting point range of 4 to  $20^\circ\text{C}$ . At room temperature, about  $18^\circ\text{C}$ , if the two phases are mechanically separated, the NMR spectra of both phases are very similar indicating that the two phases are of similar composition. The long melting range may indicate that there is a change occurring in which the solid was polymerized and on melting, becomes monomeric. This type of behaviour was observed for compounds of the type  $\text{Me}_2\text{NGaMe}_2$  (62).

The molecular weights of  $\text{Me}_3\text{NGaMe}_2\text{H}$  and  $\text{Me}_3\text{NGaMeH}_2$  were both determined cryoscopically in benzene solution. The molecular weight of  $\text{Me}_3\text{NGaMe}_2\text{H}$  was found to be 172 in a 0.0341 molal solution, this compares to the theoretical

molecular weight for a monomer of 160, to give the degree of association as 1.08. The molecular weight of  $\text{Me}_3\text{NGaMeH}_2$  was found to be 175 in a 0.0423 m solution. This compares to the theoretic molecular weight of the monomer of 146  $\text{gms mole}^{-1}$  and gives a degree of association of 1.20. It seems as if these compounds are primarily monomers but there is no doubt some association probably through dipole-dipole interactions rather than bridged dimers. With similar aluminum compounds (40,41) the degree of association for  $\text{Me}_3\text{NAlMeH}_2$  is 1.95 and for  $\text{Me}_3\text{NAlMe}_2\text{H}$  is 1.34. Substituting a better bridging ligand such as chloride in place of methyl in the aluminum compounds results in an irregular effect on the degree of association,  $\text{Me}_3\text{NAlH}_3$  and  $\text{Me}_3\text{NAlH}_2\text{Cl}$  show degrees of association of 1.43 and 1.32 respectively, whereas bridging ability is in the sequence  $\text{Cl} > \text{H} > \text{Me}$ . Neither dipole-dipole interactions nor bridged dimers have been generally accepted to explain the association of Group IIIB coordination compounds and there is still a good deal of controversy (53) because the real nature of the bonding forces effecting the compounds are little understood and therefore no predictions can be made about the degree of association in other Group IIIB coordination compounds.

(b) NMR Data

Proton NMR data were obtained using both cyclohexane and benzene as solvents. In both solvents the solvent peak was taken as the internal standard, cyclohexane  $\tau_{\text{C}_6\text{H}_{12}} = 8.54$  and benzene  $\tau_{\text{C}_6\text{H}_6} = 2.84$ . Cyclohexane has the advantage that all proton peaks in this solvent are concentration independent, but it has the disadvantage that the solvent peak at  $\tau = 8.54$  often obscures the Me-N peak which appears at about  $\tau = 8$ . Benzene solutions on the other hand show a concentration dependence at higher concentrations.

Fortunately at low concentrations, around 0.1 M to 1 M, the shifts observed due to solvent interaction are very small and benzene has the advantage that its resonance peak appears at low enough field to be free from interference with any other proton peaks in the samples. Most samples were run at a concentration of about 0.5 M to 1 M.

Table 1  
Proton NMR Data in Cyclohexane Solvent

Species	Me-N ( $\tau$ )	Ga-Me ( $\tau$ )
$\text{Me}_3\text{NGaMe}_3$	7.72	10.57
$\text{Me}_3\text{NGaMe}_2\text{H}$	7.63	10.51
$\text{Me}_3\text{NGaMeH}_2$	7.61	10.42
$\text{Me}_3\text{NGaMeCl}_2$	7.66	10.27

Table 2  
Proton NMR Data in Benzene Solvent

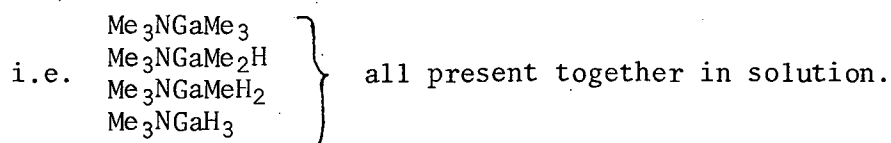
Species	Me-N ( $\tau$ )	Ga-Me ( $\tau$ )
$\text{Me}_3\text{NGaMe}_3$	8.34 $\rightarrow$ 8.10 (sat.)	10.22 $\rightarrow$ 10.46 (sat.)
$\text{Me}_3\text{NGaMe}_2\text{H}$	8.22	10.17
$\text{Me}_3\text{NGaMeH}_2$	8.10	10.08
$\text{Me}_3\text{NGaH}_3$	8.02	--
$\text{Me}_3\text{NGaMe}_2\text{Cl}$	8.31	10.11
$\text{Me}_3\text{NGaMeCl}_2$	8.36	9.92
$\text{Me}_3\text{NGaCl}_3$	8.19	--
$\text{GaMe}_3$	--	10.15
$\text{MeGaCl}_2$	--	9.90 <sup>a</sup>
$\text{Me}_3\text{NGaHMeCl}$	8.20	10.03
$\text{Me}_3\text{NGaMeD}_2$	8.10	10.09
$\text{Me}_3\text{NGaMe}_2\text{D}$	8.20	10.17
$\text{Me}_3\text{NGaH}_2\text{OMe}$	8.12	6.65 <sup>b</sup>

<sup>a</sup> Schmidbaur ref. 47 gives Ga-Me  $\tau$  = 9.20 in  $\text{CCl}_4$

<sup>b</sup> This is for Ga-OMe.



The proton NMR spectra of  $\text{Me}_3\text{NGaMe}_2\text{H}$  and  $\text{Me}_3\text{NGaMeH}_2$  both show, at the same positions, three distinct signals with different areas under the three peaks for the two "compounds", see figure 1. It seems probable therefore that an equilibrium is established in solution and that all four possible species are present.



Quotation marks are put around those formula or compounds whose stoichiometry corresponds to the formula but in solution all four compounds as listed above exist together to make up this correct stoichiometry.

For " $\text{Me}_3\text{NGaMeH}_2$ " in benzene the three Ga-Me signals appear at  $\tau = 10.24$ , 10.17, 10.09 and a Me-N peak at  $\tau = 8.10$ . The signals are assigned as is in Table 3 below. The ratio of molar concentrations and the percentage of each compound in solution are also listed.

Table 3

Molar Ratios of " $\text{Me}_3\text{NGaMeH}_2$ " in Benzene

Species	Ga-Me ( $\tau$ )	Peak Area ratio	Molar Ratio	% of Each
$\text{Me}_3\text{NGaMe}_3$	10.24	1	1	3.1%
$\text{Me}_3\text{NGaMe}_2\text{H}$	10.17	4.85	7.0	22.9
$\text{Me}_3\text{NGaMeH}_2$	10.09	5.00	15.0	47.0
$\text{Me}_3\text{NGaH}_3$	--	--	8.6	27.0

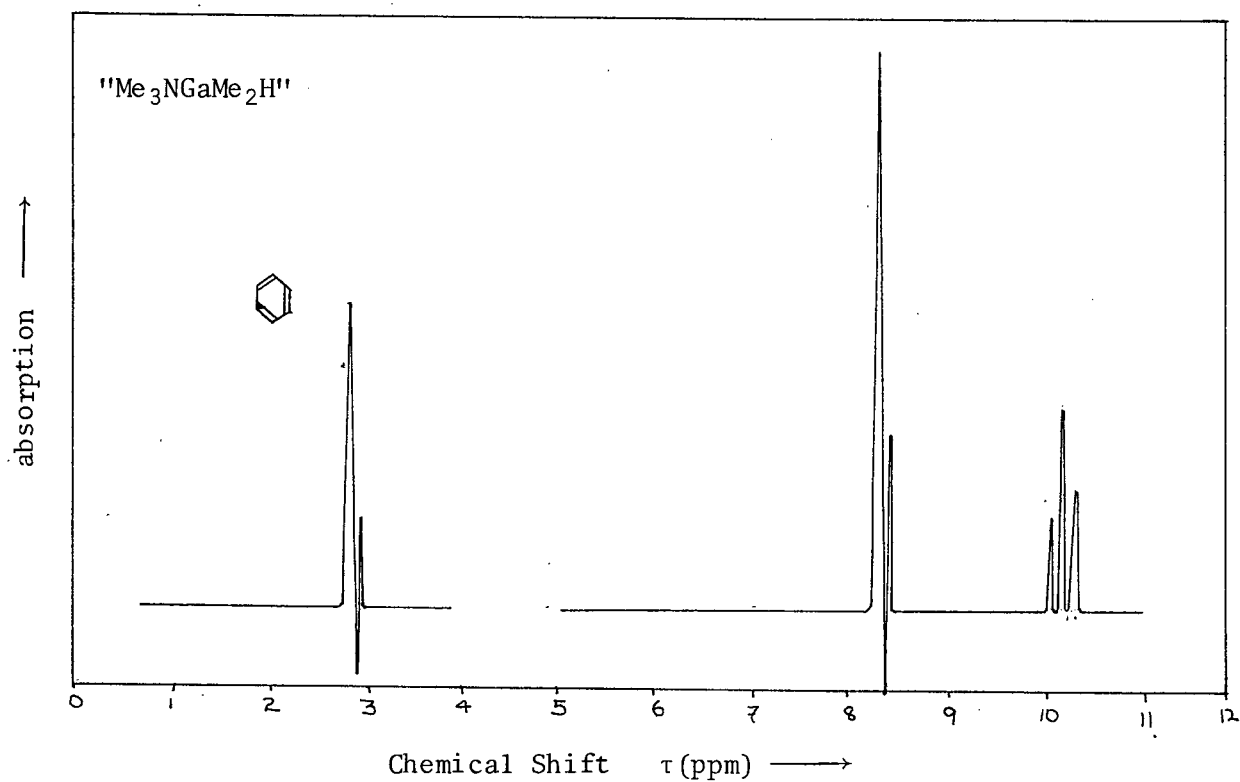
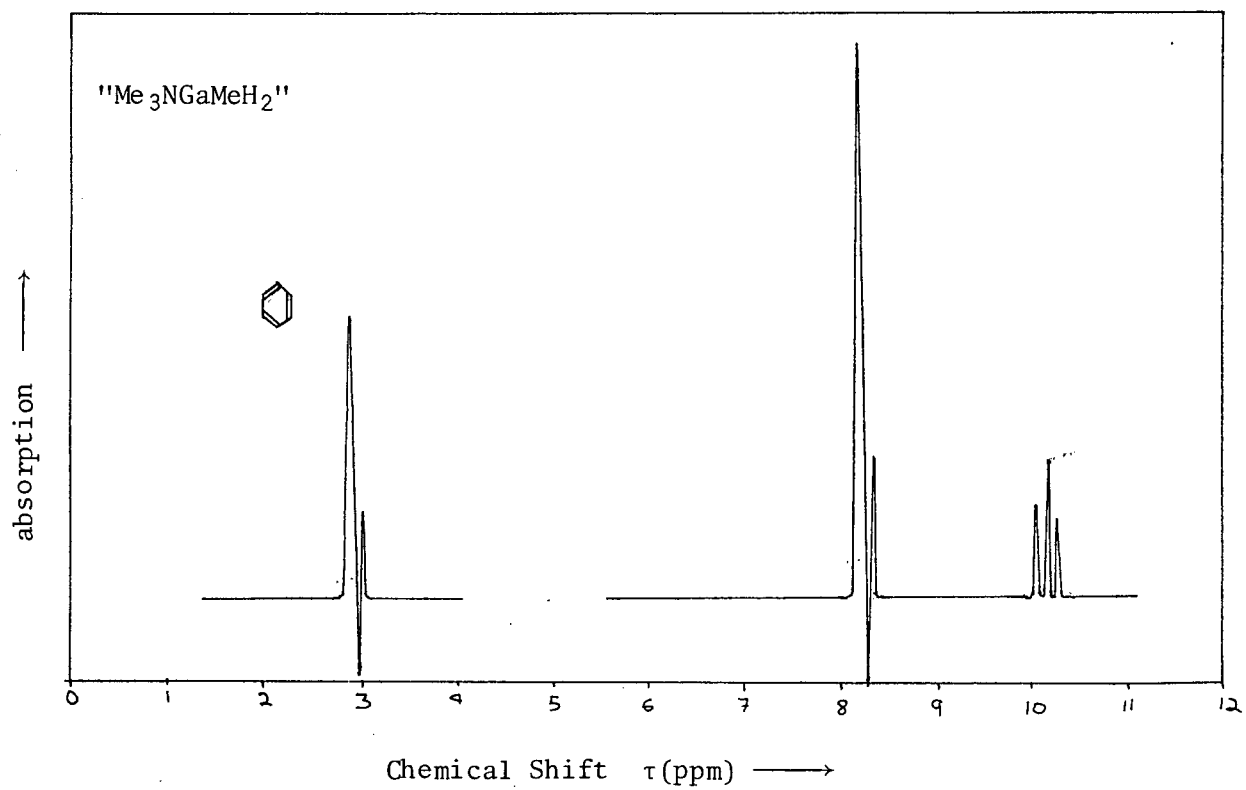


FIGURE 1

NMR Spectra of  $\text{Me}_3\text{NGaMeH}_2$  and  $\text{Me}_3\text{NGaMe}_2\text{H}$  at 60 Mc/sec.

Similarly for the compound " $\text{Me}_3\text{NGaMe}_2\text{H}$ " in benzene the following data were obtained.

Table 4  
Molar Ratios of " $\text{Me}_3\text{NGaMe}_2\text{H}$ " in Benzene

Species	Ga-Me ( $\tau$ )	Peak Area ratio	Molar Ratio	% of Each
$\text{Me}_3\text{NGaMe}_3$	10.22	1.6	2.1	16.0
$\text{Me}_3\text{NGaMe}_2\text{H}$	10.16	5.16	6.1	46.4
$\text{Me}_3\text{NGaMeH}_2$	10.07	1	3.95	30.0
$\text{Me}_3\text{NGaH}_3$	--	--	1	7.6

Similarly three Ga-Me signals were observed for each of the compounds " $\text{Me}_3\text{NGaMeH}_2$ " and " $\text{Me}_3\text{NGaMe}_2\text{H}$ " in cyclohexane solution and for the deuterated compounds " $\text{Me}_3\text{NGaMeD}_2$ " and " $\text{Me}_3\text{NGaMe}_2\text{D}$ " in benzene solution. These are listed and the different NMR signals assigned in Table 5.

Table 5  
NMR Data for " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and " $\text{Me}_3\text{NGaMeH}_2$ " in Cyclohexane and for " $\text{Me}_3\text{NGaMe}_2\text{D}$ " and " $\text{Me}_3\text{NGaMeD}_2$ " in Benzene

" $\text{Me}_3\text{NGaMe}_2\text{H}$ " in $\text{C}_6\text{H}_{12}$			" $\text{Me}_3\text{NGaMeH}_2$ " in $\text{C}_6\text{H}_{12}$		
Species	Ga-Me ( $\tau$ )	% of Each	Species	Ga-Me ( $\tau$ )	% of Each
$\text{Me}_3\text{NGaMe}_3$	10.57	27.0%	$\text{Me}_3\text{NGaMe}_3$	10.57	8.3%
$\text{Me}_3\text{NGaMe}_2\text{H}$	10.51	45.4	$\text{Me}_3\text{NGaMe}_2\text{H}$	10.51	27.5
$\text{Me}_3\text{NGaMeH}_2$	10.42	23.6	$\text{Me}_3\text{NGaMeH}_2$	10.42	35.0
$\text{Me}_3\text{NGaH}_3$	--	4.0	$\text{Me}_3\text{NGaH}_3$	--	29.2

" $\text{Me}_3\text{NGaMe}_2\text{D}$ " in $\text{C}_6\text{H}_6$			" $\text{Me}_3\text{NGaMeD}_2$ " in $\text{C}_6\text{H}_6$		
Species	Ga-Me ( $\tau$ )	% of Each	Species	Ga-Me ( $\tau$ )	% of Each
$\text{Me}_3\text{NGaMe}_3$	10.29	16.8%	$\text{Me}_3\text{NGaMe}_3$	10.26	1.7%
$\text{Me}_3\text{NGaMe}_2\text{D}$	10.22	40.9	$\text{Me}_3\text{NGaMe}_2\text{D}$	10.22	13.6
$\text{Me}_3\text{NGaMeD}_2$	10.16	34.1	$\text{Me}_3\text{NGaMeD}_2$	10.13	44.3
$\text{Me}_3\text{NGaD}_3$	--	8.2	$\text{Me}_3\text{NGaD}_3$	--	40.4

These same set of three Ga-Me peaks were found in all the compounds of the form " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and " $\text{Me}_3\text{NGaMeH}_2$ " prepared by all four experimental procedures. The compounds which were sublimed and then dissolved in benzene gave spectra exactly the same as those obtained by mixing the reagents  $\text{Me}_3\text{NGaMe}_3$  and  $\text{Me}_3\text{NGaH}_3$  together in benzene. Mixing these latter two compounds in benzene in different molar ratios i.e. at ratios of 1:2, 1:1, 2:1 etc. gave the same three peak positions but just different area ratios.

The percentages of each species present in solution must be taken as only approximate, for small amounts of impurities such as  $\text{Me}_3\text{N}$ , or gallium metal, from decomposing  $\text{Me}_3\text{NGaH}_3$  could greatly affect the concentrations, and variations as great as five percent in the amount of each species present in solution have been observed for the same "compound". Temperature would also have a marked effect on the percentages of the species present, though this was not investigated. Heating the solutions might lead to a time averaged signal for the predicted products i.e.  $\text{Me}_3\text{NGaH}_2\text{Me}$  or  $\text{Me}_3\text{NGaMe}_2\text{H}$  but low thermal stability of the species precludes such work. The equilibrium between the four compounds in solution does not seem to be time dependent for two NMR spectra were obtained from the same sample one month apart and there were no differences in intensity or position of any of the peaks.

A variation of the solvents i.e. benzene or cyclohexane, seems to have little effect on the percentage of each species in solution, compare Tables 3, 4 and 5. The percentage of that species in solution which compares to the stoichiometry of the "compound" prepared i.e.  $\text{Me}_3\text{NGaMe}_2\text{H}$  present in a solution of " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and  $\text{Me}_3\text{NGaMeH}_2$  present in a solution of " $\text{Me}_3\text{NGaMeH}_2$ " is always the greatest. The percentage of each species is only approximate, thus no solvent effect is evidenced in the two solutions used. If a strong

donor solvent such as an ether were used then there may be a change in the peak ratios caused by the solvent partly replacing amine from some of the species, but this has yet to be investigated.

The approximate Ga-Me peak separations were 5 cps at 60 Mc/sec and about 8 cps at 100 Mc/sec, thus showing the signals arise from three different species and not from spin-spin coupling.

It is interesting to note that in all the spectra run only a single sharp peak was observed for the Me-N resonance. From Table 2 it is seen that the trimethylamine group is in different electronic environments in different compounds. Thus in solutions of the compounds " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and " $\text{Me}_3\text{NGaMeH}_2$ " all trimethylamine groups must be exchanging very rapidly, and the peak positions seem to be in the average position between the extremes of  $\text{Me}_3\text{NGaMe}_3$  and  $\text{Me}_3\text{NGaH}_3$ .

The NMR spectrum of a neat sample of " $\text{Me}_3\text{NGaMe}_2\text{H}$ " was obtained. Using TMS in benzene as an external standard the following peaks, assigned as Ga-Me resonances, were observed, area under the peak is in brackets,  $\tau = 9.92$  [1], 10.02 [1.1], 10.10 [1.7], 10.18 [6.5], 10.26 [7.9]. At the probe temperature of 30°C the compound " $\text{Me}_3\text{NGaMe}_2\text{H}$ " exists as a viscous oil. It is plausible to assign the peaks at  $\tau = 10.26$ , 10.18, 10.10 to the compounds  $\text{Me}_3\text{NGaMe}_3$ ,  $\text{Me}_3\text{NGaMe}_2\text{H}$  and  $\text{Me}_3\text{NGaMeH}_2$  respectively, for these three peaks roughly parallel, in intensity and position those found for the compound " $\text{Me}_3\text{NGaMe}_2\text{H}$ " in benzene, see Table 5. The peaks at  $\tau = 9.92$  and 10.02 could be assigned to bridging methyl groups in dimeric or polymeric species. Such downfield shifts have been observed for the bridging methyl groups of  $(\text{AlMe}_3)_2$  (54). Alternatively these peaks could be assigned to methyl groups of species showing strong dipole-dipole interaction. There is a single

peak at  $\tau = 7.29$  corresponding to Me-N indicating that all the amine groups are exchanging rapidly even in the neat liquid.

The proton NMR of the chlorinated compounds  $\text{Me}_3\text{NGaMe}_2\text{Cl}$  and  $\text{Me}_3\text{NGaMeCl}_2$  in benzene show only a single resonance for Ga-Me at room temperature. Presumably the higher efficiency of chlorine as a bridging group, over methyl or hydrogen (61), leads to a stable dimer or a specific single compound or very rapid exchange.

### (c) Infrared Data

The infrared absorption spectra of the compounds " $\text{Me}_3\text{NGaMeH}_2$ ", " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and their deuterated analogues " $\text{Me}_3\text{NGaMeD}_2$ " and " $\text{Me}_3\text{NGaMe}_2\text{D}$ " were recorded in benzene solution between  $400\text{ cm}^{-1}$  and  $4000\text{ cm}^{-1}$ , see Figure 2. These compounds have a vapour pressure of about 2 mm of Hg and the gas phase infrared spectra of some were recorded. Assignments of bands can be made on the bases of the well established structures (11, 55) of the adducts of  $\text{GaH}_{3-n}\text{X}_n$ , where X is halogen and n is 0, 1, 2, 3 (11). All bands not assigned to coordinated trimethylamine or carbon-hydrogen vibrations are listed in Table 6 below. From Table 6 it is seen that the vibration frequency of Ga-H decrease by a factor of about  $\sqrt{2}$  i.e. 1.41 when going to the deuterated species as is expected from the reduced mass effect.

The infrared data of trimethylamine organogallanes generally support the NMR results. The Ga-H stretching frequencies observed for " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and " $\text{Me}_3\text{NGaMeH}_2$ " are broader bands than those observed for  $\text{Me}_3\text{NGaH}_3$  (11) and a shoulder at lower frequency is observed which is not found in the spectrum of  $\text{Me}_3\text{NGaH}_3$ . These differences could be attributed to the presence of partly methylated gallane species in solution. The gas phase of the

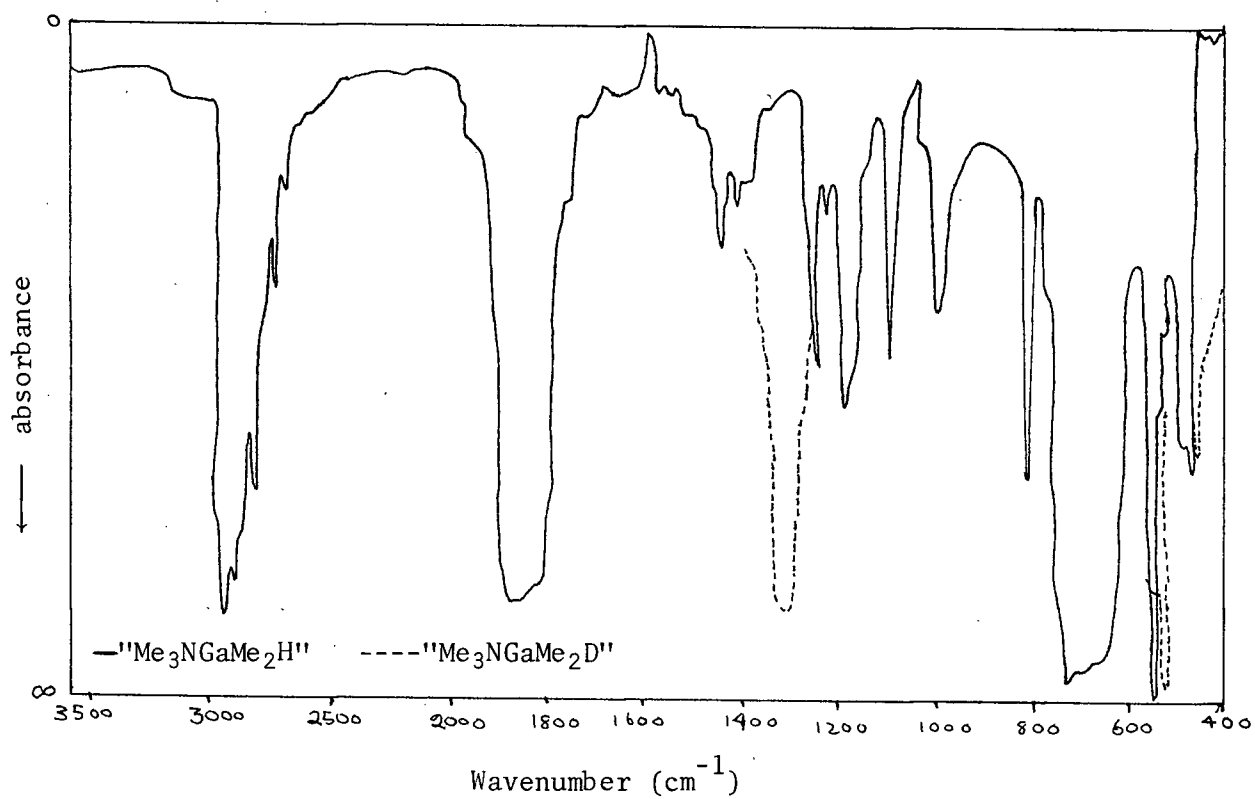
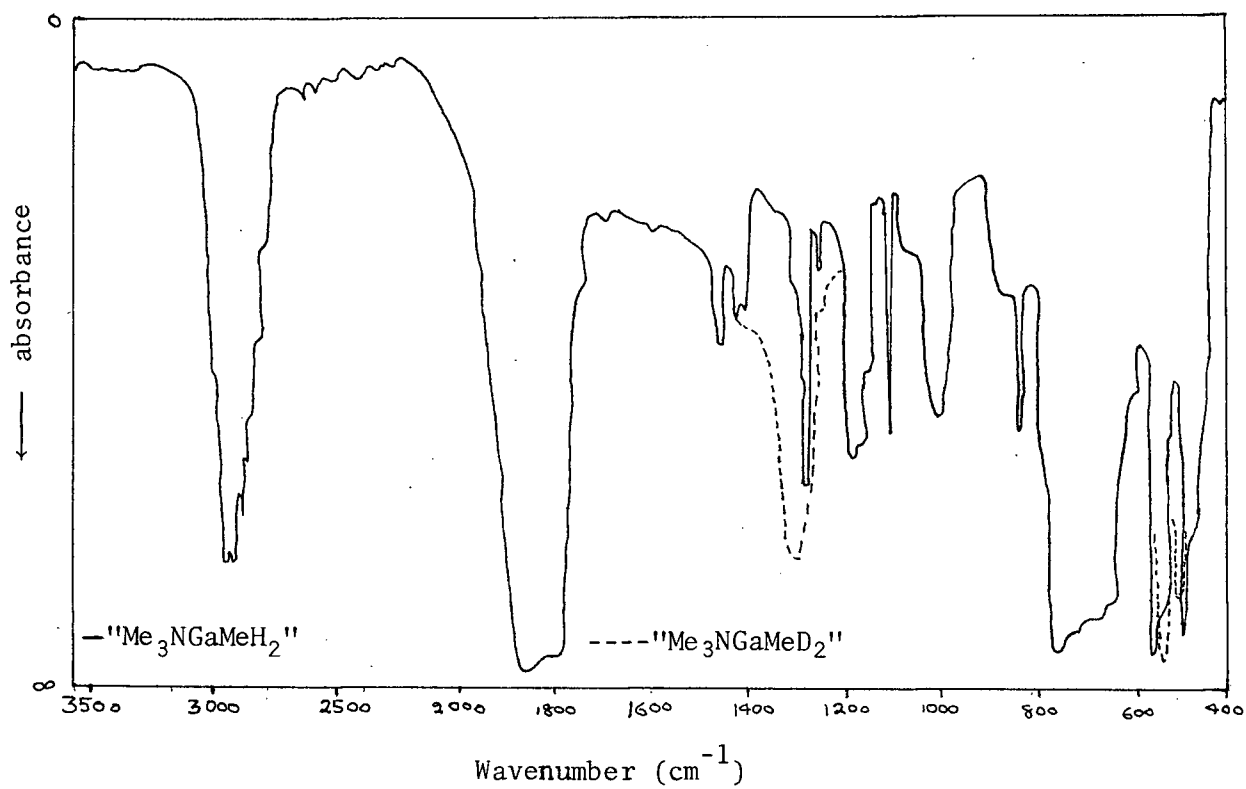


FIGURE 2

Infrared Spectra of "Me<sub>3</sub>NGaMeH<sub>2</sub>" and "Me<sub>3</sub>NGaMe<sub>2</sub>H" in C<sub>6</sub>H<sub>6</sub>

Table 6

Infrared Data for " $\text{Me}_3\text{NGaMeH}_2$ ", " $\text{Me}_3\text{NGaMeD}_2$ " and " $\text{Me}_3\text{NGaMe}_2\text{H}$ ", " $\text{Me}_3\text{NGaMe}_2\text{D}$ "

" $\text{Me}_3\text{NGaMeH}_2$ "	" $\text{Me}_3\text{NGaMeD}_2$ "	$\nu\text{H}/\nu\text{D}$	Assignment (55)
1845(vs), 1815(vs)	1313(vs)	1.41; 1.38	}antisym., sym. Ga-H stretch
1760(sh)	1270(sh)	1.39	
745(vs)	538(s)	1.37	antisym. Ga-H deformation
707(s)	490(m)	1.44	sym. Ga-H deformation
685(s,b)	680(w,b)	--	Ga-C
488(s), 495(sh)	470(m)	--	Ga-N stretch
" $\text{Me}_3\text{NGaMe}_2\text{H}$ "	" $\text{Me}_3\text{NGaMe}_2\text{D}$ "	$\nu\text{H}/\nu\text{D}$	Assignment (55)
1840(vs)	}1295(vs)	1.42	}antisym., sym. Ga-H stretch
1760(sh)			
745(s)	538(s)	1.36	antisym. Ga-H deformation
695(s) ?	490(w)	1.42	sym. Ga-H deformation
690(sh)	690(s,b)	--	Ga-C
485(m), 495(sh)	475(m)	--	Ga-N stretch

where vs; very strong; s strong; m medium; w weak; sh shoulder; b broad;  
units are in  $\text{cm}^{-1}$ .

compounds " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and " $\text{Me}_3\text{NGaMeH}_2$ " give infrared spectra that are very similar to that of pure  $\text{Me}_3\text{NGaH}_3$  (8). The infrared spectrum in the region between  $630\text{ cm}^{-1}$  and  $720\text{ cm}^{-1}$  is characterized by strong benzene solvent absorbance so the assignment of bands in this region, Ga-H symmetric deformation and Ga-C vibrations, are only tentative.

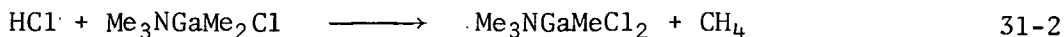
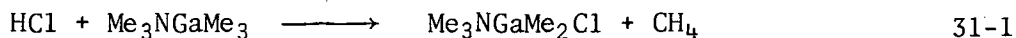


C. Reaction of Trimethylamine Organogallanes

(a) With HCl

The compound " $\text{Me}_3\text{NGaMeH}_2$ " in benzene solution reacted readily at below room temperature with one mole of hydrogen chloride to liberate one mole of gas which was shown by its infrared spectrum to be mostly hydrogen with a trace of methane, and to form the compounds " $\text{Me}_3\text{NGaHClMe}$ ". A second mole of HCl gas reacted as easily as the first with the compound " $\text{Me}_3\text{NGaMeH}_2$ ", and a second mole of gas was evolved which again was mostly hydrogen but now contained about 10% methane.

The reaction of trimethylamine gallane with HCl gas to give hydrogen and trimethylamine chlorogallane has been examined previously (11) and proceeds smoothly in solution or neat. It seems reasonable then that hydrogen can be evolved from trimethylamine adducts of organogallane. It seems that some methane is also evolved as evidenced in the infrared spectrum. This could be explained by the fact that the " $\text{Me}_3\text{NGaMeH}_2$ " compound equilibrates in solution to form some  $\text{Me}_3\text{NGaMe}_2\text{H}$  and  $\text{Me}_3\text{NGaMe}_3$  which could then react with HCl to give off methane gas, as indicated in the equations below.



The etherate of  $\text{GaMe}_3$  reacts under mild conditions with HCl gas, (see experimental section), to liberate methane; thus, it seems likely that  $\text{Me}_3\text{NGaMe}_3$  would also react with HCl. In the reaction of a trimethylamine organogallane with HCl elimination of a proton is slightly preferred

to that of a methyl group, for the amount of methane liberated is less than that expected on the bases of the percentage of  $\text{Me}_3\text{NGaMe}_3$  and  $\text{Me}_3\text{NGaMe}_2\text{H}$  in solution as calculated from the NMR data, see Table 3.

(b) With Ethylene

Ethylene gas was condensed on to a benzene solution of " $\text{Me}_3\text{NGaMeH}_2$ " and after several hours at room temperature no hydrogallation or any other reaction occurred. The ethylene gas was pumped off and identified and the NMR and infrared spectra of the benzene solution indicated that the starting material was unchanged.

Schmidbaur and coworkers (21,22) and Eisch (18,19) have shown that uncoordinated gallanes of the type  $\text{X}_2\text{GaH}$ , where X is Cl, Br or Et, hydrogallate a large variety of double and triple bonds at low or moderate temperatures. No hydrogallation reaction with a coordinated gallane has been reported and attempts usually resulted in the decomposition of the amine-gallane starting material (55).

(c) With Methanol

Trimethylamine gallane will react in benzene or ether solution or neat, at about  $0^\circ\text{C}$ , with methanol. One mole of  $\text{Me}_3\text{NGaH}_3$  will react with one, two, or three moles of methanol to liberate one, two, or three moles of hydrogen respectively. The NMR spectrum of the clear benzene solution which first results from the reaction shows two peaks, one at  $\tau = 8.12$  ( $\tau_{\text{C}_6\text{H}_6} = 2.84$  p.p.m.) corresponding to Me-N resonance, and a second peak at  $\tau = 6.65$  which is assigned to the Ga-OMe resonance. At room temperature the neat reaction product slowly evolves trimethylamine. The trimethylamine ligand is also evolved from the product mixture on removal of solvent. In both

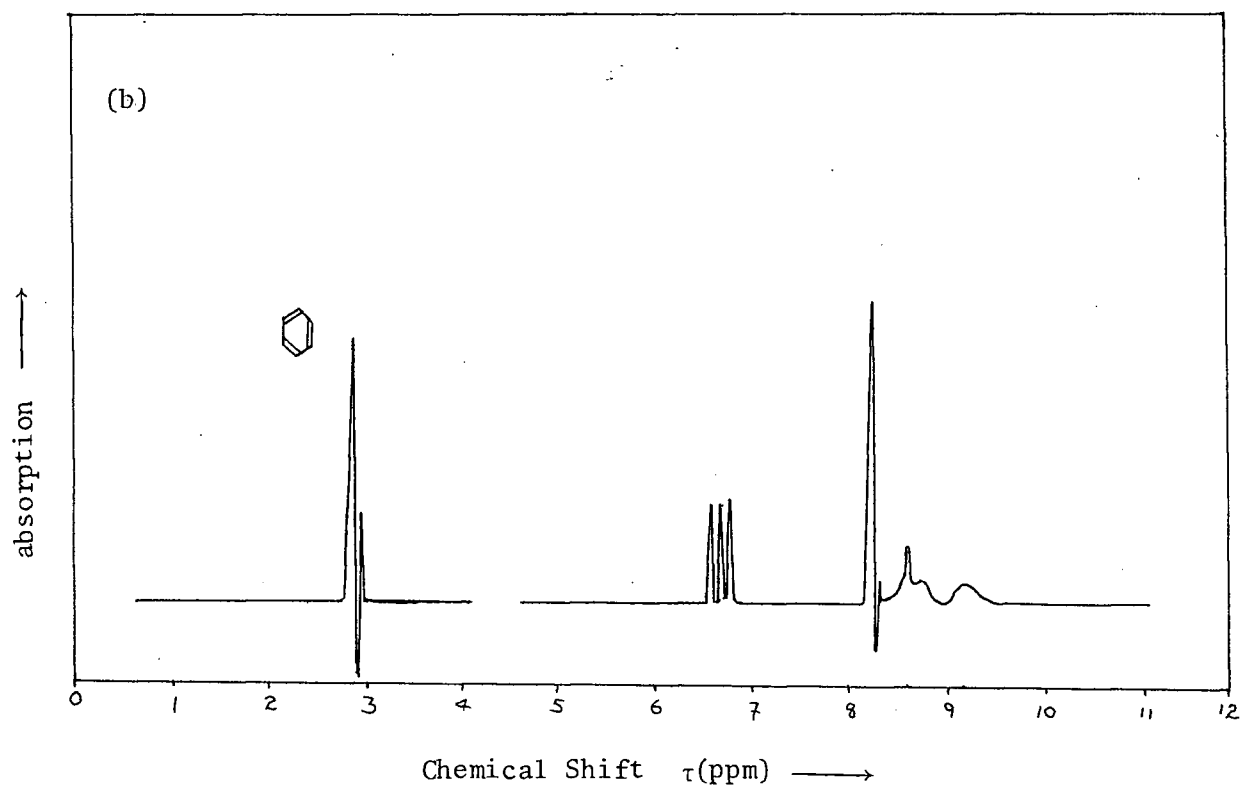
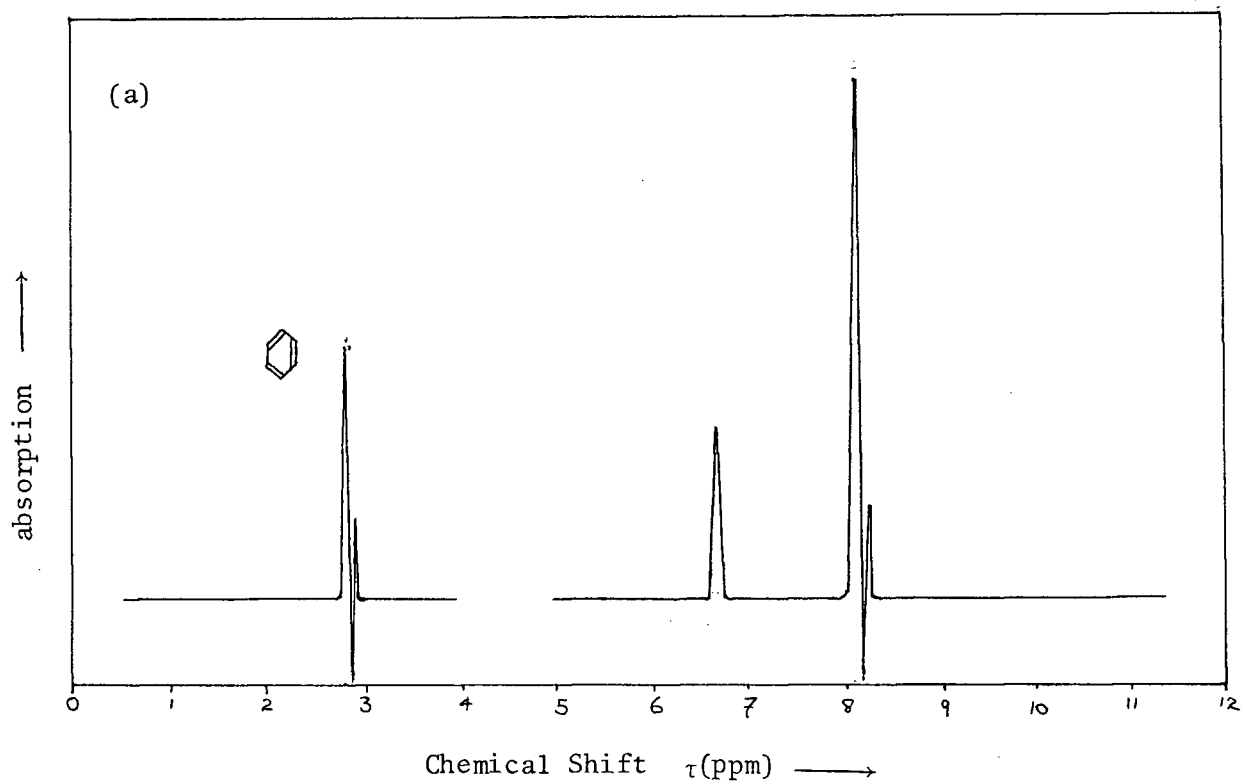


FIGURE 3

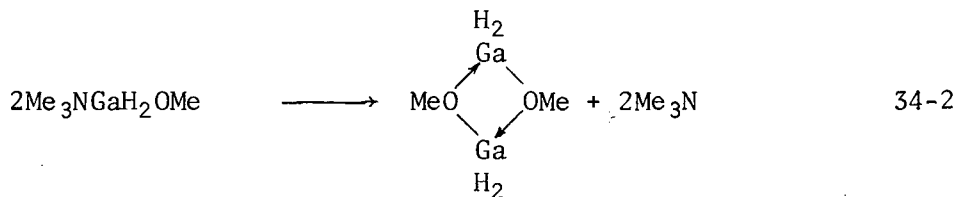
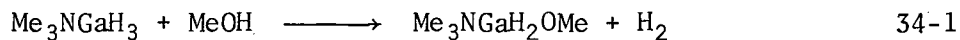
NMR Spectra of  $\text{Me}_3\text{NGaH}_2\text{OMe}$  at 60 Mc/sec.

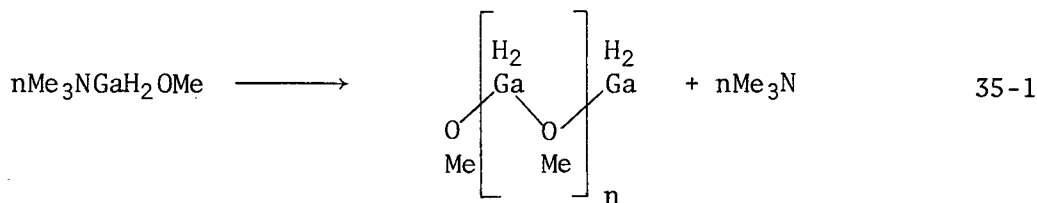
(a) Immediately after preparation

(b) After removal of solvent and redissolving in benzene

cases a white solid results which is now only partly soluble in benzene. The NMR spectrum of this partly soluble species is quite complex. The  $\text{Me}_3\text{N}$  peak decreases in intensity and two broad peaks appear at  $\tau = 8.6$  and  $\tau = 9.1$ . These could be attributed to Me-N resonance but this is uncertain. The peak assigned to Ga-OMe at  $\tau = 6.65$  also decreases in intensity and two other quite intense peaks at  $\tau = 6.57$  and  $\tau = 6.71$  appear which are field dependent and not the result of spin-spin coupling, (see Figure 3). The infrared spectra of these products, except the product from reaction with three molar equivalents of methanol, all show a complex Ga-H stretching region in the range  $1910\text{ cm}^{-1}$  to  $1825\text{ cm}^{-1}$  with the centre of the band shifting from approximately  $1850\text{ cm}^{-1}$  to  $1900\text{ cm}^{-1}$  with loss of amine.

The exact nature of the reaction of methanol with  $\text{Me}_3\text{NGaH}_3$  is only partly understood. It is known that alcohol reacts with trimethylgallium to form dimethylgallium alkoxides,  $[\text{Me}_2\text{GaOR}]_2$  (56). These compounds form very weak adducts with trimethylamine, except where  $\text{R} = \text{Me}$  in which case no adduct forms. It is argued that the -OR group acts as a stronger electron donor than trimethylamine. The reaction of  $\text{Me}_3\text{NGaH}_3$  with methanol probably proceeds thus;

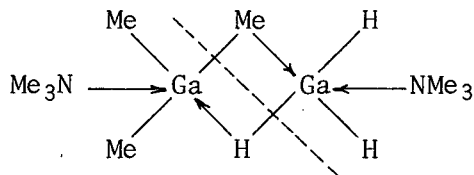




Dimers, trimers or polymers could be formed by reactions 34-2 and 35-1. Indeed some insoluble material, presumably polymeric, was obtained from the reactions in addition to the soluble compounds. These methoxy derivatives would certainly be a new class of gallanes and their preparation, structure and properties warrant further study.

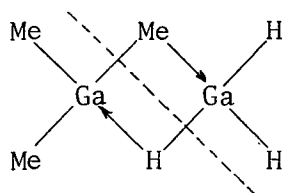
#### D. Mechanism of Exchange

From the NMR, infrared and experimental data there is strong evidence that the four compounds of the type  $\text{Me}_3\text{NGaMe}_n\text{H}_{3-n}$  where  $n = 0, 1, 2, 3$  co-exist in solution. The intermediate that gives rise to these species in solution must presumably be reached by a bridged gallium species:

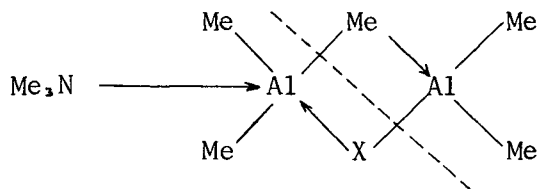


This bridged intermediate can then dissociate along the dashed line, then reform and redissociate so as to produce all four different species. A number of exchange reactions of Group IIIB alkyl addition compounds have been reported in the literature (57,58,59) but no general mechanism has been

found that applies to all or to a large number of these alkyl or Lewis base exchanges. The NMR spectra of the trimethylamine organogallanes indicate that all amines are equivalent, that is, they must be exchanging very rapidly. The bridged structure shown above could lose both its amine ligands to form the more stable four-coordinate gallium dimer species with the amine ligands reCOORDINATING as the dimer dissociates. Alternatively, in solution, the amine ligand could first dissociate from the monomeric gallane and then be free in solution. The gallane species would now be three-coordinate and could easily become four-coordinate by dimerization.

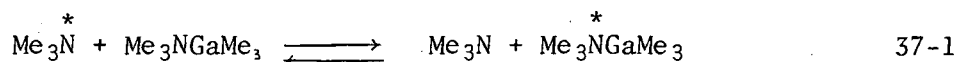


This dimer could then dissociate to again form three-coordinate gallane species which then recombines with amine ligands. Amine exchange could also occur by some modification of these two routes as is observed with aluminum alkyl exchange. Exchange between alkyl aluminum adducts of the type  $\text{Me}_3\text{NAlMe}_3$  and  $\text{Me}_3\text{NAlMe}_2\text{X}$ , where X is a halogen, occurs by two competing mechanisms (59). The first is through a bridged dimer in which the two aluminum atoms are five-coordinate similar to the bridged gallane shown above. The second is through a bridged dimer in which one aluminum atom is five-coordinate and the other is four-coordinate.

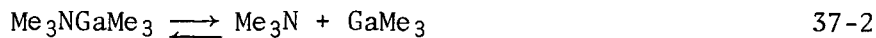


This four-coordinate part is obtained from a three-coordinate aluminum of the type  $\text{AlMe}_3$  or  $\text{AlMe}_2\text{X}$  from which the trimethylamine ligand has dissociated. It must be remembered that " $\text{Me}_3\text{NGaMeH}_2$ " does not hydrogallate olefins so, in the gallium case, the existence of an uncoordinated  $\text{GaH}_3$  species seems unlikely.

NMR studies with trimethylamine trimethylgallane (54) have shown that in the presence of excess amine a bimolecular exchange takes place as indicated in equation 37-1,



but in the presence of excess trimethylgallane a dissociation of the adduct is the rate controlling step.



Possibly both these types of exchange are occurring in solutions of trimethylamine organogallanes. No exchange studies have previously been reported involving hydride-alkyl exchange in Group IIIB compounds.

In summary, it seems that the compounds " $\text{Me}_3\text{NGaMeH}_2$ " and " $\text{Me}_3\text{NGaMe}_2\text{H}$ " roughly parallel, in properties and reactions, the chemistry of  $\text{Me}_3\text{NGaH}_3$  and  $\text{Me}_3\text{NGaMe}_3$ . The thermal stability of " $\text{Me}_3\text{NGaMe}_2\text{H}$ " and " $\text{Me}_3\text{NGaMeH}_2$ " is similar to that of  $\text{Me}_3\text{NGaH}_3$  and greater than that of the uncoordinated gallanes (20,21). However the boron and aluminum analogues possess much higher thermal stability.

## E. Exchange Reactions Involving Other Group IIIB Elements

### (a) Aluminum Alkyl-Hydride Exchange

Because of the unusual behaviour of trimethylamine adducts of organogallane in solution a re-examination of trimethylamine adducts of organoalanes was in order. Peters and coworkers (41) prepared the compounds " $\text{Me}_3\text{NAlMeH}_2$ " and " $\text{Me}_3\text{NAlMe}_2\text{H}$ " by mixing the appropriate amounts of  $\text{Me}_3\text{NAlMe}_3$  and  $\text{Me}_3\text{NAlH}_3$  in ether and then removing the solvent. Some of the properties of these compounds are listed below.

" $\text{Me}_3\text{NAlMe}_2\text{H}$ ": m.p.  $33-35^\circ\text{C}$ , b.p. (1 mm Hg)  $42-43^\circ\text{C}$ , degree of association in  $\text{C}_6\text{H}_{12}$  is 1.34,  $\nu$  Al-H  $1750\text{ cm}^{-1}$ ,  
NMR in  $\text{C}_6\text{H}_{12}$  ( $\tau_{\text{C}_6\text{H}_{12}} = 8.54$ )  $\underline{\text{Me-N}}$   $\tau = 7.59$ ,  
Al-Me  $\tau = 10.81, 10.86$ .

" $\text{Me}_3\text{NAlMeH}_2$ ": m.p.  $-35^\circ\text{C}$ , b.p. (1 mm Hg)  $25-26^\circ\text{C}$ , degree of association in  $\text{C}_6\text{H}_{12}$  is 1.95,  $\nu$  Al-H  $1750\text{ cm}^{-1}$ ,  
NMR in  $\text{C}_6\text{H}_{12}$  ( $\tau_{\text{C}_6\text{H}_{12}} = 8.54$ )  $\underline{\text{Me-N}}$   $\tau = 7.52$ ,  
Al-Me  $\tau = 10.88, 10.78$ .

The NMR doublet above  $10\tau$  has been explained in terms of a dimer with alternative methyl or hydrogen bridges. A re-examination of this NMR work led to the spectra shown in Figure 4. The NMR data are listed in the following table.



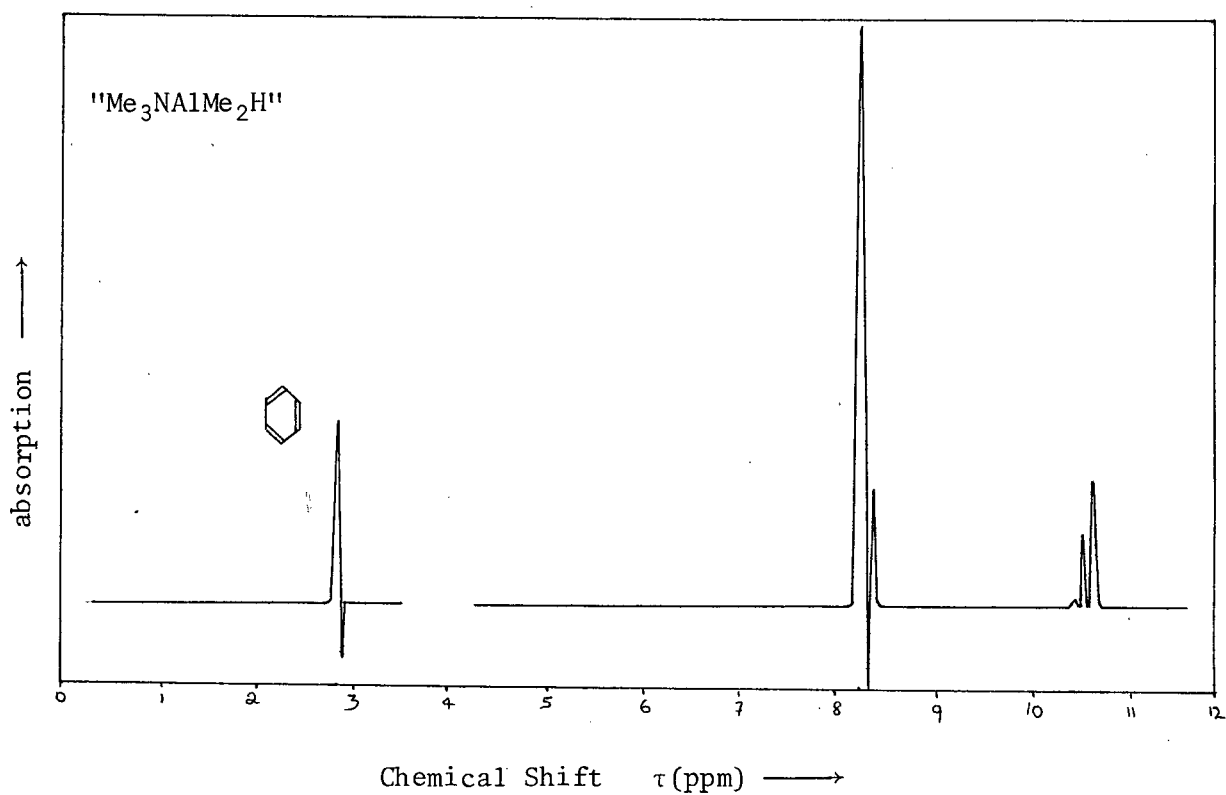
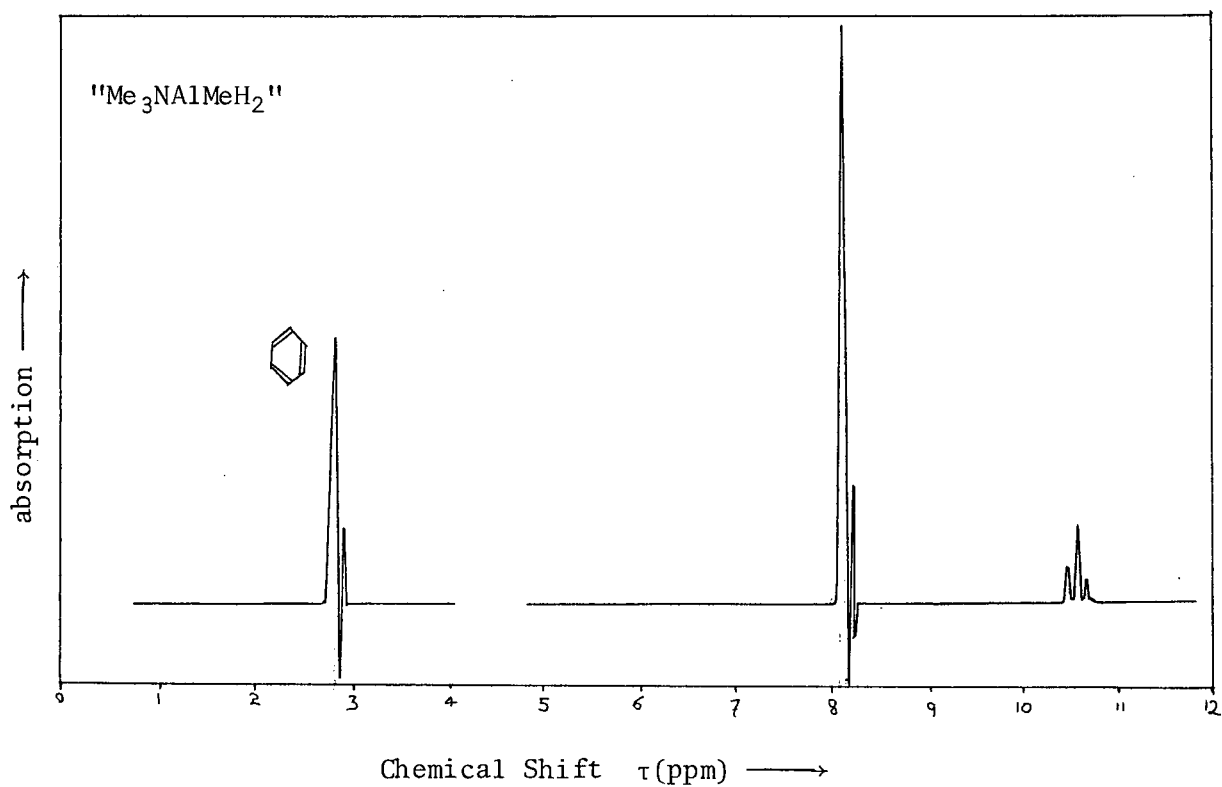


FIGURE 4

NMR Spectra of  ${}^{\text{H}}\text{Me}_3\text{NAlMe}_2$  and  ${}^{\text{H}}\text{Me}_3\text{NAlMe}_2\text{H}$  at 60 Mc/sec.

Table 7

Proton NMR Data for  $\text{Me}_3\text{NAlMe}_{3-n}\text{H}_n$  Species

Species	$\text{C}_6\text{H}_6$ Solvent		$\text{C}_6\text{H}_{12}$ Solvent	
	Me-N ( $\tau$ )	Me-Al ( $\tau$ )	Me-N ( $\tau$ )	Me-Al ( $\tau$ )
$\text{Me}_3\text{NAlMe}_3$	8.31	10.58	7.61	10.92
" $\text{Me}_3\text{NAlMe}_2\text{H}$ "	8.26	10.45, 10.51, 10.56	7.62	10.81, 10.87, 10.92
" $\text{Me}_3\text{NAlMeH}_2$ "	8.06	10.47, 10.53, 10.58	7.61	10.80, 10.87, 10.92
$\text{Me}_3\text{NAlH}_3$	7.94	---	7.71	---

An examination of these samples with a Varian HA-100 spectrometer showed the Me-Al peaks to be field dependent as were the Me-Ga peaks. These trimethylamine methylalane spectra show a remarkable similarity to the trimethylamine methylgallane spectra previously discussed and this leads to the assumption that an analogous set of aluminum compounds similar to gallium compounds are existing together in solution, thus the following assignments are made.

Table 8

Molar Ratios of " $\text{Me}_3\text{NAlMeH}_2$ " and " $\text{Me}_3\text{NAlMe}_2\text{H}$ " in Benzene

" $\text{Me}_3\text{NAlMeH}_2$ "

Species	Ga-Me ( $\tau$ )	Peak Area Ratio	Molar Ratio	% of Each
$\text{Me}_3\text{NAlMe}_3$	10.58	7	1	4.3
$\text{Me}_3\text{NAlMe}_2\text{H}$	10.53	24	5.1	21.9
$\text{Me}_3\text{NAlMeH}_2$	10.47	21	9	38.4
$\text{Me}_3\text{NAlH}_3$	--	--	8.3	35.4

" $\text{Me}_3\text{NAlMe}_2\text{H}$ "

Species	Ga-Me ( $\tau$ )	Peak Area Ratio	Molar Ratio	% of Each
$\text{Me}_3\text{NAlMe}_3$	10.56	29	1	29.3
$\text{Me}_3\text{NAlMe}_2\text{H}$	10.51	25	1.3	38.3
$\text{Me}_3\text{NAlMeH}_2$	10.45	7	0.72	21.2
$\text{Me}_3\text{NAlH}_3$	--	--	0.38	11.2

(b) Boron Alkyl-Hydride Exchange

On the bases that the trimethylamine adducts of organogallanes and organoalanes yield a series of equilibrium products in solution, an examination of the analogous boron systems was made to see if this exchange is characteristic of all Group IIIB elements. The compounds  $\text{Me}_3\text{NBMe}_3$  and  $\text{Me}_3\text{NBH}_3$  were mixed in a 1:2 and 2:1 molar ratio in benzene but no exchange was observed of either the trimethylamine groups or methyl groups on the boron, as indicated by the NMR spectra, Figure 5. The NMR data is summarized in Table 9.

Table 9

NMR Data for Mixtures of  $\text{Me}_3\text{NBMe}_3$  and  $\text{Me}_3\text{NBH}_3$  in  $\text{C}_6\text{H}_6$

Species	Me-N ( $\tau$ )	B-Me ( $\tau$ )	B-H ( $\tau$ )	$J_{\text{B-H}}$ cps
$\text{Me}_3\text{NBH}_3$	7.81	--	7.89	99
" $\text{Me}_3\text{NBH}_2\text{Me}$ "	7.91, 8.16	10.05	7.82	98
" $\text{Me}_3\text{NBHMe}_2$ "	7.96, 8.19	10.00	7.76	99
$\text{Me}_3\text{NBMe}_3$	8.24	9.99	--	--

The  $^{10}\text{B}$ -H interactions were not observed. The slight shift in the Me-N and B-Me peaks in the above compounds is probably due to dipole-dipole interactions rather than any alkyl or amine exchange.

(c) Mixing Trimethylamine Adducts of Different Group IIIB Hydrides and Alkyls

A large number of exchange reactions using 1:1 molar ratios of reagents were attempted, in benzene solution, of the type indicated by the following general equation

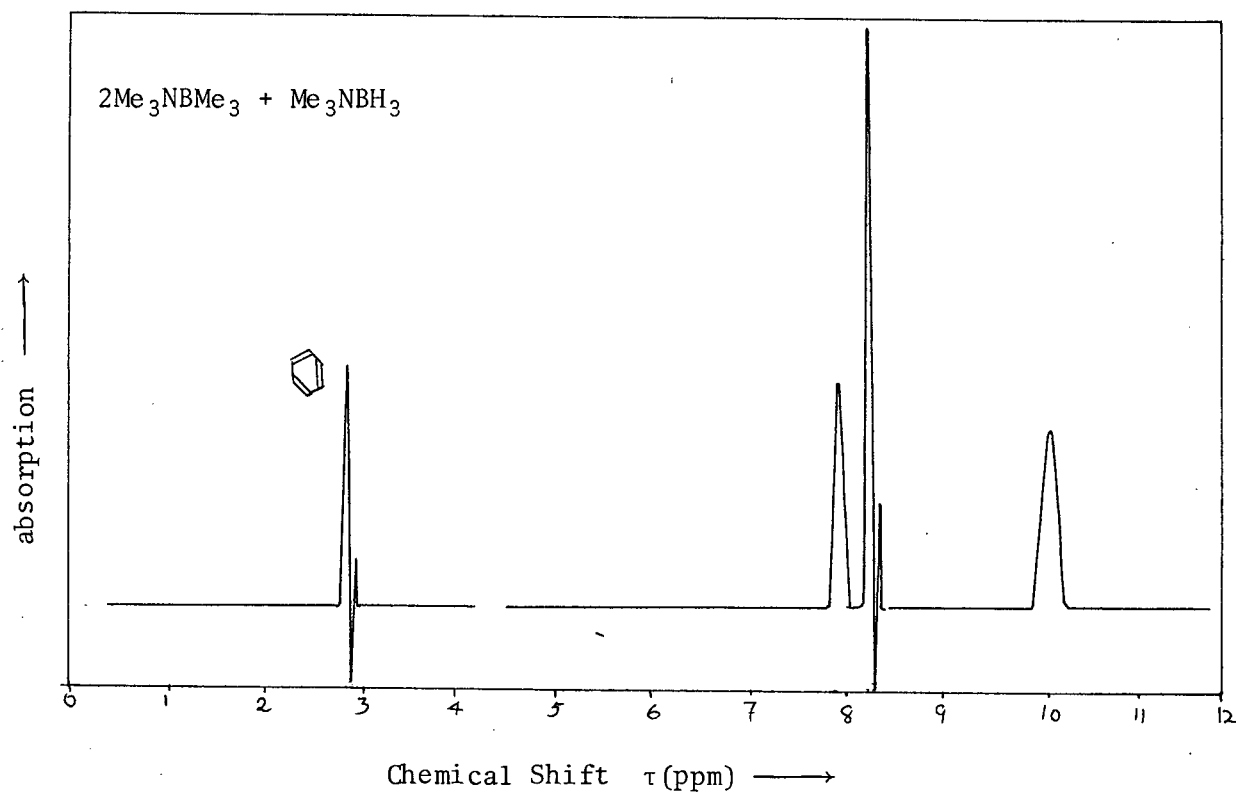
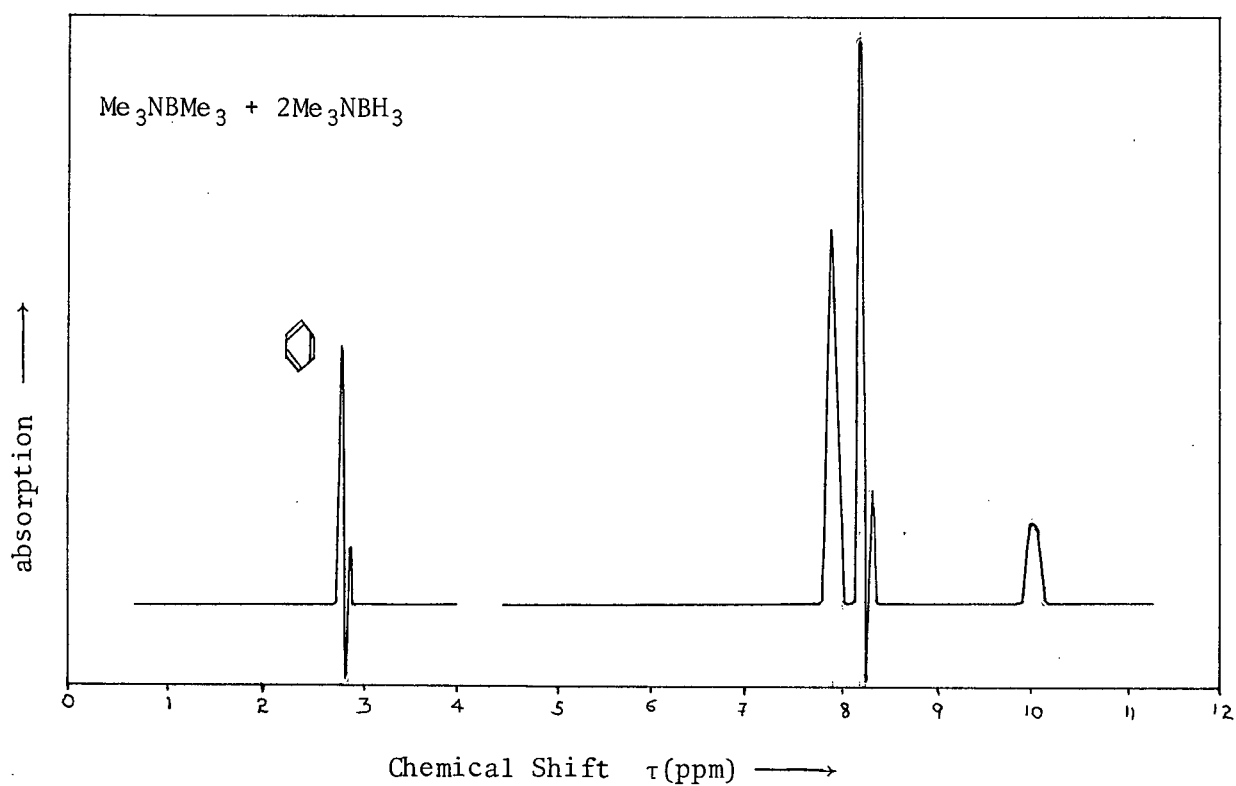
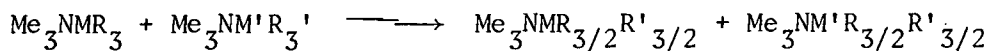


FIGURE 5

NMR Spectra of Mixtures of  $\text{Me}_3\text{NBMe}_3$  and  $\text{Me}_3\text{NBH}_3$  in  $\text{C}_6\text{H}_6$ , 60 Mc/sec



where M and M' = B, Al, Ga; R and R' = Me, H

Figure 6 gives the NMR spectra obtained from the above reactions. The NMR data are gathered in Table 10 below and whether exchange of trimethylamine or methyl groups takes place is also indicated in the table as are the NMR data of the individual reagents.

Table 10

NMR Data of the Mixed Group IIIB Alkyls and Hydrides

Reagents		N-Me			M-Me	
$\text{Me}_3\text{NMR}_3 + \text{Me}_3\text{NM}'\text{R}'_3$	Exchange	M-N-Me	M'-N-Me	Exchange	M-Me	M'-Me
a) $\text{Me}_3\text{NBH}_3 + \text{Me}_3\text{NAlMe}_3$	NO	7.97	8.24	NO	--	10.59
b) $\text{Me}_3\text{NBH}_3 + \text{Me}_3\text{NGaMe}_3$	NO	7.99	8.29	NO	--	10.29
c) $\text{Me}_3\text{NAlH}_3 + \text{Me}_3\text{NGaMe}_3$	YES		8.11	YES	10.47?	10.11
					10.51	10.17
					10.57	10.25
d) $\text{Me}_3\text{NBMe}_3 + \text{Me}_3\text{NAlH}_3$	NO	8.01	8.17	YES	9.94	10.49
						10.54
						10.60
e) $\text{Me}_3\text{NBMe}_3 + \text{Me}_3\text{NGaH}_3$	YES		8.12	NO	--	10.04
f) $\text{Me}_3\text{NAlMe}_3 + \text{Me}_3\text{NGaH}_3$	YES		8.17	NO		10.60
g) $\text{Me}_3\text{NBMe}_3 + \text{Me}_3\text{NAlMe}_3$	YES		8.22	NO	10.04	10.63
h) $\text{Me}_3\text{NBMe}_3 + \text{Me}_3\text{NGaMe}_3$	YES		8.11	NO	9.97	10.28
i) $\text{Me}_3\text{NGaMe}_3 + \text{Me}_3\text{NAlMe}_3$	YES		8.30	NO	10.28	10.59
j) $\text{Me}_3\text{NBMe}_3$			8.24			9.99
k) $\text{Me}_3\text{NAlMe}_3$			8.31			10.58
l) $\text{Me}_3\text{NGaMe}_3$			8.34			10.22
m) $\text{Me}_3\text{NBH}_3$			7.81			--
n) $\text{Me}_3\text{NAlH}_3$			7.94			--
o) $\text{Me}_3\text{NGaH}_3$			8.02			--

The solvent was used as an internal standard i.e.  $\tau_{\text{C}_6\text{H}_6} = 2.84$  p.p.m.

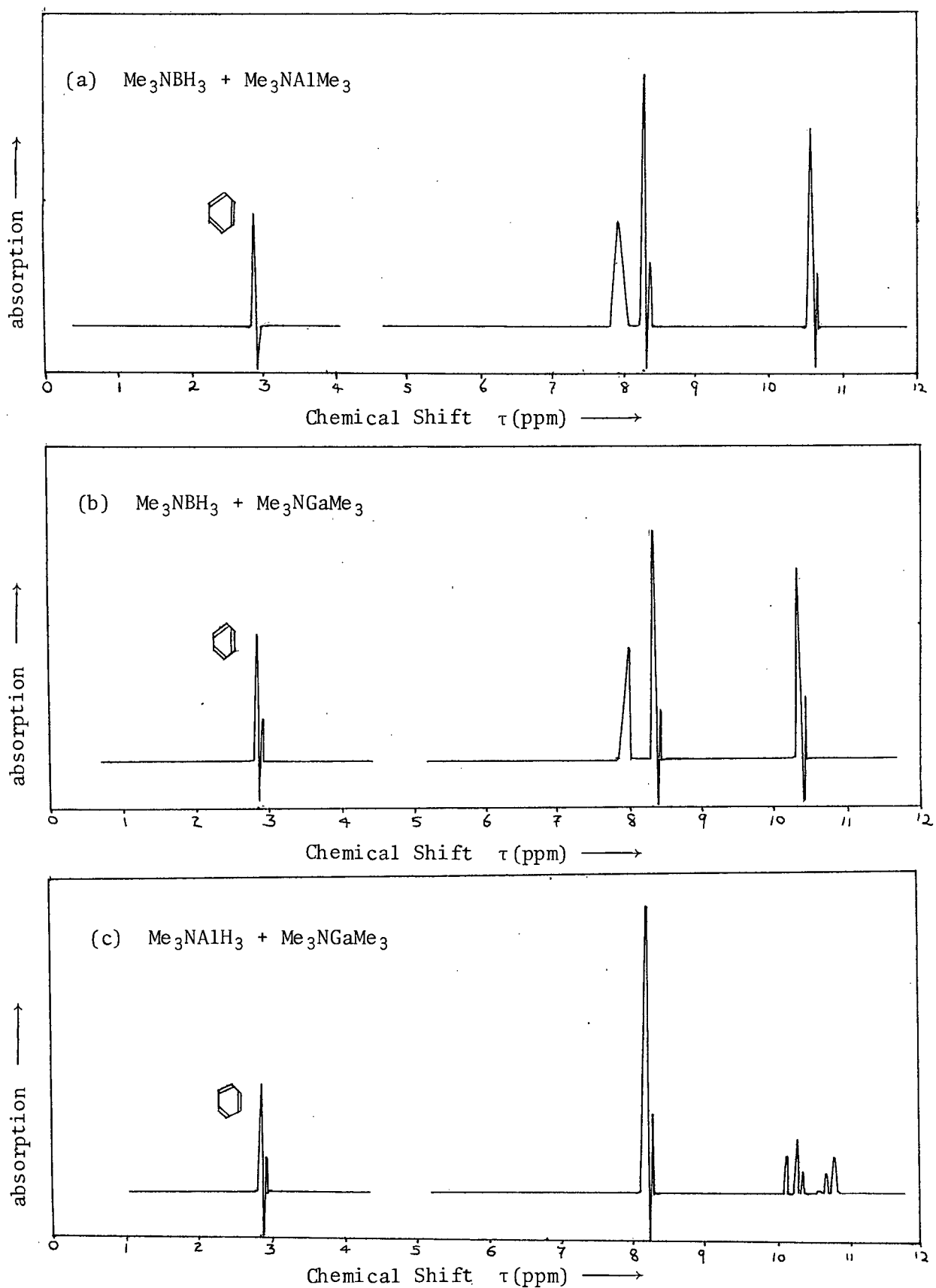


FIGURE 6

NMR Spectra of Mixed Trimethylamine Adducts of Different Group IIIB Hydrides and Alkyls at 60 Mc/sec.

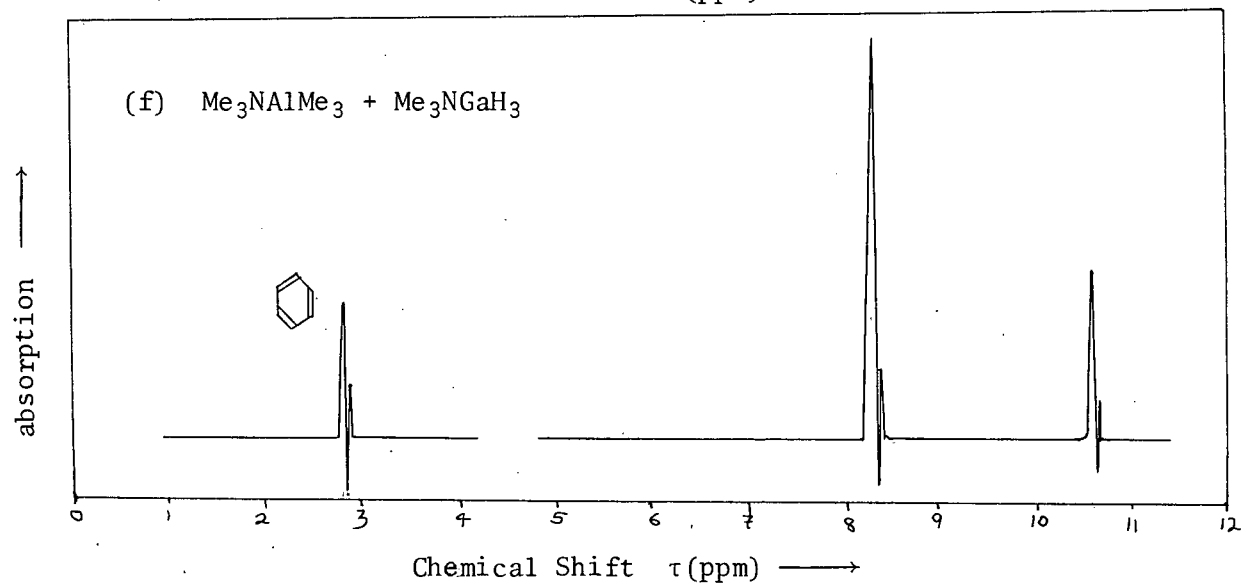
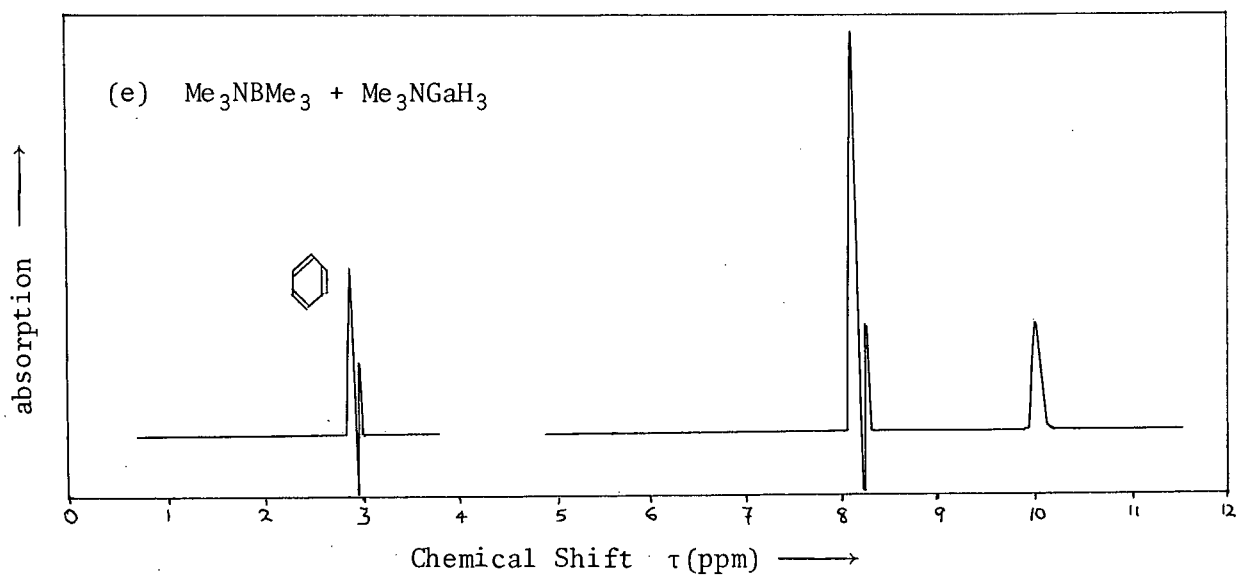
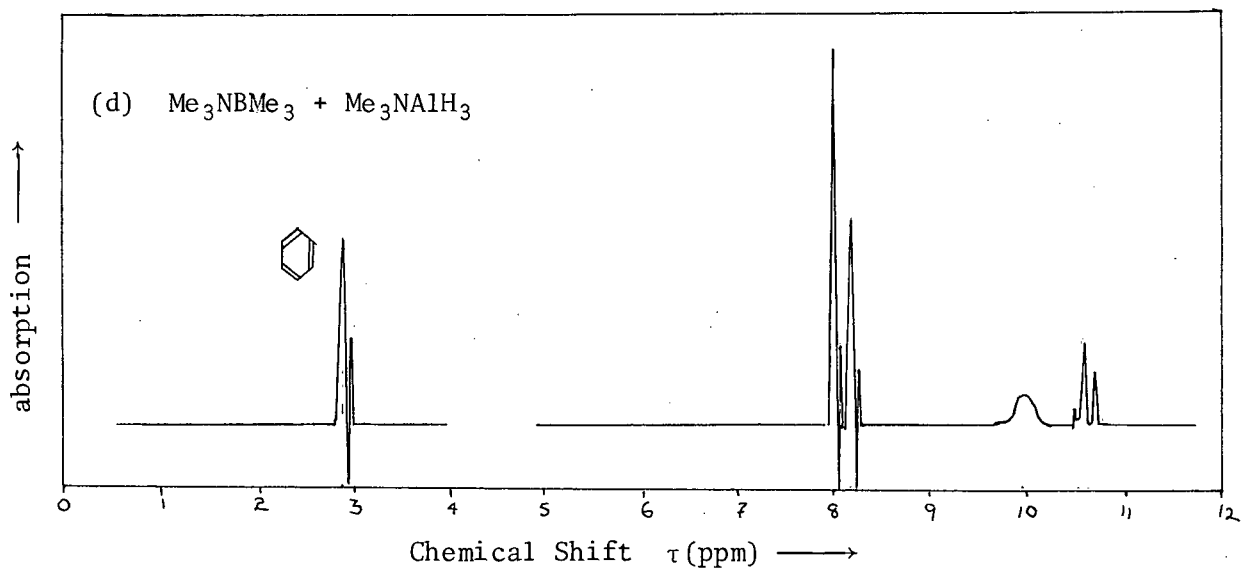


FIGURE 6 (Continued)

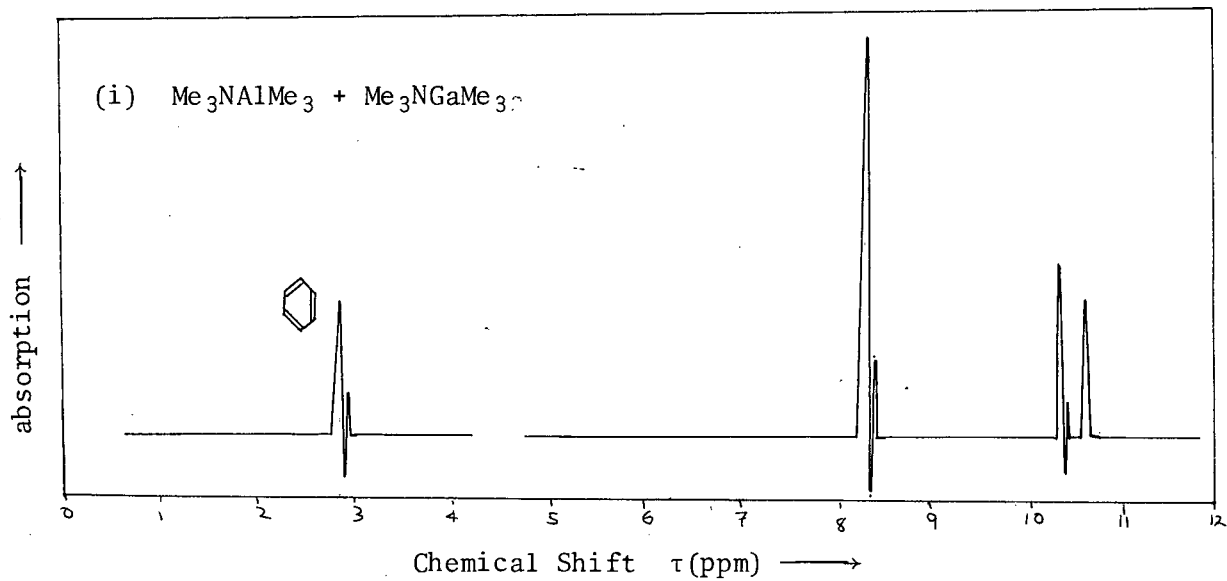
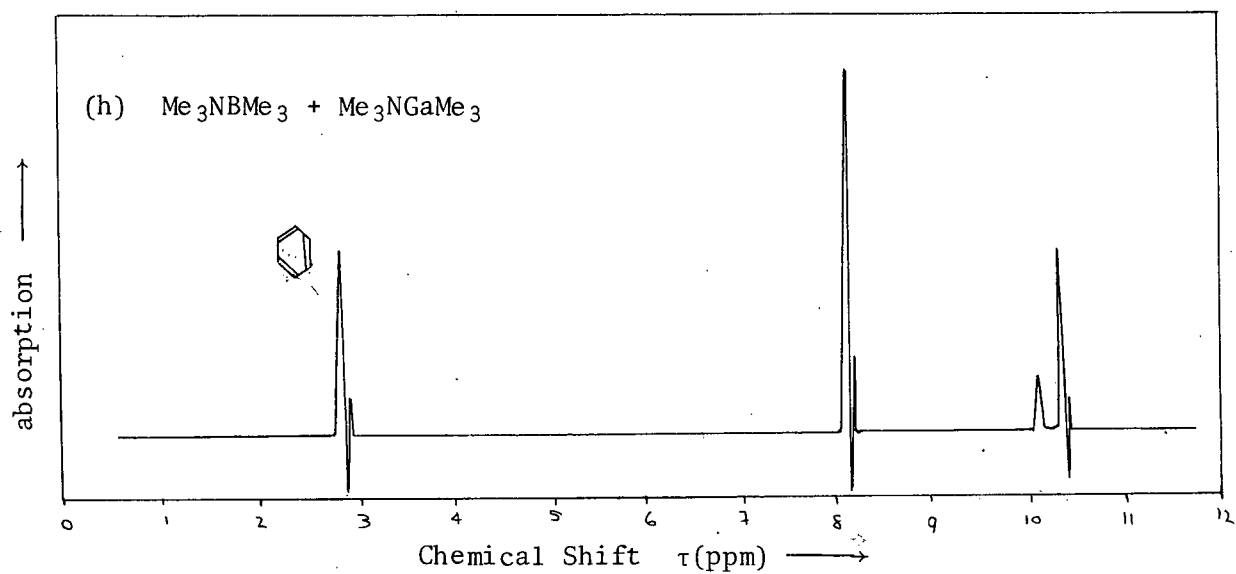
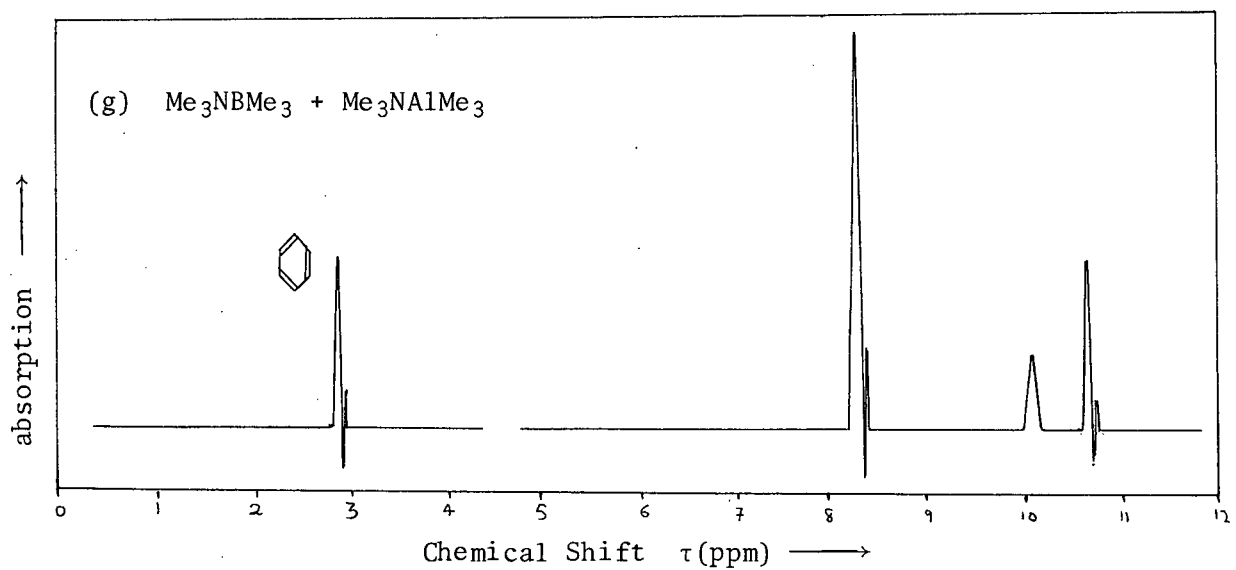


FIGURE 6 (Continued)



An examination of Table 10 indicates that no general mechanism or principal can be invoked to explain all the results and as mentioned earlier the mechanisms of exchange reactions between Group IIIB trialkyls or their adducts are little understood. In spite of the uncertainties, some observations and crude conclusions can be arrived at.

If a bridged dimer is formed as an intermediate in which one or both metal atoms are five-coordinate and one metal may be four-coordinate (as is postulated for the alkyl-hydride exchange in the trimethylamine adducts of organogallanes and organoalanes (59)), then those metals which five-coordinate or compounds which can readily lose their Lewis base adduct should show an exchange occurring. This is born out with the compound  $\text{Me}_3\text{NBMe}_3$ , which is itself largely dissociated into  $\text{Me}_3\text{N}$  gas and  $\text{BMe}_3$  at room temperature. The exchange reactions with this moiety all show  $\text{Me}_3\text{N}$  exchange and with  $\text{Me}_3\text{NAlH}_3$  show alkyl-hydride exchange. Of the three Group IIIB elements used, aluminum has the greatest tendency for five-coordination, thus, almost all the reactions involving  $\text{Me}_3\text{NAlMe}_3$  and  $\text{Me}_3\text{NAlH}_3$  show  $\text{Me}_3\text{N}$  exchange.

From the NMR spectra, two of the reactions indicate alkyl-hydride exchange. The first, that between  $\text{Me}_3\text{NAlH}_3$  and  $\text{Me}_3\text{NGaMe}_3$  to produce gallane compounds which have Ga-Me signals at  $\tau = 10.11, 10.17, 10.25$ , corresponding to  $\text{Me}_3\text{NGaMeH}_2$ ,  $\text{Me}_3\text{NGaMe}_2\text{H}$  and some starting material  $\text{Me}_3\text{NGaMe}_3$  as well as possibly some  $\text{Me}_3\text{NGaH}_3$ , all of which are in equilibrium in solution. In addition, the alane compounds produced give signals at  $\tau = 10.51, 10.57$  corresponding to  $\text{Me}_3\text{NAlMe}_2\text{H}$  and  $\text{Me}_3\text{NAlMe}_3$ . There is a shoulder at  $\tau = 10.47$  on the NMR peak at  $\tau = 10.51$ , and so we can surmise that the compound  $\text{Me}_3\text{NAlMeH}_2$  is also present, and maybe some starting material  $\text{Me}_3\text{NAlH}_3$ . The NMR spectrum shows no change over a two week period. Thus it seems that the

two sets of exchange reactions of trimethylamine adducts of organoalanes and organogallanes are existing together in solution. It is a great puzzle why the compounds  $\text{Me}_3\text{NAlMe}_3$  and  $\text{Me}_3\text{NGaH}_3$  don't exchange alkyl groups since, as postulated above, these two species exist at a steady concentration in the products of exchange between  $\text{Me}_3\text{NAlH}_3$  and  $\text{Me}_3\text{NGaMe}_3$ .

The second reaction showing alkyl exchange is between  $\text{Me}_3\text{NBMe}_3$  and  $\text{Me}_3\text{NAlH}_3$  to produce alane compounds giving signals at  $\tau = 10.49, 10.54, 10.60$  corresponding to  $\text{Me}_3\text{NAlMeH}_2$ ,  $\text{Me}_3\text{NAlMe}_2\text{H}$ , and  $\text{Me}_3\text{NAlMe}_3$ , and boron compounds giving a signal at  $\tau = 9.95$  which is about 13 cps in width at half peak height. Since there are methyl groups transferred to the alanes there should also be hydride groups transferred to the boron atom. Thus the broad peak at  $\tau = 9.95$  probably represents several compounds of the type  $\text{Me}_3\text{NBMeH}_2$ ,  $\text{Me}_3\text{NBMe}_2\text{H}$  and possibly some starting material  $\text{Me}_3\text{NBMe}_3$ . Spin-spin coupling of the methyl protons with the  $^{11}\text{B}$  nucleus, along with quadrupole broadening probably causes the loss of detail from this peak. This NMR spectrum is also unchanged over a period of time. Again it is puzzling why the compounds  $\text{Me}_3\text{NBH}_3$  and  $\text{Me}_3\text{NAlMe}_3$  do not show methyl-hydride exchange.

The  $\text{BH}_3$  moiety is a stronger Lewis acid than  $\text{BMe}_3$  and its tendency to dissociate from trimethylamine is much less than  $\text{BMe}_3$ . Boron is not known to have a coordination number greater than four, and therefore any Lewis base adduct of a trisubstituted boron atom must dissociate before a bridged dimer involving boron can be formed. Thus, in the NMR spectra it is observed that all solutions containing  $\text{Me}_3\text{NBH}_3$  show no  $\text{Me}_3\text{N}$  exchange, and in the exchange between  $\text{Me}_3\text{NBMe}_3$  and  $\text{Me}_3\text{NAlH}_3$  where it is postulated that formation of species of the type  $\text{Me}_3\text{NBMe}_2\text{H}$  and  $\text{Me}_3\text{NBMeH}_2$  and possibly  $\text{Me}_3\text{NBH}_3$  occurred, it is seen that there are two NMR signals for  $\text{Me}_3\text{N}$ , indicating that

there is restricted amine exchange here as well.

In conclusion it seems that a great deal of more work must be done, particularly on reaction kinetics, in order to understand the exchange of ligands in alkyl and hydride compound of the Group IIIB elements.

## VII. Experimental

### A. Experimental Techniques

#### (a) Desiccation

All gases were dried first by fractionating under high vacuum through a trap at  $-20^{\circ}\text{C}$ , to remove large amounts of water, and then condensed at  $-196^{\circ}\text{C}$  into one limb of a drying pistol, see Figure 7, packed with a mixture of glass-wool and phosphorus pentoxide. The gas is passed through the phosphorus pentoxide by alternately cooling one limb and then the other limb. The dried gases are then stored at less than one atmosphere in large glass bulbs attached to the vacuum line.

All solvents were dried and redistilled before use; diethyl ether over lithium hydride, n-butyl ether over molten sodium, benzene and cyclohexane over molten potassium. Methanol was distilled from a mixture of magnesium turnings and iodine.

Solid components were purified by sublimation, either by vacuum bulb-to-bulb sublimation or as with trimethylamine hydrochloride, sublimed to the cooled central finger of the apparatus shown in Figure 8. Trimethylamine gallane was sublimed under dynamic vacuum from the flask to the large vertical tube, marked as A, of the apparatus, which was cooled to  $-80^{\circ}\text{C}$ , shown in Figure 9.

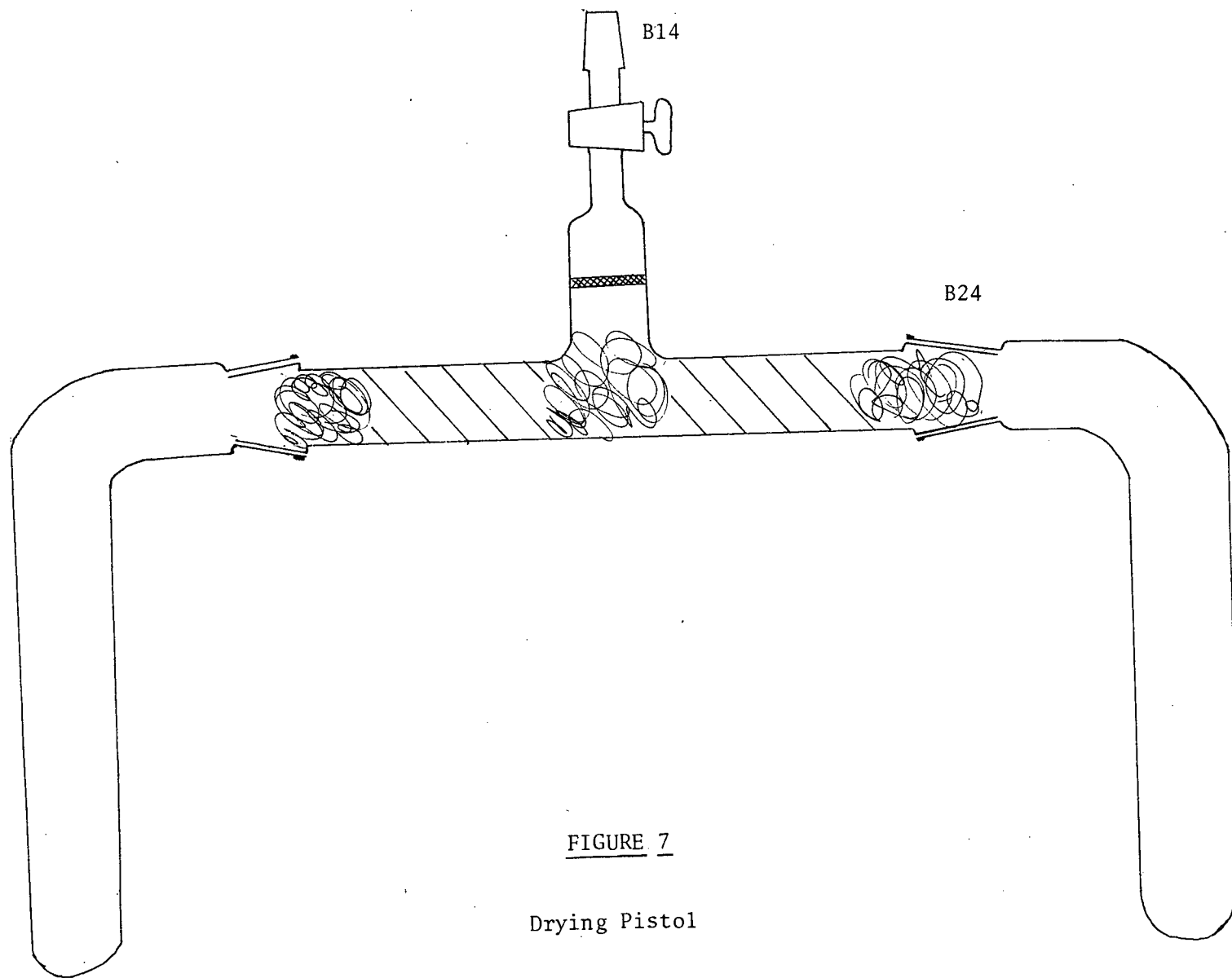


FIGURE 7

Drying Pistol

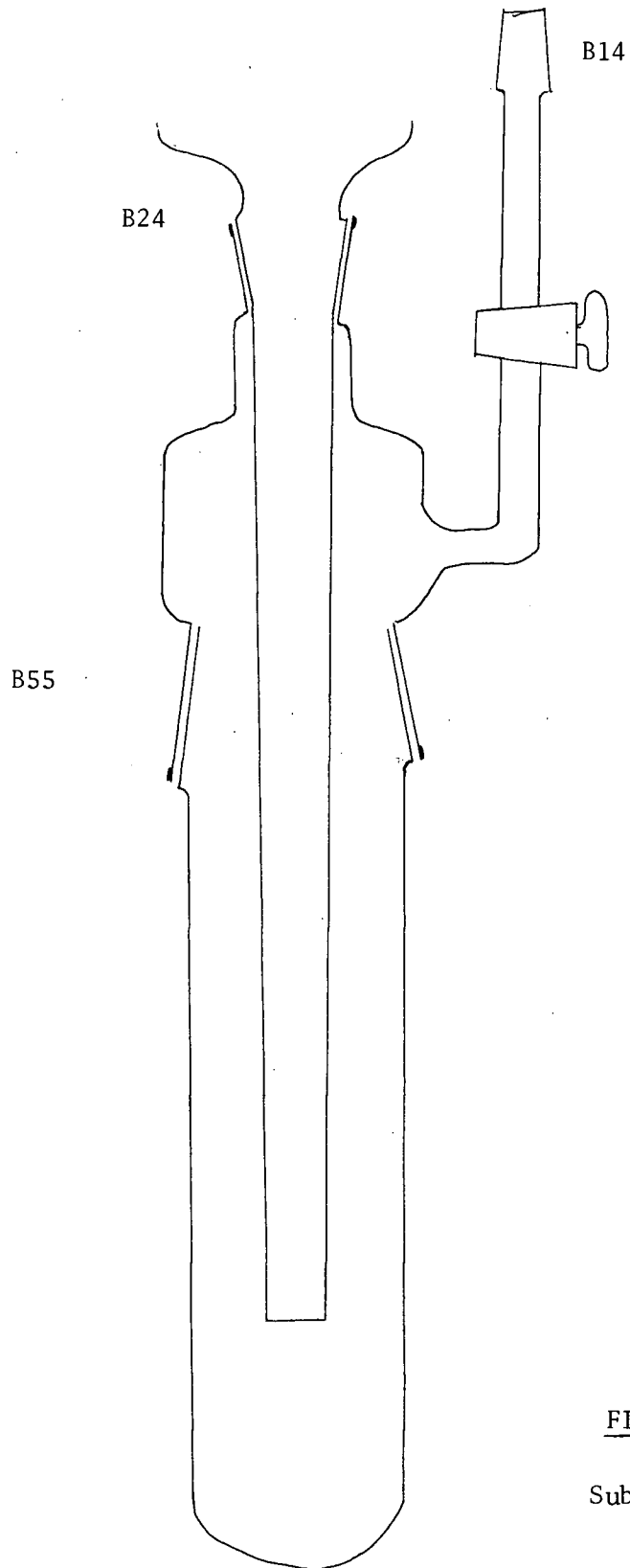


FIGURE 8

Sublimer

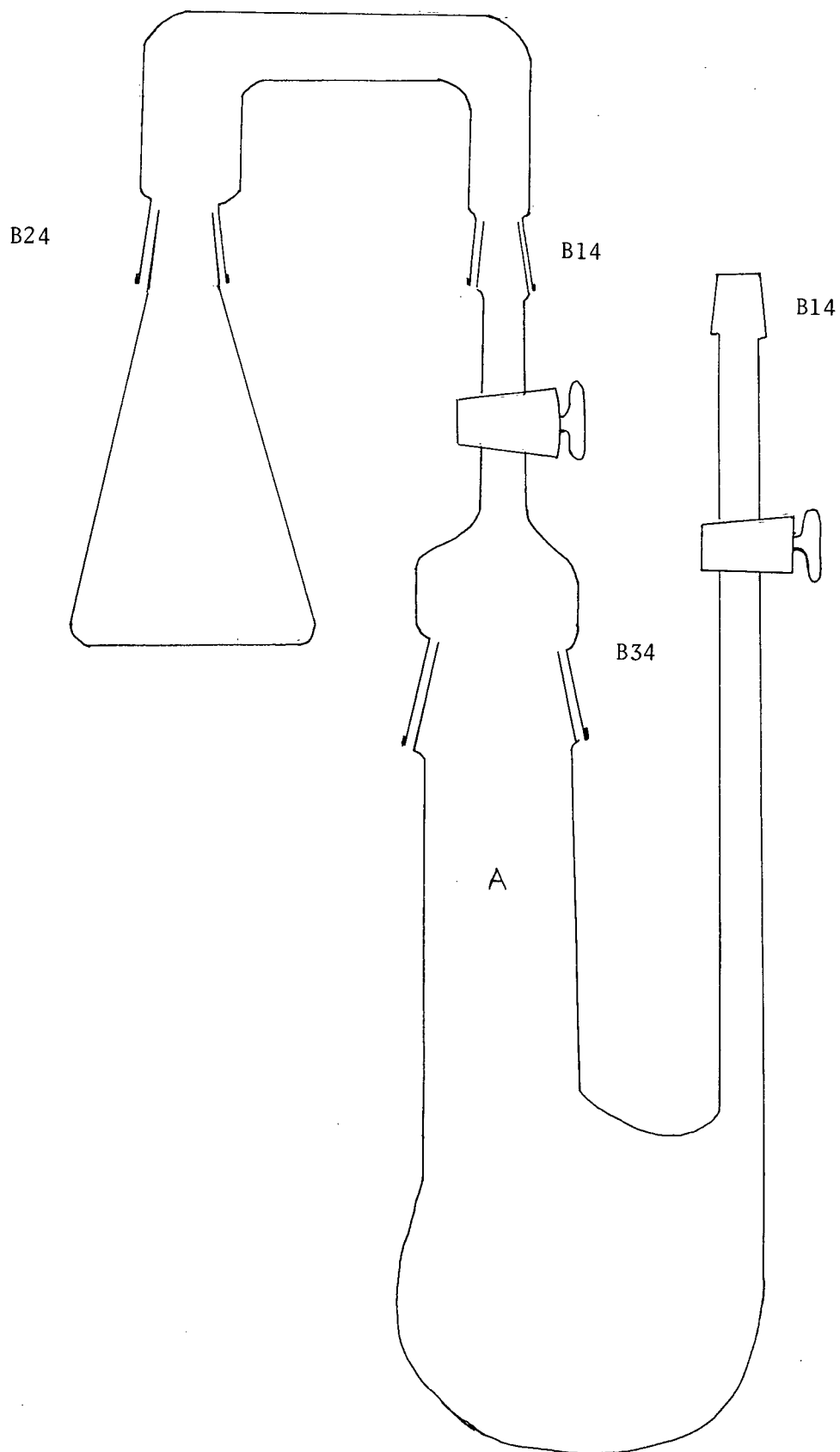


FIGURE 9

$\text{Me}_3\text{NGaH}_3$  Sublimier

All glassware was washed with acetone, oven dried, evacuated and filled with nitrogen before use. All nitrogen used was Canada Liquid Air "L" grade, purified nitrogen.

The hydride and alkyl derivatives, because of their relative instability and extreme reactivity with oxygen or water vapour were all prepared and handled in either a high-vacuum system or a nitrogen filled dry box. The high vacuum system developed for the work is shown in Figure 10. A double-stage rotary oil pump (Welch Scientific Co.) and an electrically heated single stage mercury diffusion pump were used to obtain a vacuum of greater than  $10^{-4}$  mm of Hg.

The dry box (Kewaunee Scientific Equipment) had a special ante-chamber that could be evacuated by a double-stage rotary oil pump and then filled with dry nitrogen to ensure the purity of the atmosphere in the box. The dry box is also connected to a circulating pump which circulates the box's atmosphere through a drying train containing molecular sieve (Fisher type 5A) and a copper furnace to remove any oxygen.

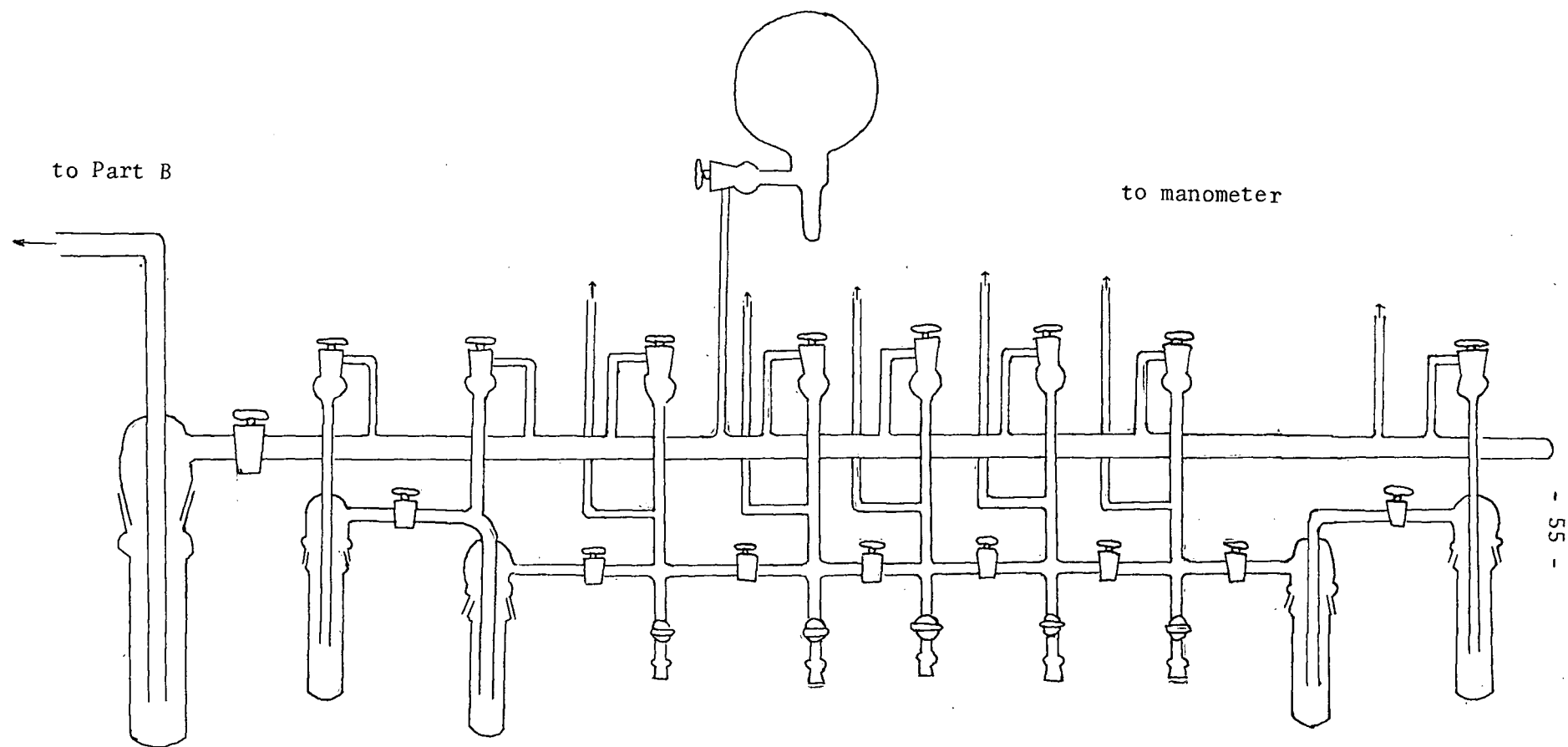
(b) Grease

Apiezon "N" grease was used in the summer and Apiezon "L" in the winter on all joints unless otherwise stated. On apparatus that was warmed above room temperature Apiezon "T" grease was used. The principal thought behind the design and use of any apparatus in the research was to have a few greased joints as possible.

(c) Reaction-Filtration Apparatus

The apparatus shown in Figure 11 found extensive use in our work. The apparatus is evacuated filled with dry nitrogen, and the reactants are placed in flask A. Additional reagents may be added during the course of a reaction





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FIGURE 10

Vacuum Line, Part A

[illegible]

Vacuum Line, Part B

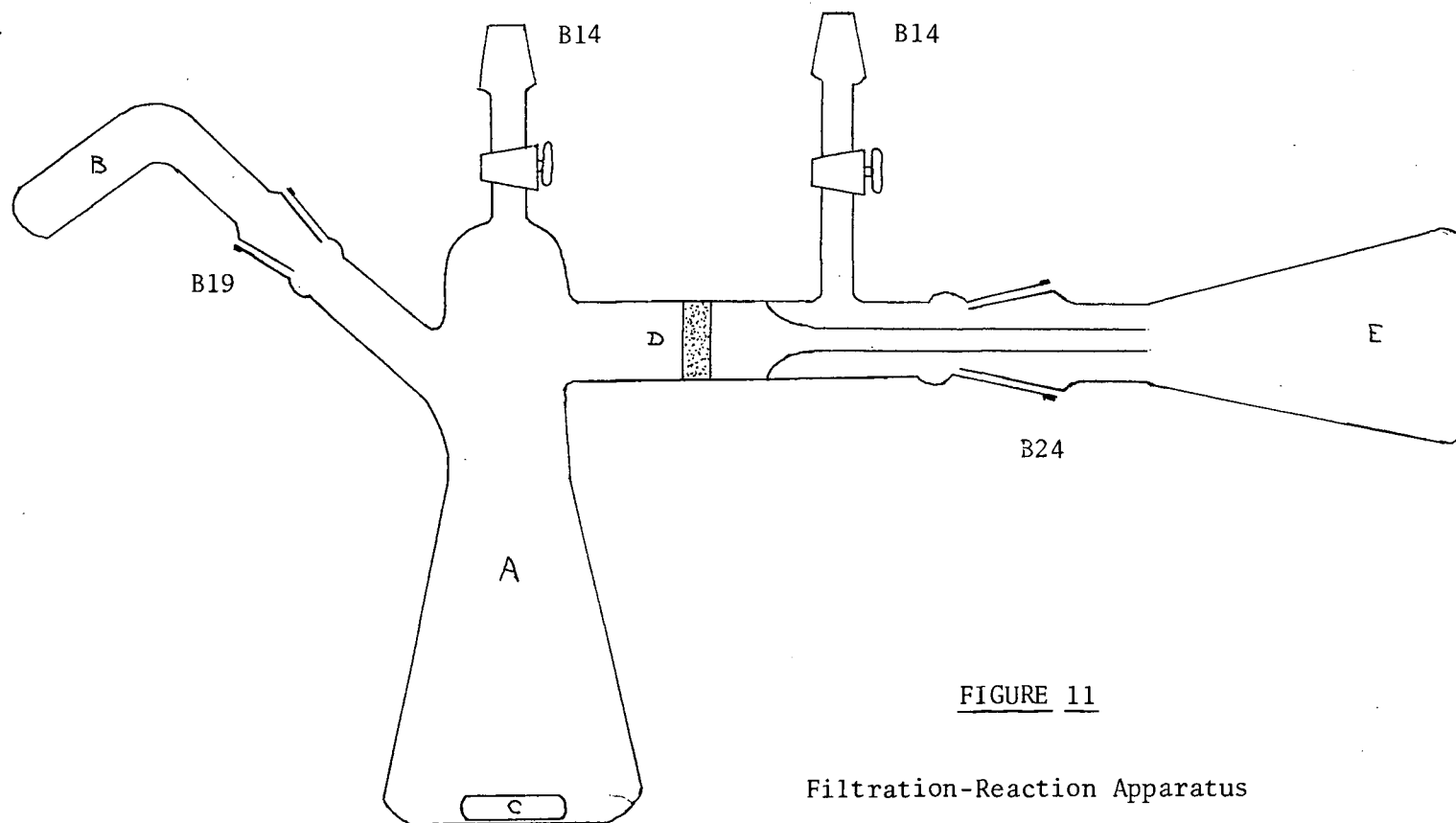


FIGURE 11

Filtration-Reaction Apparatus

by rotating the dumper tube B, the reaction mixture is stirred by a magnetic bar C. The products, if gaseous may be removed by a Topley pump through one of the stopcocks, or if in solution can be filtered through the sintered disc D (medium porosity) by cooling or evacuating the receiver flask E.

(d) Molecular Weights

Molecular weights were determined by the cryoscopic method. In the dry box an accurately known weight of pure compound was dissolved in a weighed sample of pure benzene (about 15 ml). The benzene solution was poured into the molecular weight apparatus, see Figure 12, and removed from the dry box. A slow stream of pure nitrogen was flushed through the apparatus as it was cooled in an ice bath. The freezing point of the solution was recorded and compared with that of pure benzene solvent and with standard solutions of biphenyl in benzene solvent. The following empirical formula was used to calculate the molecular weights.

$$\text{molecular weight} = \frac{[K_f]X[\text{weight of sample (gms)}]}{[\text{weights of benzene solvent (gms)}]X[\text{change in temperature (}^\circ\text{C)}]}$$

$K_f$  = freezing point depression constant  $5.10^\circ\text{C per molal.}$

(e) Spectroscopy

Infrared spectroscopy was used throughout this work for semi-quantitative analysis and for structural determination of compounds. Infrared spectra were recorded on the following Perkin-Elmer instruments; 137, NaCl range  $4000 - 650 \text{ cm}^{-1}$ , 137, KBr, range  $800 - 400 \text{ cm}^{-1}$ , 457 range  $4000 - 250 \text{ cm}^{-1}$ , 21 range  $4000 - 550 \text{ cm}^{-1}$ . The observable range for both liquid and gas samples was between  $4000$  and  $400 \text{ cm}^{-1}$  because KBr windows were used.

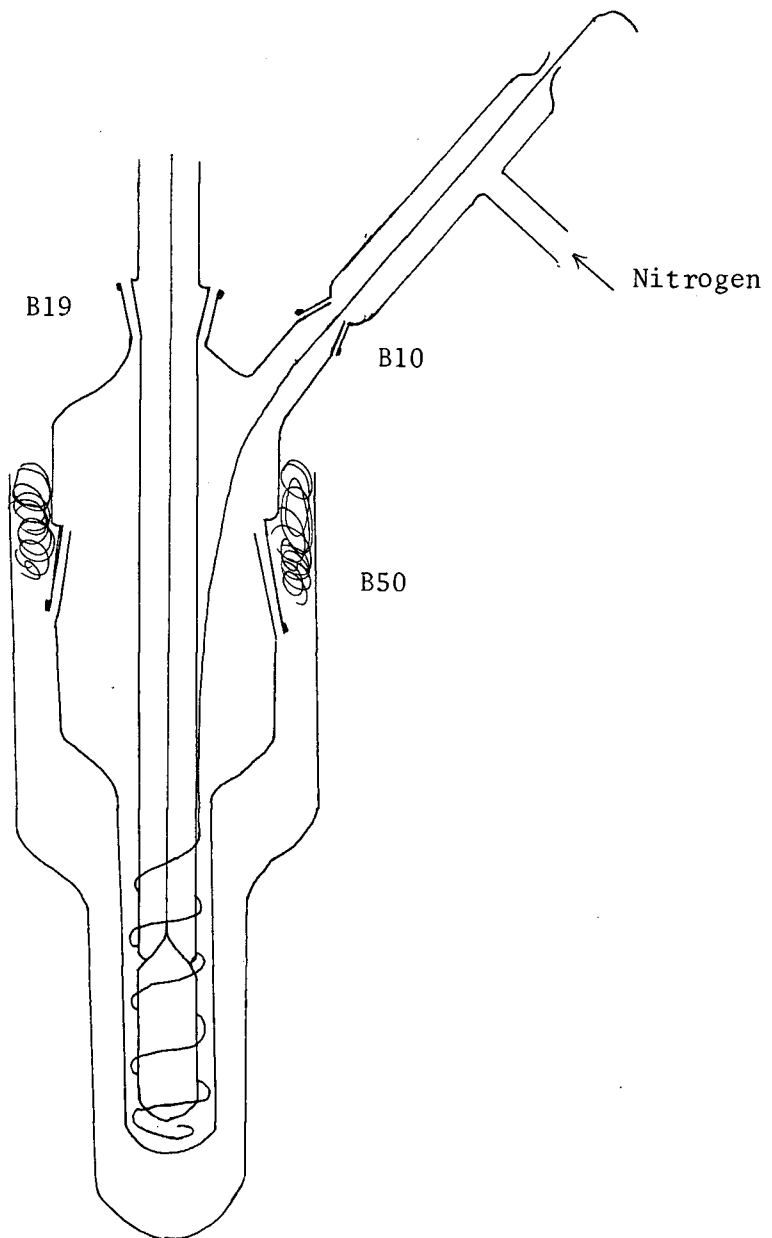


FIGURE 12

Molecular Weight Apparatus

For gaseous or volatile samples a 10 cm gas cell was used with KBr windows. For liquid or solution samples a 0.05 cm fixed path length solution cell with KBr windows was used and a variable-thickness cell filled with pure solvents (usually benzene) was placed in the reference beam to compensate for solvent absorption. Because of the instability of most of the gallium hydride adducts prepared, all infrared solution cells were loaded in the dry box and a spectrum run as rapidly as possible.

As with infrared spectroscopy, nuclear magnetic resonance spectroscopy, NMR, was used as a tool to investigate reactions and for structural determination. The instruments used were a Varian A-60 and Jelco C-60 both operating with a radiofrequency of 60 megacycles per second and a Varian HA-100 which operates at a radiofrequency of 100 megacycles per second. Most samples were run in benzene solution with a concentration of about 0.1 M to 1 M. The benzene proton signal was used as an internal standard and was defined as  $\tau = 2.840$  p.p.m. Tetramethylsilane, TMS, was used as an external standard on several samples and is defined as  $\tau_{\text{TMS}} = 10.000$  p.p.m.

The NMR sample tubes were specially fitted with a flame-seal constriction and a B-10 quick-fit cone so that the samples could be loaded and sealed under an atmosphere of nitrogen. As with the infrared samples, the NMR spectra were run as rapidly as possible since steady decomposition at room temperature often impeded prolonged investigation.

(f) Lithium Methyl Standardization

On standing ether solutions of lithium methyl slowly decompose (35), and consequently these solutions were standardized just before use. The apparatus in Figure 13 was used for the standardization.

In a typical standardization 5.0 ml of the lithium methyl ether solution

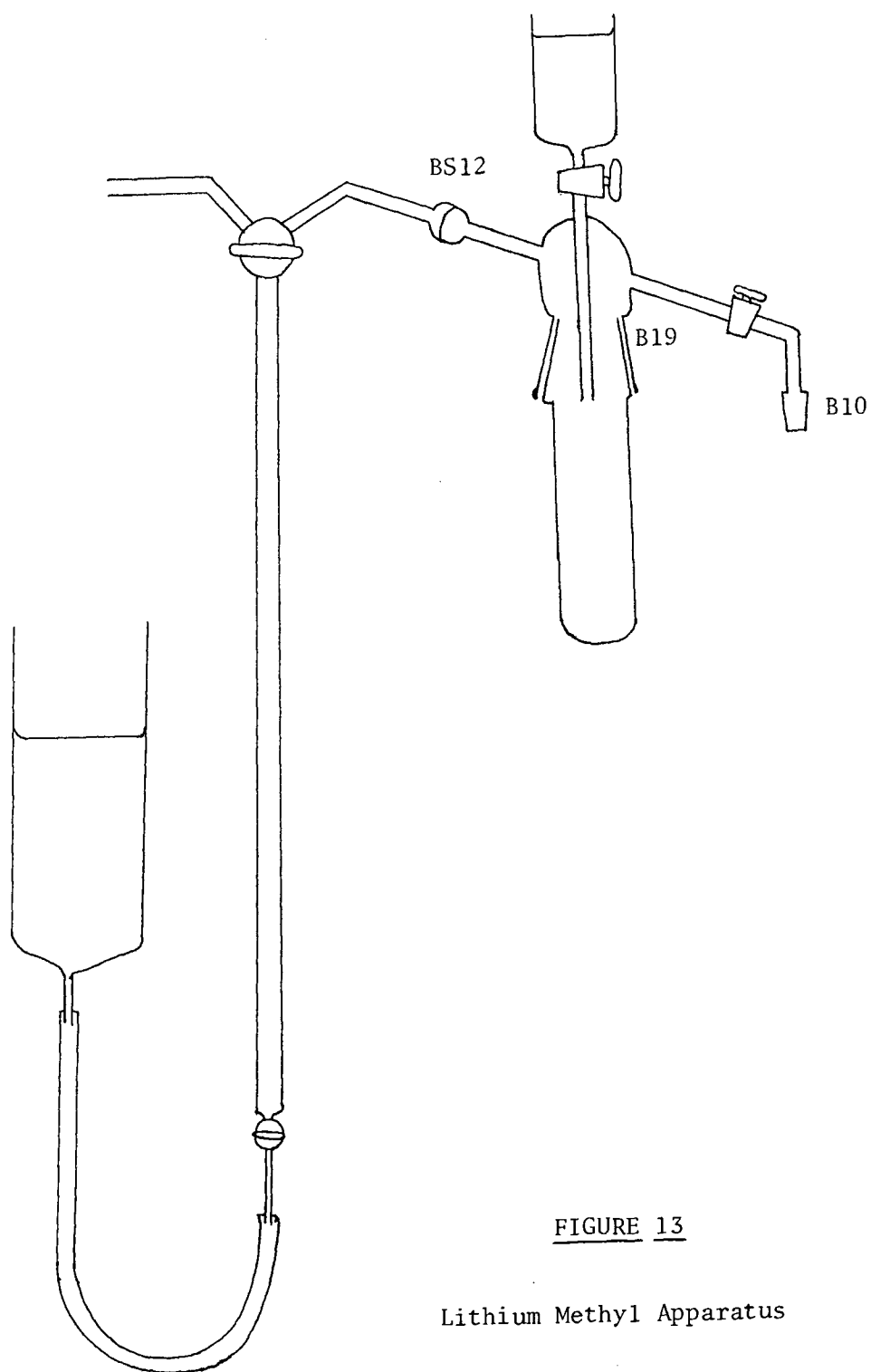


FIGURE 13

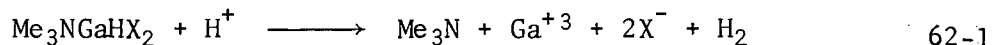
Lithium Methyl Apparatus

was added to the apparatus in the glove box. The apparatus was then removed from the glove box, the ether solution frozen in liquid nitrogen, the apparatus evacuated and then attached to the gas burette which was completely full of concentrated sulfuric acid. A mixture of 70% p-dioxane and 30% water was slowly added from the top reservoir hydrolysing the lithium methyl and forcing all the methane gas into the gas burette. The gas burette was removed and shaken several times to remove traces of ether and then the volume of gas measured. this procedure was repeated several times and the results averaged. Volume of gas was 71.6 ml at 19°C thus molarity was 0.598 M.

(g) Elemental Analysis

i) Active Hydrogen:

Active hydrogen was measured by placing a small weighed amount of compound in a round bottom flask in the dry box, attaching a stopcock adaptor and evacuating on the vacuum line. A small volume of degassed, dilute aqueous HNO<sub>3</sub> solution was then condensed onto the solid at -196°C. The mixture was allowed to reach room temperature and left to react for about one hour with stirring.



The volume of hydrogen gas, non-condensable at -196°C, was then measured using a Töpler pump. The amount of active hydrogen in the compound was then calculated.

This aqueous solution was made up to a known volume and aliquots were used in the determination of chloride and gallium as indicated below.



ii) Chloride

A measured aliquot of the solution prepared above was made slightly acidic with dilute nitric acid, then a slight excess of aqueous silver nitrate solution was added, whereupon silver chloride is precipitated. The precipitate was then heated to 80°C and stirred vigorously to coagulate the initially colloidal precipitate. The precipitate was collected in a filtering crucible, washed with very dilute nitric acid and dried at 120°C. The precipitate was weighed as AgCl which contains 24.74% chlorine by weight.

iii) Gallium

A measured aliquot of the solution prepared in section (i) was measured out into a beaker. The solution was first made neutral with dilute ammonia solution, then was made slightly acidic, pH 5-7, with dilute aqueous HCl. The solution was then heated to 80°C and a slight excess of a 5% solution of 8-hydroxyquinoline in glacial acetic acid was added followed by an aqueous solution of saturated ammonium acetate until precipitation of  $\text{Ga}(\text{C}_9\text{H}_6\text{NO})_3$  is complete. After digestion at 80°C for one hour, the yellow precipitate was collected in a filtration crucible and the precipitate washed, first with hot, then cold water. The precipitate was then dried at 120°C and weighed and its gallium content calculated from the formula  $\text{Ga}(\text{C}_9\text{H}_6\text{NO})_3$  which is 13.89% gallium by weight. This method has been found to give accurate determinations for a minimum concentration of 10 mg of gallium in 50 ml of solution.

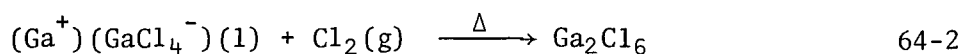
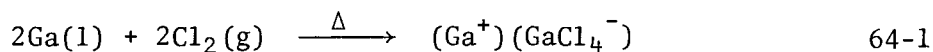
If the gallium compound had a methyl ligand attached to it then this ligand was not removed under mild hydrolysing conditions such as in dilute  $\text{HNO}_3$  solutions, and gallium was precipitated as  $\text{GaMe}(\text{C}_9\text{H}_6\text{NO})_2$  which contains 18.78% gallium. If the gallium compound had two or more methyl ligands

attached to it then these were also often not removed under mild hydrolysing conditions. Attempts to precipitate gallium as a 8-hydroxyquinoline complex were not too successful for the complexes formed tended to be colloids and difficult to filter off. Gravimetric determinations of gallium in these latter compounds was difficult and the results poor. Wade and coworkers (69) have proposed a method of analysing these compounds, by titrating with EDTA after the removal of organic ligands by boiling the sample for several hours in concentrated hydrochloric acid.

## B. Preparative

### (a) Preparation of Gallium Trichloride (63) GaCl<sub>3</sub>

Gallium trichloride was prepared by direct combination of the elements. Pure chlorine gas (Matheson Ltd.) was dried by passing through concentrated sulphuric acid in a bubbler and was then passed into the all glass apparatus shown in Figure 14. The gallium metal, about 15 gms, (Alfa Inorganics Inc.) placed in A soon melted on warming with a bunsen burner, and reacted with the chlorine, first to give a colourless liquid, gallium tetrachlorogallate (64), Ga<sub>2</sub>Cl<sub>4</sub> (melting point 170.5°C (65)). On adding more chlorine this liquid Ga<sub>2</sub>Cl<sub>4</sub> disappeared and the liquid gallium burned with a grey-white flame giving a volatile white solid, gallium trichloride GaCl<sub>3</sub>, (melting point 79°C).



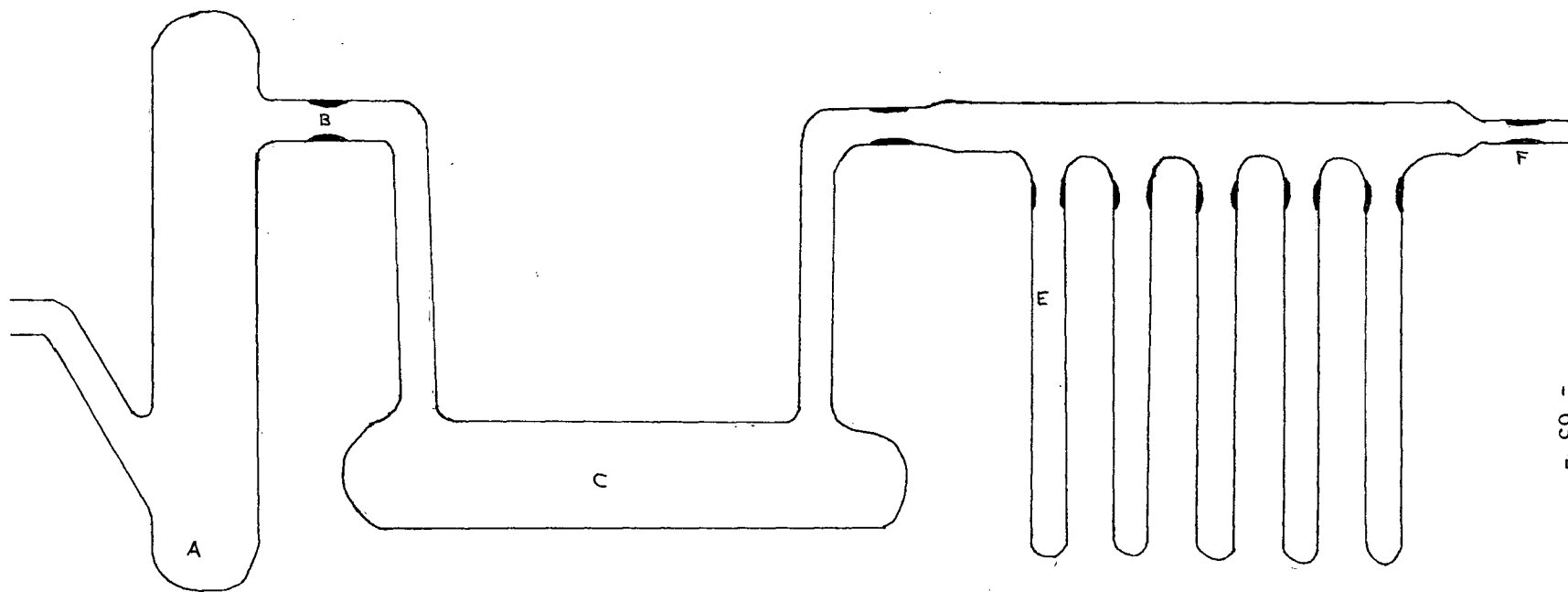
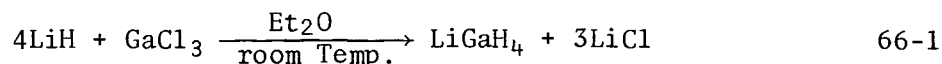


FIGURE 14

Gallium Trichloride Apparatus

The rate of flow of chlorine gas and rate of heating the molten gallium were adjusted so that most of the volatile  $\text{GaCl}_3$  was deposited in the cooled receiver boat C. After all the gallium had reacted (essentially 100%), any sublimate in A was driven into C by warming and then flame sealing the constriction at B. The apparatus was then evacuated and flame sealed at F. The crude halide was then resublimed into the ampoules E and then these were sealed at their constrictions. The gallium trichloride was found to remain stable indefinitely when stored this way.

(b) Preparation of Lithium Gallium hydride (66),  $\text{LiGaH}_4$



An ampoule of  $\text{GaCl}_3$ , was weighed and broken open in the dry box and placed in a conical flask. The gallium trichloride was then dissolved in diethyl ether and the ampoule washed several times to ensure quantitative removal of  $\text{GaCl}_3$ . The empty ampoule was reweighed and the weight of  $\text{GaCl}_3$  determined. The ethereal solution of  $\text{GaCl}_3$  and all the washings were now added to the nitrogen filled reaction-filtration apparatus (see Figure 11) and the solution brought up to about 150 ml.

From the weight of  $\text{GaCl}_3$  calculated, (8.59 gms; 48.8 mmoles) the weight of about 16 molar equivalents of finely ground lithium hydride (7.45 gms; 938 mmoles) (Alfa Inorganics Inc.), enough for a four-fold excess, was weighed out under nitrogen into the dumper tube.

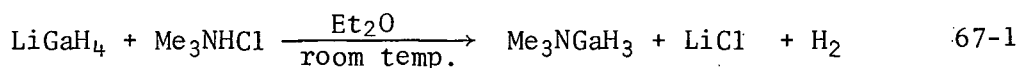
The reaction flask was cooled to  $-50^\circ\text{C}$  in an acetone-solid  $\text{CO}_2$  bath and the dumper tube rotated upwards to permit the slow addition of  $\text{LiH}$  to the reaction flask over a period of about thirty minutes. A bubbler was

attached to the apparatus so that the reaction could be carried out under a constant pressure of one atmosphere of nitrogen. The coolant was allowed to warm up to room temperature and the mixture was stirred for about fifty hours to ensure complete reaction.

The resulting reaction mixture was filtered through the glass sintered disc and a clear colourless filtrate resulted. This filtrate was then transferred, in the dry box, to a conical flask fitted with a break seal and an extended neck which was flame sealed for storage. The  $\text{LiGaH}_4$  ether solution was observed to be indefinitely stable if stored in all glass ampoules under a nitrogen atmosphere and cooled below  $0^\circ\text{C}$ .

Lithium gallium deuteride,  $\text{LiGaD}_4$ , was prepared and stored in exactly the same manner as  $\text{LiGaH}_4$ , only lithium deuteride,  $\text{LiD}$ , (Alfa Inorganics Inc.) was substituted in the preparation for lithium hydride.

(c) Preparation of Trimethylamine Gallane (9),  $\text{Me}_3\text{NGaH}_3$



A known amount of lithium gallium hydride (2.38 gms; 29.4 mmoles) in ether solution was placed in the reaction-filtration apparatus, see Figure 11. Slightly less than the stoichiometric amount of trimethylamine hydrochloride,  $\text{Me}_3\text{NHCl}$ , (2.644 gms; 27.6 mmoles) (Alfa Inorganics Inc.) dried and purified by sublimation, was placed in the dumper tube of the reaction vessel which contained a nitrogen atmosphere.

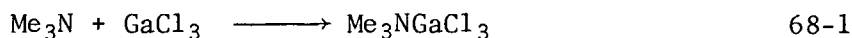
The ether solution of  $\text{LiGaH}_4$  was first cooled to  $-50^\circ\text{C}$  in a dry-ice cooled acetone bath, as the trimethylamine hydrochloride was added over a period of about 10 minutes. Then the solution was allowed to warm up to

room temperature and stirred for about four hours to ensure complete reaction.

The solution was next filtered through the glass sinter and the receiver flask containing the clear ether solution was attached to the sublimation apparatus, see Figure 9. This apparatus was attached to the vacuum line and the ether was pumped off at  $-50^{\circ}\text{C}$ . When most of the ether was removed, the residue was allowed to warm up to room temperature while the large bulb part of the sublimation apparatus was immersed in an acetone-solid  $\text{CO}_2$  slush bath. The pure trimethylamine gallane was vacuum sublimed as long needle-like crystals into the cooled receiver. The overall yield in going from gallium trichloride to trimethylamine gallane was about 60%.

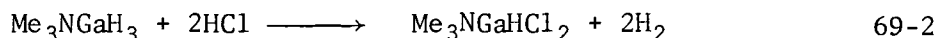
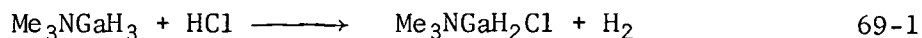
The deuterated compound, trimethylamine trideuterogallane,  $\text{Me}_3\text{NGaD}_3$  was prepared in the same manner only lithium gallium deuteride was substituted for lithium gallium hydride.

(d) Preparation of Trimethylamine Trichlorogallane,  $\text{Me}_3\text{NGaCl}_3$



An ampoule containing 5.318 gms (30.2 mmoles) of  $\text{GaCl}_3$  was broken open in the glove box and placed in a conical flask fitted with a stopcock adaptor. The flask was removed from the dry box and evacuated on the vacuum line. A very large excess of  $\text{Me}_3\text{N}$  was then condensed onto the  $\text{GaCl}_3$  at liquid nitrogen temperature and then the mixture was slowly warmed up to  $0^{\circ}\text{C}$  and kept at this temperature for four hours. The excess  $\text{Me}_3\text{N}$  is then pumped off at  $-20^{\circ}\text{C}$  and a white solid of  $\text{Me}_3\text{NGaCl}_3$  is left behind which was then examined by NMR and infrared spectroscopy. The yield is essentially 100% and the compound can be stored indefinitely in the dry box.

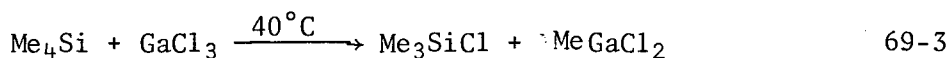
(e) Preparation of Trimethylamine Adducts of Monochlorogallane,  $\text{Me}_3\text{NGaH}_2\text{Cl}$ , and Dichlorogallane,  $\text{Me}_2\text{NGaHCl}_2$  (11)

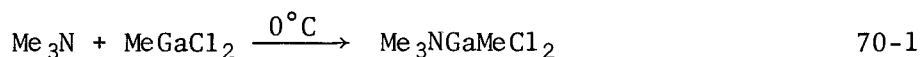


Trimethylamine monochlorogallane,  $\text{Me}_3\text{NGaH}_2\text{Cl}$  was prepared by weighing out 0.2414 gms (1.83 mmoles) of  $\text{Me}_3\text{NGaH}_3$ , into a conical flask fitted with a stopcock adaptor and then evacuating the flask on the vacuum line. 41.9 ml at NTP (1.83 mmoles) of HCl gas was condensed into the conical at liquid nitrogen temperature and then the flask was allowed to warm up to room temperature. After about two hours the flask was frozen in liquid nitrogen and the noncondensable gas, hydrogen, pumped off with a Töpler pump. Yield of gas 42.1 ml at NTP (1.84 mmoles). The product  $\text{Me}_3\text{NGaH}_2\text{Cl}$ , could be sublimed under a dynamic vacuum at room temperature to a cold finger of a sublimator cooled to  $-78^\circ\text{C}$  and collected as a white solid.

The trimethylamine dichlorogallane,  $\text{Me}_3\text{NGaHCl}_2$  was similarly obtained from the product of trimethylamine gallane (0.1608 gms; 1.22 mmoles) and HCl gas (56.0 ml at NTP, 2.44 moles). The hydrogen evolved was measured by the Töpler pump as 55.8 ml at NTP. The product is a white involatile solid, only slightly soluble in benzene.

(f) Preparation of Trimethylamine Adducts of Dichloromonomethylgallane  $\text{Me}_3\text{NGaMeCl}_2$  and Monochlorodimethylgallane,  $\text{Me}_2\text{NGaMe}_2\text{Cl}$  Method I  
(22, 47, 68):

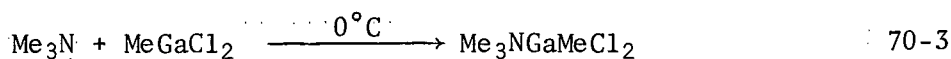




In the dry box an ampoule of  $\text{GaCl}_3$  was weighed, broken open and placed in the apparatus as shown in Figure 15. The  $\text{GaCl}_3$  was then sublimed into the reaction vessel by warming the outside of the tube and cooling the reaction vessel in acetone-solid  $\text{CO}_2$  slush bath, and the constriction flame sealed. The empty ampoule was then reweighed and the amount of  $\text{GaCl}_3$  determined (5.60 gms; 31.7 mmoles). Excess tetramethylsilane,  $\text{Me}_4\text{Si}$ , (3.44 gms; 39.0 mmoles) was condensed onto the  $\text{GaCl}_3$  and the mixture warmed up to  $40^\circ\text{C}$  and allowed to react for two hours. The reaction vessel was then cooled to  $0^\circ\text{C}$  and the volatile components, excess  $\text{Me}_4\text{Si}$  and  $\text{Me}_3\text{SiCl}$ , were pumped off and the desired product methyldichlorogallane,  $\text{MeGaCl}_2$ , as a white solid, stable under nitrogen at room temperature was left in the flask.

On the vacuum line an excess of  $\text{Me}_3\text{N}$  gas (1.17 l at NTP; 50.9 mmoles) was then condensed onto the solid  $\text{MeGaCl}_2$  and the mixture held at  $0^\circ\text{C}$  for several hours after which the excess  $\text{Me}_3\text{N}$  was pumped off, leaving a white solid. The product was then examined by infrared and NMR spectroscopy. The yield in going from  $\text{GaCl}_3$  to  $\text{Me}_3\text{NGaMeCl}_2$  is quite high. Only the dichloro gallium species is prepared by this method.

#### Method II



An ampoule containing  $\text{GaMe}_3$  (0.199 gms; 1.73 mmoles) was broken open in the dry box and dissolved in about 25 ml of diethyl ether in a conical



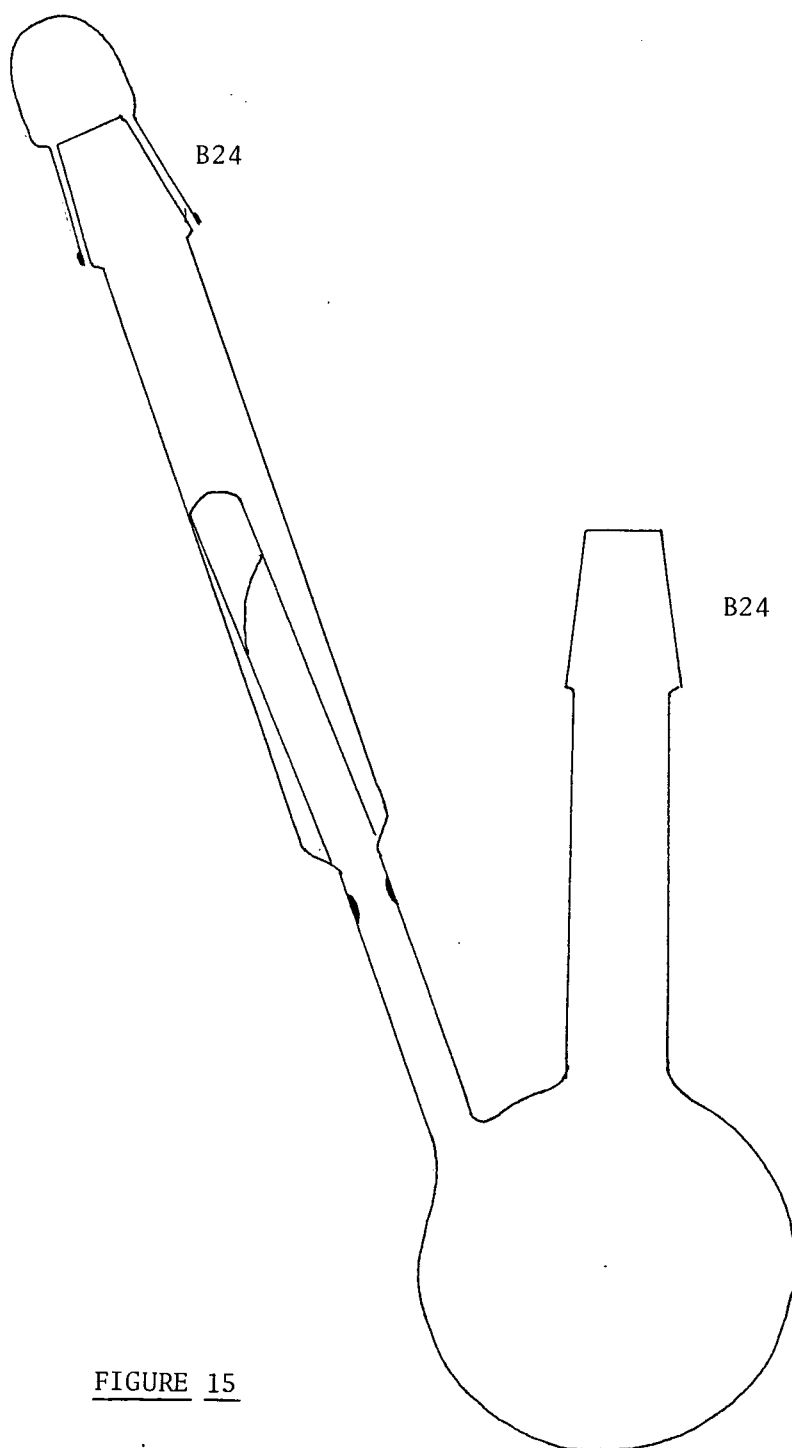
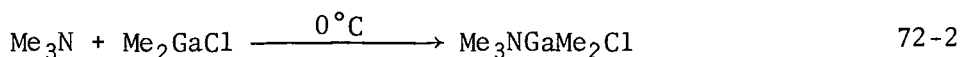
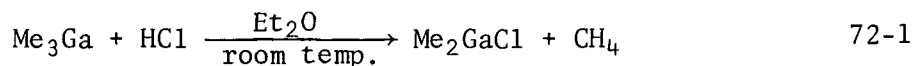


FIGURE 15

Apparatus for Reacting  $\text{Me}_4\text{Si}$  and  $\text{GaCl}_3$

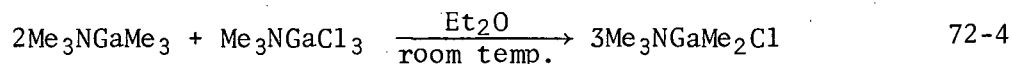
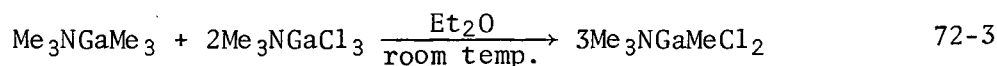
flask fitted with a stopcock adaptor. The flask was removed from the dry box, attached to the vacuum line and HCl gas (77.5 ml at NTP; 3.46 mmoles) was condensed into the flask. The flask was warmed up to room temperature and kept at this temperature for about one hour before being frozen in liquid nitrogen and the volatile components, CH<sub>4</sub>, (identified by its infrared spectrum) pumped off through a Töpler pump. Yield of gas 76.9 ml at NTP.

Into this ether solution of MeGaCl<sub>2</sub> was then condensed excess Me<sub>3</sub>N and allowed to react at room temperature for two hours. The unreacted Me<sub>3</sub>N and ether solvent were then removed at -20°C to leave a white powder behind whose spectra compares favorably with the infrared and NMR spectra of Me<sub>3</sub>NGaMeCl<sub>2</sub> prepared by other methods.



Using one mole of HCl (37.7 ml at NTP; 1.73 mmoles) with one mole of Me<sub>3</sub>Ga (0.198 gms; 1.73 mmoles) and condensing on excess Me<sub>3</sub>N, the compound Me<sub>3</sub>NGaMe<sub>2</sub>Cl was easily prepared by a method analogous to that for the preparation of Me<sub>3</sub>NGaMeCl<sub>2</sub>. The yield of these reactions was high.

### Method III



To prepare the Me<sub>3</sub>NGaMeCl<sub>2</sub> compound, Me<sub>3</sub>NGaCl<sub>3</sub> (0.349 gms; 1.48 mmoles)

and  $\text{Me}_3\text{NGaMe}_3$  (0.129 gms; 0.74 mmoles) were weighed out in the dry box, dissolved in ether and put into a conical flask fitted with a stopcock adaptor. This flask was removed from the dry box, attached to the vacuum line and the solvent removed at  $-20^\circ\text{C}$  leaving a white powder behind which analysed by infrared and NMR spectroscopy as  $\text{Me}_3\text{NGaMeCl}_2$ .

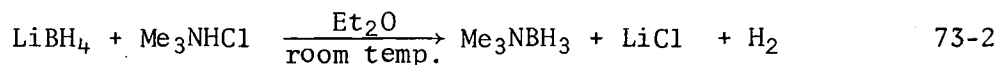
$\text{Me}_3\text{NGaMe}_2\text{Cl}$  was prepared in the same manner only using 0.159 gms (0.68 mmoles) of  $\text{Me}_3\text{NGaCl}_3$  and 0.233 gms, (1.34 mmoles) of  $\text{Me}_3\text{NGaMe}_3$ .

(g) Preparation of Trimethylamine Trimethylgallane,  $\text{Me}_3\text{NGaMe}_3$



An ampoule of  $\text{GaMe}_3$  containing 2.16 gms (18.8 mmoles), prepared in the laboratory, was broken open in the glove box and placed in a conical flask fitted with a stopcock adaptor. On the vacuum line  $\text{Me}_3\text{N}$  gas, about ten times excess, was condensed onto the  $\text{GaMe}_3$  and allowed to react for about two hours at  $0^\circ\text{C}$ . The excess  $\text{Me}_3\text{N}$  was then pumped off at  $-20^\circ\text{C}$  and a white solid, slightly sticky, was left behind. The pure  $\text{Me}_3\text{NGaMe}_3$  could be stored indefinitely in a nitrogen filled flask at room temperature.

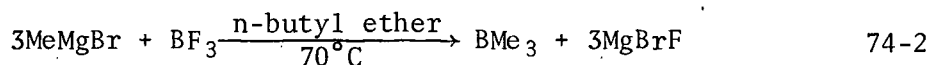
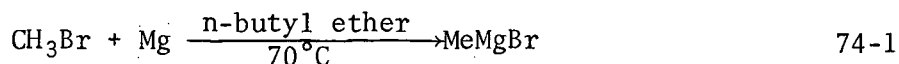
(h) Preparation of Trimethylamine Borane,  $\text{Me}_3\text{NBH}_3$



Trimethylamine borane was prepared by a procedure similar to that for the preparation of  $\text{Me}_3\text{NGaH}_3$ , The differences being, lithium borohydride,  $\text{LiBH}_4$ , was used in place of  $\text{LiGaH}_4$ , and the entire reaction was carried out at room temperature, if the  $\text{Me}_3\text{NHCl}$  was added below room temperature no

reaction was observed.

(i) Preparation of Trimethylborane (67),  $\text{Me}_3\text{B}$



In the three-necked flask of the apparatus shown in Figure 16 a Grignard,  $\text{MeMgBr}$ , was prepared in the following manner. Clean magnesium turnings, (7.20 gms; 0.292 mmoles) (B & A Ltd.), 100 ml of dry n-butyl ether, and a few crystals of iodine were added to the flask and the entire apparatus was purged with nitrogen. Then 16.5 ml (0.302 moles (BDH Ltd.) of methyl bromide dissolved in 50 ml of n-butyl ether was added very slowly so that the reaction mixture was kept at a temperature of  $50^\circ\text{C}$ . The mixture was vigorously stirred for about six hours, the magnesium was all consumed and the solution turned black. The two traps were then immersed in an acetone-solid  $\text{CO}_2$  slush bath and 6.1 gms (0.090 moles) (Matheson Co.) of boron trifluoride,  $\text{BF}_3$ , measured out in a calibrated gas bulb and condensed into 50 ml of n-butyl ether was added dropwise over a 4 hour period from the dropping funnel into the Grignard solution. The mixture was then warmed to  $70^\circ\text{C}$ , a slow stream of nitrogen bubbled through and the system maintained this way for an additional two hours, allowing the product to condense into the cold traps.

The traps were removed from the rest of the apparatus and attached to the vacuum line. The  $\text{BMe}_3$  was purified by fractionation on the vacuum line and stored in a large gas bulb. The yield was low.

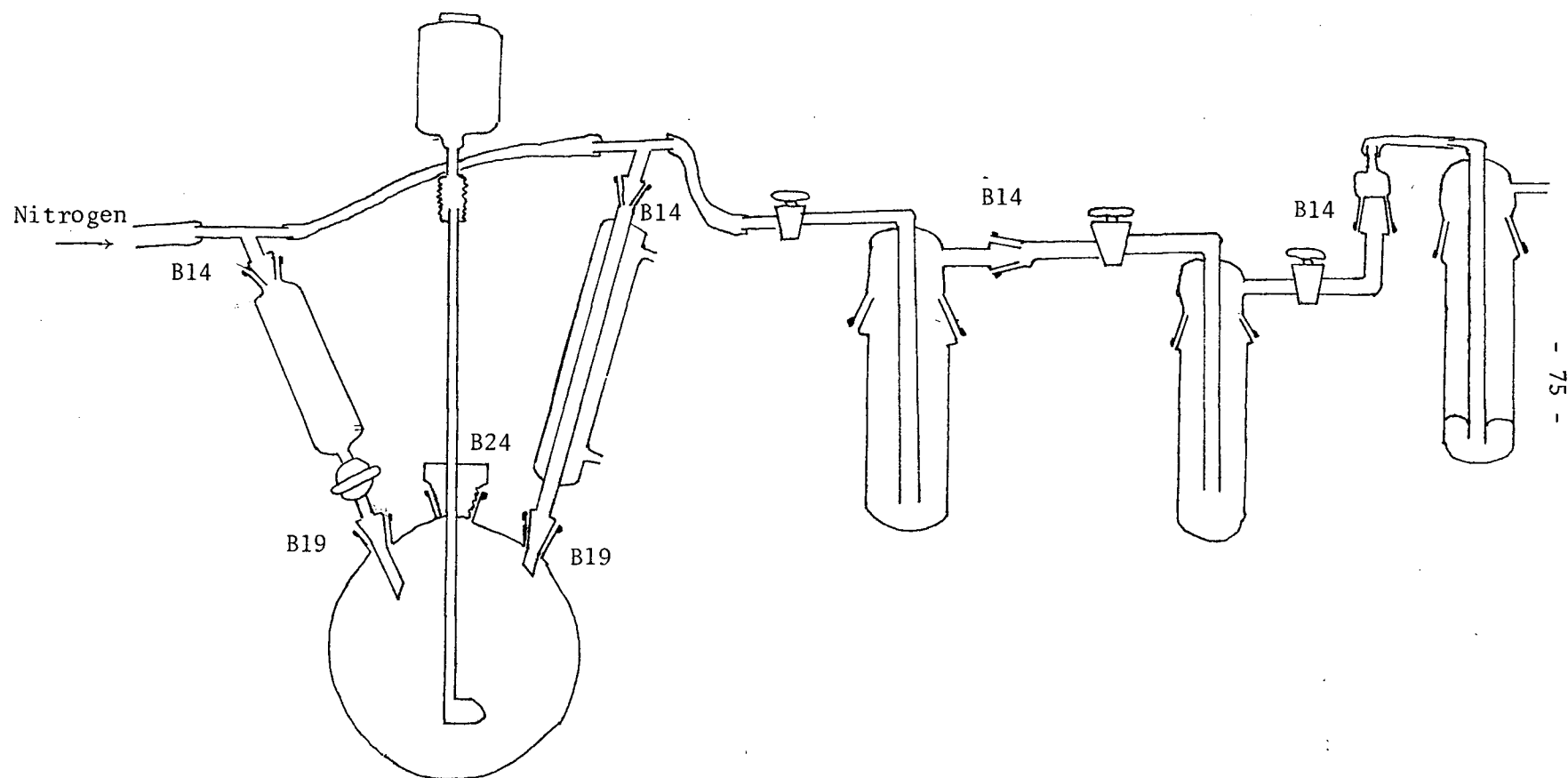


FIGURE 16

Boron Trimethyl Apparatus

(j) Preparation of Trimethylamine Trimethylborane,  $\text{Me}_3\text{NBMe}_3$



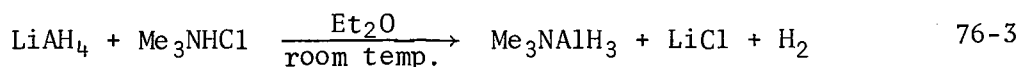
A sample of  $\text{BMe}_3$  was measured out in a gas bulb (2.61 cm of Hg in 3.19 l volume at  $23^\circ\text{C}$ ) (4.92 mmoles) and condensed into a conical flask attached to the vacuum line. A slight excess of  $\text{Me}_3\text{N}$  (2.80 cm of Hg in a 3.19 l volume at  $23^\circ\text{C}$ ) (5.08 mmoles) was condensed onto the  $\text{BMe}_3$  and allowed to react and warm up to room temperature. The excess  $\text{Me}_3\text{N}$  was then pumped off at  $-20^\circ\text{C}$  and a white solid of  $\text{Me}_3\text{NBMe}_3$  remained which was stored under a nitrogen atmosphere at room temperature. The yield was 100%.

(K) Preparation of Trimethylamine Trimethylalane,  $\text{Me}_3\text{NAlMe}_3$



Trimethylamine trimethylalane,  $\text{Me}_3\text{NAlMe}_3$ , was prepared by a procedure similar to that used to prepare  $\text{Me}_3\text{NGaMe}_3$ . The difference in the procedure was that trimethylaluminum (Alfa Inorganics Inc.) was used in place of  $\text{GaMe}_3$  and only a slight excess of  $\text{Me}_3\text{N}$  gas was used.

(l) Preparation of Trimethylamine alane,  $\text{Me}_3\text{NAlH}_3$

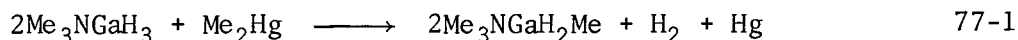


Trimethylamine alane  $\text{Me}_3\text{NAlH}_3$ , was prepared and purified in the same way as  $\text{Me}_3\text{NGaH}_3$ , only  $\text{LiAlH}_4$  (Alfa Inorganics Inc.) was used in place of  $\text{LiGaH}_4$ . Care was taken to avoid the formation of the bis-amine adduct which is quite stable, by using excess  $\text{LiAlH}_4$ .

C. Reactions to Prepare Coordinated Organogallanes

(a) Reaction of Trimethylamine Gallane,  $\text{Me}_3\text{NGaH}_3$  with Dimethyl Mercury

$\text{Me}_2\text{Hg}$

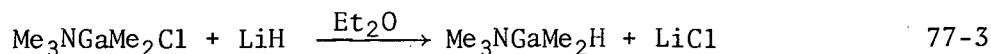
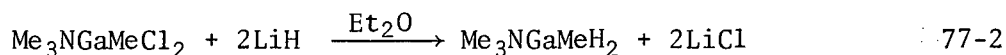


In a typical reaction 0.373 gms (2.85 mmoles) of  $\text{Me}_3\text{NGaH}_3$  and 0.338 gms (1.47 mmoles) of  $\text{Me}_2\text{Hg}$  (Alfa Inorganics Inc.) were mixed in a conical flask with 50 ml of benzene in the dry box. The conical was removed from the dry box, fitted with a reflux condenser and flushed with a slow stream of nitrogen while the benzene solution was refluxed. After 75 minutes graying of the solution was observed and the reaction was stopped. The conical flask was then capped and the solution filtered in the dry box. Then the conical flask was fitted with a stopcock adaptor and the solution was concentrated by removing most of the benzene at  $-20^\circ\text{C}$  by pumping it off on the vacuum line. The solution was then examined by infrared and NMR spectroscopy to be certain a definite product does exist.

(b) Reaction of Trimethylamine Adducts of Monochlorodimethylgallane,

$\text{Me}_3\text{NGaMe}_2\text{Cl}$ , and Dichloromonomethylgallane  $\text{Me}_3\text{NGaMeCl}_2$ , with

Lithium Hydride,  $\text{LiH}$ .

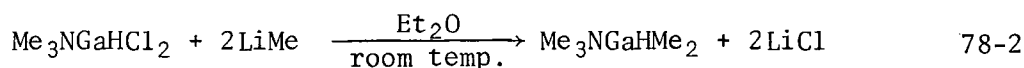
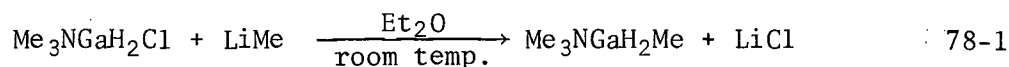


Trimethylamine dichloromonomethylgallane,  $\text{Me}_3\text{NGaMeCl}_2$  (0.178 gms;

0.919 mmoles) was weighed out, dissolved in ether and placed in the reaction-filtration apparatus, see Figure 11. Excess LiH (0.032 gms; 4.0 mmoles) placed in the dumper tube was slowly added at  $-20^{\circ}\text{C}$  and the reaction mixture stirred for a period of two hours at room temperature. The reaction mixture was then filtered and the ether removed at  $-40^{\circ}\text{C}$  leaving a paste or oil like material behind, which was then examined by infrared and NMR spectroscopy to confirm that a definite product did form.

Trimethylamine monochlorodimethylgallane,  $\text{Me}_3\text{NGaMe}_2\text{Cl}$ , (0.271 gms; 1.26 mmoles) was reacted with 0.0274 gms (3.42 mmoles) of LiH in a similar manner. Again a paste or oil like material resulted from the reaction which was then analysed by infrared and NMR spectroscopy. The yield from these reactions was quite low.

(c) Reaction of Trimethylamine Adducts of Monochlorogallane,  $\text{Me}_3\text{NGaH}_2\text{Cl}$ , and Dichlorogallane,  $\text{Me}_3\text{NGaHCl}_2$ , with Lithium Methyl, LiMe



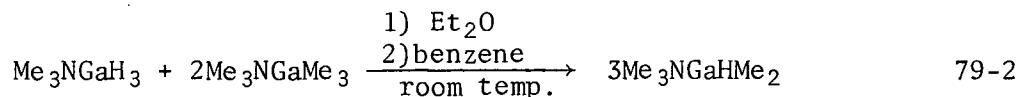
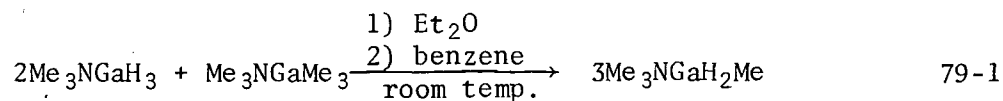
A quantity of  $\text{Me}_3\text{NGaH}_2\text{Cl}$  (0.369 gms; 2.21 mmoles) was weighed out in the dry box and dissolved in 30 ml of ether in a conical flask. Lithium methyl in ether solution (3.51 ml of 0.63 M; 2.21 mmoles) was also added to this flask. The flask was allowed to stand for several hours at room temperature and then, the white precipitate that formed was filtered off and the clear solution put into a different flask. It was then fitted with a stopcock adaptor, removed from the dry box attached to the vacuum line and the ether



pumped off at  $-70^{\circ}\text{C}$ . An oil remained in the flask and when analysed by infrared and NMR compared favorably to  $\text{Me}_3\text{NGaH}_2\text{Me}$  prepared by other routes.

In an analogous manner  $\text{Me}_3\text{NGaHCl}_2$  (0.247 gms; 1.23 mmoles) and  $\text{LiMe}$  (1.3 ml of 1.89 M; 2.46 mmoles) were mixed together in ether solution, filtered and then the solvent removed to yield a sticky oil product. The infrared and NMR analysis indicates that some  $\text{Me}_3\text{NGaHMe}_2$  was formed.

(d) Equilibrium Reactions of Trimethylamine Gallane  $\text{Me}_3\text{NGaH}_3$  with Trimethylamine Trimethylgallane,  $\text{Me}_3\text{NGaMe}_3$



These methylgallane species are prepared by mixing the two reagents in a suitable solvent at room temperature in the glove box. For monomethylgallane trimethylamine adduct,  $\text{Me}_3\text{NGaH}_2\text{Me}$ , a typical preparation was mixing 0.398 gms (2.30 mmoles) of  $\text{Me}_3\text{NGaMe}_3$  and 0.608 gms (4.60 mmoles) of  $\text{Me}_3\text{NGaH}_3$  in benzene. For trimethylamine dimethylgallane,  $\text{Me}_3\text{NGaHMe}_2$  0.612 gms (3.51 mmoles) of  $\text{Me}_3\text{NGaMe}_3$  and 0.232 gms (1.76 mmoles) of  $\text{Me}_3\text{NGaH}_3$  were mixed in benzene. The solutions were then examined by NMR and infrared spectroscopy.

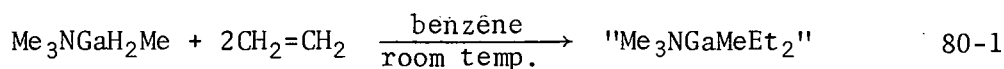
To prepare a solvent of free pure compound diethylether was a better solvent to use. In these cases, the ether solutions were placed in a conical flask fitted with a stopcock adaptor, attached to the vacuum line and the ether removed at  $-40^{\circ}\text{C}$  leaving the product as an oil or past like substance.

The deuterated analogs; trimethylamine monomethylbideuterogallane,  $\text{Me}_3\text{NGaD}_2\text{Me}$ , and trimethylamine dimethyldeuterogallane,  $\text{Me}_3\text{NGaDMe}_2$ , are

prepared in the same manner. 0.126 gms (0.938 mmoles) of  $\text{Me}_3\text{NGaD}_3$  was weighed out and dissolved in a benzene solution containing 0.0815 gms (0.469 mmoles) of  $\text{Me}_3\text{NGaMe}_3$ , to prepare the  $\text{Me}_3\text{NGaD}_2\text{Me}$  compound. To prepare the  $\text{Me}_3\text{NGaDMe}_2$  compound, 0.0512 gms (0.379 mmoles) of  $\text{Me}_3\text{NGaD}_3$  and 0.132 gms (0.758 mmoles) of  $\text{Me}_3\text{NGaMe}_3$  were mixed in benzene solution. The infrared and NMR data were collected on these compounds.

D. Miscellaneous Reactions of Coordinated Gallanes

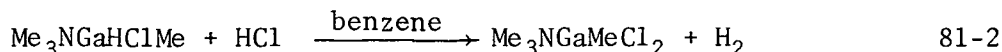
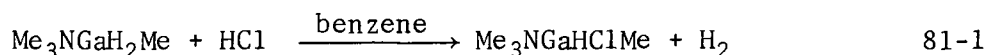
(a) Reaction of Trimethylamine Monomethylgallane,  $\text{Me}_3\text{NGaH}_2\text{Me}$  with Ethylene,  $\text{CH}_2=\text{CH}_2$



$\text{Me}_3\text{NGaH}_2\text{Me}$  (0.562 gms; 3.85 mmoles) was dissolved in benzene in the dry box, placed in a conical flask fitted with a stopcock adaptor and then the flask was attached to the vacuum line. Ethylene gas (172.5 ml at NTP; 7.70 mmoles) was condensed onto the benzene solution of  $\text{Me}_3\text{NGaH}_2\text{Me}$  at liquid nitrogen temperatures and then the solution was allowed to warm up to room temperature and magnetically stirred.

After seven hours at room temperature some graying of the solution was observed but the manometer of the vacuum line showed little gas uptake. An NMR spectrum of the volatile components collected in a NMR tube connected to the vacuum line was obtained and an infrared and NMR spectra of the benzene solution were also recorded.

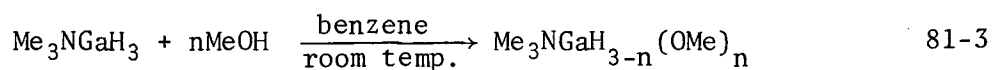
(b) Reaction of Trimethylamine Monomethylgallane  $\text{Me}_3\text{NGaH}_2\text{Me}$  with Hydrogen Chloride,  $\text{HCl}$



A benzene solution of  $\text{Me}_3\text{NGaH}_2\text{Me}$  (0.242 gms; 1.66 mmoles) was made up in a conical flask in the dry box. The flask was fitted with a stopcock adaptor, cooled to  $-196^\circ\text{C}$  and evacuated on the vacuum line. The  $\text{HCl}$  gas (37.2 ml at NTP; 1.66 mmoles) was condensed into the benzene solution and the mixture allowed to warm up to room temperature for about two hours, then the solution was frozen down again. The non-condensable gas was removed via a Töpler pump, yield of gas 35.4 ml at NTP. Infrared and NMR spectra of the gas liberated and of the benzene solution were recorded.

A second portion of  $\text{HCl}$  gas (36.9 ml at NTP; 1.65 mmoles) was condensed into the above solution in the same manner as the first. The non-condensable gas was removed by a Töpler pump and its infrared spectrum obtained, also the infrared and NMR spectra of benzene solution were obtained. The benzene solvent was then removed at  $0^\circ\text{C}$  on the vacuum line and a white solid was left in the flask.

(c) Reaction of Trimethylamine Gallane,  $\text{Me}_3\text{NGaH}_3$ , with Methanol,  $\text{MeOH}$

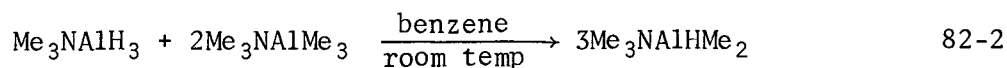
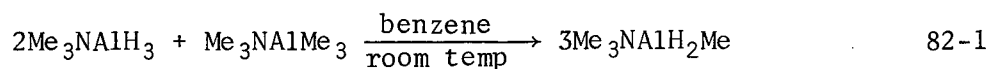


where "n" = 1, 2, 3

In a typical reaction 0.101 gms (0.77 mmoles) of  $\text{Me}_3\text{NGaH}_3$  was weighed

out and dissolved in about 15 ml of benzene in a conical flask fitted with a stopcock adaptor. This flask was then evacuated on the vacuum line and 0.0486 gms (1.52 mmoles) of MeOH was condensed onto the benzene solution. After reacting the reagents for two hours at room temperature the flask was frozen in liquid nitrogen and the non-condensable gas, hydrogen, pumped off and measured with a Töpler pump. Yield of gas 31.5 ml at NTP. A white solid remained in the flask on removal of benzene at low temperature.

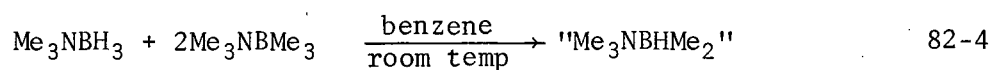
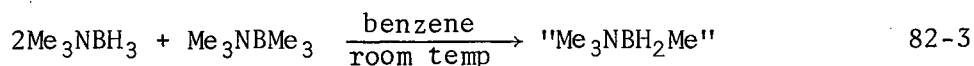
(d) Rearrangement Reaction Between Trimethylamine Alane,  $\text{Me}_3\text{NAlH}_3$ , and Trimethylamine Trimethylalane,  $\text{Me}_3\text{NAlMe}_3$



Trimethylamine monomethylalane,  $\text{Me}_3\text{NAlH}_2\text{Me}$ , was prepared by mixing  $\text{Me}_3\text{NAlH}_3$  (0.0699 gms; 0.785 mmoles) and  $\text{Me}_3\text{NAlMe}_3$  (0.0516 gms; 0.395 mmoles) in 2 ml of pure benzene in the dry box. Trimethylamine dimethylalane,  $\text{Me}_3\text{NAlHMe}_2$ , was prepared similarly by mixing  $\text{Me}_3\text{NAlH}_3$  (0.0263 gms; 0.296 mmoles) and  $\text{Me}_3\text{NAlMe}_3$  (0.0773 gms; 0.592 mmoles) in 3 ml of benzene.

Infrared and NMR spectra were recorded of all the products and the spectra compared to the literature results (41).

(e) Rearrangement Reaction Between Trimethylamine Borane,  $\text{Me}_3\text{NBH}_3$  and Trimethylamine Trimethylborane,  $\text{Me}_3\text{NBMe}_3$

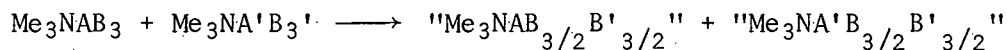


In a typical preparation 0.0700 gms (1.01 mmoles) of  $\text{Me}_3\text{NBH}_3$  and 0.0561 gms (0.506 mmoles) of  $\text{Me}_3\text{NBMe}_3$  were mixed together in a few mls of benzene in the dry box to prepare the compound trimethylamine monomethylborane,  $\text{Me}_3\text{NBH}_2\text{Me}$ . To prepare trimethylamine dimethylborane,  $\text{Me}_3\text{NBHMe}_2$ , 0.121 gms (1.09 mmoles) of  $\text{Me}_3\text{NBMe}_3$  and 0.0375 gms (0.545 mmoles) of  $\text{Me}_3\text{NBH}_3$  were similarly mixed together in a few mls of benzene. Infrared and NMR spectra were recorded on all the solutions.

(f) Mixed Rearrangement Reactions Using Different Group IIIB

Coordination Compounds

A number of rearrangement reactions were attempted with different Group IIIB hydrido- and alkyl-trimethylamine adducts. All reaction mixtures were prepared in the same manner. The solid hydride compounds were weighed out in a small beaker in the dry box and a calculated volume of a standard benzene solution of one of the trialkyl trimethylamine adduct, to make a one to one molar mixture, was syringed into the beaker containing the known weight of hydride or calculated volumes of the standard solutions of the trialkyl compounds were mixed together in a beaker. The resultant solutions were then examined by infrared and NMR spectroscopy. The following gives a list of the reactions attempted and quantities of reagents used.



where A, or A' = B, Al, Ga; and B or B' = Me or H.

$\text{Me}_3\text{NAB}_3$		quantity	$\text{Me}_3\text{NA'B'}_3$		quantity
1	$\text{Me}_3\text{NBMe}_3$	0.58 ml of 0.490 M (0.282 mmoles)	$\text{Me}_3\text{NGaMe}_3$		2.0 ml of 0.141 M (0.282 mmoles)
2	$\text{Me}_3\text{NBMe}_3$	0.80 ml of 0.490 M (0.394 mmoles)	$\text{Me}_3\text{NAlMe}_3$		2.0 ml of 0.197 M (0.394 mmoles)
3	$\text{Me}_3\text{NAlMe}_3$	0.72 ml of 0.197 M (0.141 mmoles)	$\text{Me}_3\text{NGaMe}_3$		1.0 ml of 0.141 M (0.141 mmoles)
4	$\text{Me}_3\text{NGaMe}_3$	1.0 ml of 0.141 M (0.141 mmoles)	$\text{Me}_3\text{NAlH}_3$		0.0126 gms (0.141 mmoles)
5	$\text{Me}_3\text{NAlMe}_3$	1 ml of 0.197 M (0.197 mmoles)	$\text{Me}_3\text{NGaH}_3$		0.0258 gms (0.197 mmoles)
6	$\text{Me}_3\text{NAlMe}_3$	1 ml of 0.197 M (0.197 mmoles)	$\text{Me}_3\text{NGaD}_3$		0.0264 gms (0.197 mmoles)
7	$\text{Me}_3\text{NBMe}_3$	1 ml of 0.490 M (0.490 mmoles)	$\text{Me}_3\text{NAlH}_3$		0.0436 gms (0.490 mmoles)
8	$\text{Me}_3\text{NBMe}_3$	1 ml of 0.490 M (0.490 mmoles)	$\text{Me}_3\text{NGaH}_3$		0.0642 gms (0.490 mmoles)
9	$\text{Me}_3\text{NAlMe}_3$	1 ml of 0.197 M (0.197 mmoles)	$\text{Me}_3\text{NBH}_3$		0.0143 gms (0.197 mmoles)
10	$\text{Me}_3\text{NGaMe}_3$	1 ml of 0.141 M (0.141 mmoles)	$\text{Me}_3\text{NBH}_3$		0.0103 gms (0.141 mmoles)

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