620. *Halogen Derivatives of Co-ordinated Gallium Hydride*

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The compounds, $Me_3NGaH_{3-n}X_n$ and $Me_3NGaD_{3-n}X_n$ (where $n = 0, 1, 2,$ or 3 and X = Cl, Br, or I) have been prepared and their infrared spectra recorded in benzene solution in the range 200—4000 cm.$^{-1}$. These spectra show several interesting features that are related to the substitution of hydrogen by halogen. The methyl-proton nuclear magnetic resonance spectra of these compounds in benzene solution have also been recorded.

The monosubstituted halogenogallanes, Me_3NGaH_2X, are white, slightly volatile solids, which can be purified by vacuum sublimation. The disubstituted halogenogallanes, Me_3NGaHX_2, and the fully halogenated compounds, Me_3NGaX_3, are all involatile white solids.

Displacement of trimethylamine from the adduct Me_3NGaH_2Cl by boron trifluoride resulted in the liberation of unco-ordinated GaH_2Cl which subsequently decomposed at low temperatures even in solution. An attempt to prepare the borohydride derivative, $Me_3NGaH_2(BH_4)$, led to decomposition to gallium metal and hydrogen.

As part of an investigation into the possibility of preparing an unco-ordinated gallium hydride[1] the reaction of trimethylamine–gallane and anhydrous hydrogen chloride was investigated. Instead of displacement of trimethylamine, however, a substitution reaction occurred in which hydrogen was evolved and the new compound trimethylamine–monochlorogallane, Me_3NGaH_2Cl, was isolated by vacuum sublimation. This experiment led to a systematic investigation of the preparation of halogen-substituted gallanes, and the present Paper discusses the various methods that have been used to synthesise these compounds, and also presents infrared data for this new group of compounds.

The trimethylamine–halogenogallanes were first prepared by treating solid trimethylamine–gallane with the stoicheiometric quantity of dry hydrogen halide gas. Reaction occurred at temperatures as low as −78° to give an equivalent amount of hydrogen and the halogen derivative,

$$Me_3NGaH_3(s) + nHX(g) \longrightarrow Me_3NGaH_{3-n}X_n(s) + nH_2(g)$$

where $n = 1$ or 2, and X = Cl or Br.

A parallel series of deuterio-compounds was prepared by using trimethylamine–trideuteriogallane and deuterium chloride gas or hydrogen bromide gas in stoicheiometric quantities. The action of hydrogen bromide gas on trimethylamine–trideuteriogallane liberated HD quantitatively and substituted bromine for deuterium in the adduct; no deuterium–hydrogen exchange was observed. In experiments with an excess of hydrogen halide, three moles of hydrogen were evolved, but the usual method of preparing the fully substituted compounds was directly from the gallium halide and excess of anhydrous trimethylamine, followed by removal of excess of ligand under vacuum,

$$Me_3N(l) + GaX_3(s) \xrightarrow{0^\circ} Me_3NGaX_3(s)$$

where X = Cl, Br, or I. The trimethylamine adducts of gallium trichloride and tribromide have previously been prepared in this way.[2] It was found that in the substitution reactions both ether and benzene could be used as solvent and then separated from the product by sublimation.

A second method of introducing halogen atoms into trimethylamine–gallane was by reaction with an excess of trimethylammonium halide in ether; two moles of hydrogen were produced as required by the equation,

$$Me_3NGaH_3 + 2Me_3NHX \xrightarrow{Et_2O} Me_3NGaHX_2 + 2Me_3N + 2H_2$$

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[1] N. N. Greenwood and M. G. H. Wallbridge, *J.*, 1963, 3912.

[2] R. E. Van Dyke and H. E. Crawford, *J. Amer. Chem. Soc.*, 1950, 72, 2829.

for the chloro-system, but only one and one half moles for the bromo-system. It appears that further reaction does not occur, even after prolonged periods at room temperature, and this may indicate some shielding of the third hydrogen by the two halogens already present. This reaction was investigated as a result of observations made during the preparation of triethylamine–gallane from lithium gallium hydride,[3] when it was found that the use of an excess of triethylammonium chloride produced more hydrogen than was required by the equation,

$$Et_3NHCl + LiGaH_4 \xrightarrow{Et_2O} Et_3NGaH_3 + LiCl + H_2$$

In a quantitative experiment, it was found that equimolar proportions of trimethylamine–trideuteriogallane and trimethyldeuterioammonium chloride in ether solution yielded the monochloro-compound, Me_3NGaD_2Cl,

$$Me_3NGaD_3 + Me_3NDCl \xrightarrow{Et_2O} Me_3NGaD_2Cl + Me_3N + D_2$$

Analogous behaviour has not been reported in either borane or alane chemistry.

A third method of preparation of the mixed hydride–halide compounds involves direct reaction of trimethylamine–gallane or –trideuteriogallane with the appropriate amount of trimethylamine–gallium trihalide. The monosubstituted derivatives can be prepared from stoicheiometric ratios according to the equation,

$$2Me_3NGaH_3 + Me_3NGaX_3 \xrightarrow{C_6H_6} 3Me_3NGaH_2X$$

where $X = Cl$, Br, or I.

For disubstitution, however, an excess of the trihalides appears to be necessary before all the hydride is converted into the species Me_3NGaHX_2.

Cryoscopic measurements in benzene solution indicated that trimethylamine–gallane and –monochlorogallane were only slightly associated (degree of association 1·1), whereas trimethylamine–gallium trichloride was appreciably dimerised (degree of association 1·8).

In an attempt to prepare a free chlorogallium hydride, boron trifluoride was added to trimethylamine–monochlorogallane,

$$Me_3NGaH_2Cl(s) + BF_3(g) \longrightarrow GaH_2Cl(l) + Me_3NBF_3(s)$$

The reaction resulted in the formation of an oil, which decomposed rapidly under vacuum below room temperature. The infrared spectrum of the vapour showed a medium-strong band in the Ga–H stretching region [1,4,5] at 2000 cm.$^{-1}$, which suggests the formation of "GaH_2Cl" by comparison with the observed stretching frequency for the Ga–H band in unco-ordinated gallane [1] at ~2000 cm.$^{-1}$. In benzene solution, the reactants again yielded an unstable product, and gallium metal was deposited from the solution below room temperature.

The reaction of excess of lithium borohydride with trimethylamine–monochlorogallane yielded an unstable oil which decomposed below room temperature but showed infrared absorption bands in benzene solution characteristic of Ga–H (1910 and 1840 cm.$^{-1}$) and B–H (2300 cm.$^{-1}$) stretching frequencies,

$$Me_3NGaH_2Cl + LiBH_4 \xrightarrow[Et_2O]{C_6H_6\text{ or}} Me_3NGaH_2(BH_4) + LiCl$$

This is in contrast to similar work on the corresponding aluminium system [6] where a stable compound, $Me_3NAlH_2(BH_4)$, was isolated. However, the instability of the gallium borohydride derivative, $Me_3NGaH_2(BH_4)$, may be expected since gallium borohydride itself is much less stable than aluminium borohydride.[7,8]

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[3] A. Storr, Ph.D. Thesis, University of Newcastle upon Tyne, 1963.

[4] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 1963, **2**, 1036.

[5] N. N. Greenwood, E. J. F. Ross, and A. Storr, *J.*, 1965, 1400.

[6] J. K. Ruff, *Inorg. Chem.*, 1963, **2**, 515.

[7] H. I. Schlesinger, H. C. Brown, and G. W. Schaeffer, *J. Amer. Chem. Soc.*, 1943, **65**, 1786.

[8] E. Wiberg, *Angew. Chem.*, 1953, **65**, 26.

TABLE 1

Infrared spectra of trimethylamine–halogenogallanes, $Me_3NGaH_{3-n}X_n$, in benzene solution

Me_3N	Me_3NGaH_3	Me_3NGaH_2Cl	$Me_3NGaHCl_2$	Me_3NGaCl_3	Me_3NGaH_2Br	$Me_3NGaHBr_2$	Me_3NGaBr_3	Me_3NGaH_2I	Me_3NGaHI_2	Me_3NGaI_3	Assignment
	2996w										CH_3 stretches
2965sh m	2975m	2970sh m	2975sh m	2979sh w	2971m		2975sh w	2975w		2980w	
	2949sh w		2953sh s	2960sh m		2953sh w	2955sh w	2952sh m		2955sh m	
	2930m	2936m	2935vs	2941s	2936s	2938m	2939m	2938m		2940s	
2920s	2909m	2914m	2920vs	2918m	2915m	2917w	2915m	2915m		2916m	
	2883w	2883m	2892sh s	2888m	2885m	2886w	2885w	2888w		2888m	
2868m	2859w	2864m	2865s	2866m	2863m	2862w	2864w	2865m		2865m	
	2834w	2840w	2856s	2844w	2840w	2840w	2841w	2843w		2843w	
2819s	2818w	2818w			2820m			2822w		2813w	
	2798w	2804w	2805m	2809w	2803sh w	2802w	2805w	2805w		2805w	
2770vs	2768w	2770m			2770m			2770w			
2730m		2729w		2700br w	2730w		2650br w	2739w		2720w	
			2510m								
	1959w	1965w	2458m	1960br m	1960br w	1967m	1960br w	1960br m	1960m	1960br w	?
			1825m								
		1810w	1808m	1820br w	1815br m	1815br w	1815br w	1815br w		1815br w	?
1448m	1460m	1447m	1450s	1448s	1446m	1444m	1449m	1447m		1448s	CH_3 antisym. defn.
1439m	1448sh w	1438sh w	1438sh m	1439sh m	1437sh m	1435sh w	1438sh w	1438sh w		1439m	
1420w											
	1409w	1409m	1411s	1412s	1408m	1407m	1411s	1409m		1411s	CH_3 sym. defn.
		1395sh w	1398sh m	1399m	1393w	1392w	1395m	1395w		1395m	
1271m					1269w						CH_3 rock
	1252m	1250m	1245s	1243s	1247m	1240m	1241s	1247m		1241s	
1172br w	1230w	1235w			1233w			1233w			
1100m	1119w				1116w						
1084w	1105m	1105m	1108s	1109s	1104m	1104m	1108s	1104m		1106s	
1040br w	1006s	996m	986vs	981s	989m	983m	980s	994m		981s	C–N antisym. stretch
826s	824w	824m	818vs	815vs	823m	815s	812vs	823m		810vs	C–N sym. stretch
		819sh m	810sh vs		816sh m			811w			
					810s						
	1835vs	1905vs	1968vs		1907vs			1906vs			Ga–H stretch
	1819vs	1899sh vs	1949vs			1931s			1925s		
	745vs	730vs	748m		721s	722w		714s			Ga–H defn.
		710sh s	730w								
		603m	604vs		594m	595vs		583m	585vs		H–Ga–X defn.
	528m	504s			505m			505s			Ga–H_x rock
			520vs	538s		515m	531m			525m	Ga–N stretch
	494m	491s		514sh m	478m		520m	463m		500sh w	
			420s	417vs		415w	420m				Ga–X stretches
			403vs	**400vs**		365m	397w			422m	
			370vs	373s		303w	**305vs**				
		345m	**362vs**	357vs	**258m**	**286vs**		**229m**		**262m**	
			336m			265s					

w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; br, broad.

TABLE 2

Infrared spectra of trimethylamine–halogenodeuteriogallanes, $Me_3NGaD_{3-n}X_n$, in benzene solution

Me_3NGaD_3	Me_3NGaD_2Cl	$Me_3NGaDCl_2$	$Me_3NGaDBr$	$Me_3NGaDBr_2$	Me_3NGaD_2I	Me_3NGaDI_2	Assignment
	2964sh m	2974sh m	2972sh m	2970sh w	2973w		CH_3 stretches
2949sh m			2953sh w		2953sh m		
2926m	2934m	2935m	2930sh m	2924m	2938m		
2910sh m	2913m	2914m	2912m	2911m	2916m		
2887sh m	2885m	2885m	2893m	2890m	2887w		
2855m	2860m	2865w	2861w	2854m	2863w		
	2840sh w	2845sh w	2843sh w		2843w		
2815w	2815w	2820w	2816w	2820w			
2800w	2804w	2805w	2803w		2803w		
2768m	2764w	2765w	2763w				
2725w	2724w				2738w		
1965br w	1950br w	1940br w	1950br w	1950br w	1950br w		
1830br w	1810br w	1810br w	1800br w	1800br w	1800br w		?
1440m	1447m	1448m	1446w	1447m	1448m		CH_3 antisym. defn.
	1438sh m		1438sh w				
1396m	1396m	1374m	1395m		1398m		CH_3 sym. defn.
1374m							
1268w	1249m		1323w				CH_3 rock
1249m	1238m	1247m	1247m	1243m	1247m		
1227w	1220w		1233sh w				
1140w			1148br w	1143w	1145br w		
1115sh m	1115sh w	1115sh w					
1105m	1106m	1107m	1104m	1107m	1106m		
996w	991m	989m	993m	989m	993sh m		C–N antisym. stretch
964w			968sh w		987m		
845w			843w		819s		C–N sym. stretch
828m	822s	818s	820m	817s	814s		
		1408s		1400s	1373s	1395sh s	Ga–D stretch
1324s	1370vs	1393s	1380s	1390s	1369s	1380s	
538s	529s	526m	536sh w	528w	522m		Ga–D defn.
			524m				
505m	510s	510m	505s	508w	503s		
487m	485vs	484m	479s	481w	476s		Ga–N stretch
	440m	441vs	434w	440s	439m	436s	D–Ga–X defn.
					424w?		
					412w?		
364w	372w		340w				GaD_x rock
		407s		427s			Ga–X stretches
		396sh m		410sh m			
		371vs		403s			
	345m	**365vs**	**253m**	**282s**	**227m**		
		333s		263w			

TABLE 3

Methyl-proton chemical shifts in benzene solution

Compound	P.p.m.	Compound	P.p.m.	Compound	P.p.m.
Me_3N	7·940	$Me_3NGaHCl_2$	8·175	$Me_3NGaHBr_2$	8·307
Me_3NGaH_3	8·073	Me_3NGaCl_3	8·207	Me_3NGaBr_3	8·173
Me_3NGaH_2Cl	7·990	Me_3NGaH_2Br	8·023	Me_3NGaI_3	8·107

The vapour pressures of the substituted gallanes were too low to permit gas-phase spectra to be recorded over the full range of frequencies, but it was observed that when a sample of trimethylamine–monochlorogallane, Me_3NGaH_2Cl, was heated in a gas cell, weak absorption bands appeared at 1900, 734, and 694 cm.$^{-1}$ corresponding to the Ga–H stretching and deformation modes.[4]

The detailed infrared spectra of the trimethylamine–halogenogallanes, trimethylamine–halogenodeuteriogallanes, and their parent compounds were recorded in benzene solution and the results, together with an assignment of bands, are listed in Tables 1 and 2.

The methyl-proton magnetic resonance spectra for the majority of the compounds in benzene solution were also recorded and the chemical shifts observed are given in Table 3 as τ values relative to benzene, $\tau = 2{\cdot}840$ p.p.m. [*i.e.*, τ (Me_4Si) $= 10$ p.p.m.]. The resonance signals for all the adducts occur at higher fields than for the free ligand. This is contrary to the expected shift on the basis of electron drift away from the methyl groups as a result of complex formation, but is in the same direction as recently found for trimethylphosphine–gallane.[5]

DISCUSSION

The infrared spectra of the trimethylamine–halogenogallanes and –halogenodeuteriogallanes show several interesting features. It was observed that the Ga–H stretching frequencies move successively to higher values on progressive substitution of halogen for hydrogen in the compounds; likewise for the corresponding Ga–D frequencies, which occur at positions moved by a factor of approximately 1/1·4 from the normal compounds. Substitution of one halogen atom increases the Ga–H stretching frequency by about 70 cm.$^{-1}$ independent of the halogen (X = Cl, Br, or I).

Disubstitution, however, effects a larger shift of the Ga–H stretching frequency for the dichloride (130 cm.$^{-1}$) than for the dibromide (112 cm.$^{-1}$), and this, in turn, is larger than for the di-iodide (106 cm.$^{-1}$). In addition, the band appears to be split in the case of the dichloride, and this may indicate partial dimerisation of the compound in benzene solution. These changes in the Ga–H stretching frequency of substituted gallanes can be understood in terms of the electron-withdrawing effect of the halogen atom on the electronegativity of the gallium atom; this results in an increase in the strength of the Ga–H bond, and hence an increase in the stretching frequency. A similar shift in the Al–H stretching frequencies was noticed for the triethylamine–halogenoalane compounds,[9] $Et_3NAlH_{3-n}X_n$, (where X = Cl or Br and $n = 1$ or 2), and also for the trimethylamine–mercaptoalanes,[10] $Me_3NAlH_{3-n}(SR)_n$, (where R = Pr^n or Ph and $n = 1$ or 2). Corresponding infrared data on the trialkylamine–halogenoboranes could not be found in the literature, but recent work [11] in these laboratories on the triethylamine–chloroboranes has shown a similar shift to higher frequencies of the B–H stretching modes on substitution of hydrogen by halogen.

In the unsubstituted gallane adduct, Me_3NGaH_3, the bands attributable to the ligand are of much lower intensity than those due to the Ga–H modes. However, on substitution of halogen for hydrogen, the intensities of the ligand absorption bands increase relative to those of the Ga–H bands; this is presumably a concentration effect following the reduction of the number of Ga–H bonds throughout the series.

The progressive decrease in the value of the C–N symmetric and antisymmetric stretching frequencies on successive substitution of halogen for hydrogen is possibly due to the greater electronegativity of the halogen groups, which enhances the electron drift away from the ligand and hence weakens the C–N bonds.

The assignment of the intense bands in the range 585—605 cm.$^{-1}$ to the H–Ga–X deformation modes follows from their position and from the fact that these bands do not appear in the spectra of trimethylamine–gallane, Me_3NGaH_3, or of the trimethylamine–gallium trihalides. The intensities of these bands are considerably greater in the dihalogen derivatives, but the band occurs in essentially the same position for both the mono- and di-substituted compounds. On deuteration the bands move by a factor of approximately $1/\sqrt{2}$ (see Tables 1 and 2) as predicted from a mass effect. With increase in atomic number of halogen there is a corresponding decrease in the frequency of this mode, again indicating the operation of a mass effect. A similar trend is noticed with the Ga–N stretching frequencies of the monohalogenogallanes.

The Ga–X stretching vibrations in compounds containing a single Ga–X bond have been observed for the first time in this work. There is a general decrease in this stretching frequency in the compounds Me_3NGaH_2X and Me_3NGaD_2X in passing from chlorine to iodine, as might be expected from increased atomic mass of the halogen, but the position of the band remains approximately the same in the normal and deuterio-derivatives of the same halogen (see Tables 1 and 2). With increase in the halogen content, however, the

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[9] E. G. Hoffmann and G. Schomburg, *Z. Elektrochem.*, 1957, **61**, 1110.

[10] W. Marconi, A. Mazzei, F. Bonati, and M. de Malde, *Z. Naturforsch.*, 1963, **18b**, 3.

[11] J. H. Morris, private communication.

gallium–halogen stretching modes move to higher frequencies. The most intense bands are shown in bold type in Tables 1 and 2. A similar effect was observed in a study of the addition compounds of organotin halides.[12] Assignment of these bands is complicated by partial association in solution. Thus, the infrared spectrum of trimethylamine–gallium trichloride showed more bands than expected for a monomeric species in the range investigated (200—4000 cm.$^{-1}$). For a monomeric $N\rightarrow GaCl_3$ unit of C_{3v} symmetry there are six infrared active modes expected, but on the basis of Raman work [13,14] on the tetrahedral ion, $GaCl_4^-$, only the two Ga–Cl stretching vibrations and the Ga–N stretching mode would be expected to be in the range investigated, the deformation modes occurring at frequencies below 200 cm.$^{-1}$. However, six bands attributable to the $N\rightarrow GaCl_3$ part of the molecule were observed in the benzene solutions, which suggests the presence of a further species. Molecular weight studies show a degree of association of 1·8 for the compound in this solvent. Dimerisation could occur either through chlorine bridges, as in gallium trichloride, giving in this case five-co-ordinate gallium atoms, or by the formation of ion pairs, similar to those postulated for pyridine–gallium trichloride,[15] *i.e.*, $[(Me_3N)_2GaCl_2]^+[GaCl_4]^-$.

EXPERIMENTAL

Materials were handled in a conventional vacuum line or in a glove box under an atmosphere of oxygen-free, dry nitrogen. All solvents after preliminary desiccation were dried over lithium aluminium hydride or lithium hydride and redistilled before use. Gas volumes quoted are at s.t.p.

Trimethylamine–gallane and –trideuteriogallane and deuterium chloride were prepared as previously described.[4] The gallium trihalides were prepared and purified by standard procedures.[16–18] Hydrogen halide gases were dried by repeated passage over phosphorus pentoxide, followed by low temperature fractionation.

Trimethylamine–Monochlorogallane.—In a typical experiment trimethylamine–gallane (0·3577 g., 2·71 mmoles) was weighed into a 100 ml. Quickfit conical flask fitted with a tap adapter. The apparatus was attached to the vacuum line, cooled in liquid nitrogen, and evacuated. Hydrogen chloride (61·0 ml., 2·72 mmoles) was condensed into the vessel which was then isolated and immersed in a bath at −78°. A considerable amount of hydrogen was evolved at this temperature and, on warming to room temperature for a short time, one mole equivalent of hydrogen was liberated (Found: 60·5 ml.; Calc., 61·0 ml.). Similar results were obtained by using ether or benzene as solvent in the reaction, but here the rate of hydrogen evolution was increased. The product, *trimethylamine–monochlorogallane,* was sublimed under dynamic vacuum from a bath at room temperature into a trap cooled to −78°, where it collected as a white solid, m. p. 65—66° (Found: Ga, 42·3; hydrolysable H, 1·2; Cl, 22·0; N, 8·5. Me_3NGaH_2Cl requires Ga, 41·9; hydrolysable, H, 1·2; Cl, 21·4; N, 8·4%). The molecular weight for the compound in benzene solution was 182; the monomer requires 166·2.

Trimethylamine–Monochlorodideuteriogallane Me_3NGaD_2Cl.—This was obtained similarly from trimethylamine–trideuteriogallane (0·1362 g., 1·01 mmoles) and deuterium chloride (22·55 ml., 1·005 mmoles), 22·5 ml. of deuterium being evolved. The product was again obtained by sublimation. The reaction of trimethylamine–trideuteriogallane (0·1211 g., 0·897 mmole) with an equimolar quantity of trimethyldeuterioammonium chloride (0·0867 g., 0·897 mmole) in ether (30 ml.) liberated 1 molar portion of deuterium (Found: 20·0 ml.; Calc. 20·1 ml.) and gave the *monochloro-compound,* Me_3NGaD_2Cl, in solution.

Trimethylamine–Monobromogallane.—This was prepared from trimethylamine–gallane (0·1483 g., 1·124 mmoles) and hydrogen bromide (25·15 ml., 1·122 mmoles). The hydrogen evolved was measured (Found: 25·3 ml.; Calc., 25·15 ml.) and the *product* sublimed (Found: Ga, 33·4; hydrolysable H, 0·95; Br, 38·9; N, 6·6. Me_3NGaH_2Br requires Ga, 33·1; hydrolysable H, 0·95; Br, 37·9; N, 6·7%). The corresponding *deuterio-compound,* Me_3NGaD_2Br, was

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[12] I. R. Beattie and G. P. McQuillan, *J.*, 1963, 1519.

[13] L. A. Woodward and A. A. Nord, *J.*, 1956, 3721.

[14] L. A. Woodward, G. Garton, and H. L. Roberts, *J.*, 1956, 3723.

[15] N. N. Greenwood and K. Wade, *J.*, 1958, 1663.

[16] N. N. Greenwood and K. Wade, *J.*, 1956, 1527.

[17] N. N. Greenwood and I. J. Worrall, *Inorg. Synth.*, 1960, **6**, 21.

[18] N. N. Greenwood and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

obtained from trimethylamine–trideuteriogallane (0·0506 g., 0·376 mmole) and hydrogen bromide (8·42 ml., 0·376 mmole). An equivalent amount of hydrogen deuteride was evolved (Found, 8·39 ml.; Calc., 8·42 ml.) and identified by mass spectrometry.

Trimethylamine–Monoiodogallane.—This was prepared by mixing 2 : 1 molar amounts of trimethylamine–gallane (0·1442 g., 1·095 mmoles) and trimethylamine–gallium tri-iodide (0·297 g., 0·547 mmole) in benzene solution. The corresponding *deuterio-derivative*, Me_3NGaD_2I, was prepared similarly from trimethylamine–trideuteriogallane (0·0356 g., 0·264 mmole) and trimethylamine–gallium tri-iodide (0·0673 g., 0·132 mmole). The monosubstituted chloro- and bromo-derivatives could be prepared similarly.

Trimethylamine–Dichlorogallane.—This was obtained by the reaction between trimethylamine–gallane (0·1625 g., 1·234 mmoles) and hydrogen chloride (55·3 ml., 2·467 mmoles) in benzene solution at room temperature. The hydrogen evolved was measured (Found, 54·9 ml.; Calc., 53·3 ml.) and the solution used directly for spectroscopic measurements. The dichloro-derivative could also be prepared by treating trimethylamine–gallane (0·3434 g., 2·605 mmoles) with an excess of trimethylammonium chloride (1·23 g., 12·87 mmoles) in ether. After 46 hr. at room temperature the hydrogen evolved during the reaction was measured (Found, 118 ml.; Calc., 117 ml.).

Trimethylamine–Dichloromonodeuteriogallane, $Me_3NGaDCl_2$.—This was prepared from trimethylamine–trideuteriogallane (0·046 g., 0·344 mmole) and deuterium chloride (15·4 ml., 0·687 mmole) in benzene. The deuterium evolved was measured (Found, 15·3 ml.; Calc., 15·4 ml.).

Trimethylamine–Dibromogallane.—Trimethylamine–gallane (0·054 g., 0·412 mmole) and hydrogen bromide (18·5 ml., 0·825 mmole) were isolated in benzene and the hydrogen evolved measured after the reaction had ceased (Found, 18·2 ml.; Calc., 18·5 ml.). Similarly, the reaction between trimethylamine–trideuteriogallane (0·0327 g., 0·243 mmole), and hydrogen bromide (10·9 ml., 0·486 mmole) in benzene gave the *deuterio-derivative* $Me_3NGaDBr_2$. The liberated hydrogen deuteride was measured (Found, 10·7 ml.; Calc., 10·9 ml.). The reaction of trimethylamine–gallane (0·2040 g., 1·545 mmoles) and excess of trimethylammonium bromide (2·45 g., 13·5 mmoles) in ether liberated less hydrogen than in the corresponding chloro-system. Thus, after 7 days at room temperature, the volume of hydrogen evolved was 50·0 ml. (2·23 mmoles; Calc. for complete reaction, 3·09).

Trimethylamine–Di-iodogallane.—Excess of trimethylamine–gallium tri-iodide was required to convert trimethylamine–gallane into the *di-iodo-complex*, Me_3NGaHI_2, and trimethylamine–trideuteriogallane into the *deuterio-derivative*, Me_3NGaDI_2. The benzene solutions were used for spectroscopic measurements for the Ga–H(D) modes only.

Trimethylamine–Gallium Trihalides.—Reaction of trimethylamine–gallane (0·028 g., 0·213 mmole) with an excess of hydrogen chloride (16·0 ml., 0·714 mmole) in benzene liberated three molar equivalents of hydrogen (Found, 14·2 ml.; Calc., 14·3 ml.). Similarly, with trimethylamine–gallane (0·0366 g., 0·278 mmole) and hydrogen bromide (20·1 ml., 0·897 mmole) three molar equivalents of hydrogen were liberated (Found, 18·5 ml.; Calc., 18·7 ml.).

Trimethylamine–gallium trichloride was prepared by condensing excess of trimethylamine on gallium trichloride and allowing the mixture to warm to between −5 and 0° for about 1 hr. The excess of amine was pumped off and the white chalky powder evacuated for a further 6 hr. at room temperature to remove all traces of free amine. The product was analysed (Found: Ga, 29·8; Cl, 45·4; N, 5·9. Calc. for Me_3NGaCl_3: Ga, 29·6; Cl, 45·3; N, 5·9%). The molecular weight for the compound in benzene solution was 423; the monomer has a calculated value of 235·2. Similar procedures were used for the corresponding *bromide* (Found: Ga, 19·0; Br, 64·8; N, 3·75. Calc. for Me_3NGaBr_3: Ga, 18·9; Br, 65·1; N, 3·8%), and *iodide* (Found: Ga, 13·9; N, 2·7. Calc. for Me_3NGaI_3: Ga, 13·7; N, 2·7%) complexes.

Trimethylamine–Monochlorogallane + Boron Trifluoride.—When an excess of boron trifluoride was condensed on to trimethylamine–monochlorogallane in the side-arm of an infrared gas cell and the cell warmed, a sludge and a mobile oil were formed which, after removal of excess of boron trifluoride, showed a strong Ga–H band in the vapour phase at 2000 cm.$^{-1}$. The oil rapidly decomposed under vacuum depositing gallium metal and liberating hydrogen; it was vigorously hydrolysed by water. The use of benzene as solvent in the reaction did not prevent decomposition of the product below room temperature.

Trimethylamine–Monochlorogallane + Lithium Borohydride.—An excess of lithium borohydride was added to a stirred ethereal solution of the chlorogallane adduct. Stirring was continued below room temperature for about 1 hr. when decomposition was noticed. The ether was removed at low temperature (−40°) and the paste-like product, which started to deposit gallium below room temperature, was treated with benzene. The infrared spectrum of the solution showed both Ga–H and B–H stretching modes, but decomposition, even in the solution, concluded the experiment.

Analytical Methods.—The samples were analysed for gallium and hydrolysable hydrogen as previously described.[4] Nitrogen was determined by the Kjeldahl method and the halogens gravimetrically by precipitation with silver nitrate.

Molecular weight determinations in benzene solution were carried out in a nitrogen-flushed system under strictly anhydrous conditions.

Spectra.—The infrared spectra were recorded on a Perkin-Elmer S.P. 125 grating infrared spectrometer (4000—400 cm.$^{-1}$), which was calibrated with a polystyrene film, and on a Grubb–Parsons DM4 spectrometer (450—200 cm.$^{-1}$) with cæsium iodide optics.

Methyl-proton magnetic resonance spectra were recorded at 60 Mc./sec. with an A.E.I. RS2 spectrometer.

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