Cyclogallazanes. Part III.[1] (*N*-Polymethylene)cyclogallata-azonianes

By **A. Storr,* B. S. Thomas,** and **A. D. Penland,** Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

A series of novel, volatile, cyclogallata-azonianes $[CH_2{\cdot}(CH_2)_x{\cdot}N{\cdot}GaH_2]_n$, (where $x = 1, 2, 3,$ or 4; $n = 2$ or 3), has been prepared and characterized. Analogous aluminium and boron compounds have been prepared and comparative studies have been made on the three series of compounds. Factors governing the degree of association, *n*, of the compounds are discussed and ring strain and additional arguments are invoked to explain the tendency of some of the compounds to undergo ring fission and polymerization.

THE reaction of trimethylamine–gallane with primary amines at room temperature readily leads to the elimination of molar equivalents of hydrogen and trimethylamine, and to the formation of the cyclic derivatives, $[RNH{\cdot}GaH_2]_n$.[1,2] The factors involved in determining the degree of association, *n*, are, most importantly, steric interactions between the R groups, but also include valency-angle strain and entropy considerations.[1,2] This series has now been extended to include (*N*-polymethylene)cyclogallata-azoniane derivatives in an attempt to elucidate ring strain characteristics and steric requirements in this new class of compounds. The compounds are readily prepared by the room temperature reaction of the cyclic amine vapour with trimethylamine–gallane and form colourless crystals on sublimation:

$$CH_2{\cdot}(CH_2)_x{\cdot}NH(g) + Me_3N{\cdot}GaH_3(s) \longrightarrow 1/n[CH_2{\cdot}(CH_2)_x{\cdot}N{\cdot}GaH_2]_n + H_2 + Me_3N$$

Similar aluminium derivatives were prepared from bistrimethylamine–alane and the cyclic amines in benzene at room temperature, when a molar equivalent of hydrogen was readily evolved. The compounds were isolated by removal of solvent and trimethylamine at low temperatures:

$$CH_2{\cdot}(CH_2)_x{\cdot}NH + (Me_3N)_2{\cdot}AlH_3 \xrightarrow{C_6H_6} 1/n[CH_2{\cdot}(CH_2)_x{\cdot}N{\cdot}AlH_2]_n + H_2 + 2Me_3N$$

Earlier workers[3] successively isolated the pyrollidinyl- and piperidinyl-derivatives by this method and the same two compounds were prepared more recently by a direct synthesis.[4]

The formation of the analogous boron compounds required more forcing conditions. The amine–boranes initially formed by the reaction of diborane with the ligand, required elevated temperatures for the elimination of hydrogen:

$$2CH_2{\cdot}(CH_2)_x{\cdot}NH + B_2H_6 \longrightarrow 2CH_2{\cdot}(CH_2)_x{\cdot}NH{\cdot}BH_3$$

$$CH_2{\cdot}(CH_2)_x{\cdot}NH{\cdot}BH_3 \xrightarrow{\Delta} 1/n[CH_2{\cdot}(CH_2)_x{\cdot}N{\cdot}BH_2]_n + H_2$$

A much earlier investigation[5] of this series of compounds was unsuccessful only in its attempt to isolate the aziridinyl-derivative, which was regarded as highly unstable because of double-ring strain about the nitrogen atoms, with consequent formation of ring-opened products. A more recent attempt to prepare this compound successfully demonstrated its trimeric constitution in the gas phase by mass spectral analysis.[6]

The tendency of amine derivatives of alanes, gallanes, and boranes to eliminate hydrogen has been discussed previously,[1,7] and follows the pattern expected from a consideration of the electronegativity values of the three Group III atoms and the consequent electrical strains set up in the parent adducts. Similar arguments, evidently, are also applicable to the present series of compounds, with ease of formation decreasing from aluminium through gallium to the boron systems. The gallane series, in particular, illustrates the role of the cyclic amine in determining the speed of reaction. Thus the speed of hydrogen elimination in the reactions follows the order: aziridine > azetidine ≫ pyrollidine > piperidine. The sequence observed must indicate a decrease in the polarity of the NH bond, on adduct formation, as the amine ligands go to larger ring size. If this were so then the observed order would fit the electrical strain postulates outlined previously.

Analytical data for all three series of compounds are summarized in Table 1.

Degree of Association.—From a consideration of the degrees of association of the compounds in benzene solution (Table 1) it is clear that, in general, the α-methylene groups of the cyclic amine rings larger than that of aziridine have steric requirements which are significantly critical to yield angularly strained dimers as the preferred oligomers. Thus with the three aziridinyl-compounds, $[CH_2{\cdot}CH_2{\cdot}N{\cdot}MH_2]$ (M = Ga, Al, or B), there is a preference for trimer formation in solution, but with the higher (*N*-polymethylene)cycloborata-azonianes and the analogous gallium compounds there is a marked tendency towards the formation of dimers. The analogous aluminium compounds, however, are anomalous and only with the piperidinyl-derivative is there a drop in the degree of association from a trimeric value.

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[1] Part II, A. Storr and A. D. Penland, *J. Chem. Soc.* (*A*), 1971, 1237.

[2] A. Storr, *J. Chem. Soc.* (*A*), 1968, 2605.

[3] W. Marconi, A. Mazzei, F. Bonati, and M. de Maldé, *Gazzetta*, 1962, **92**, 1062.

[4] R. A. Kovar and E. C. Ashby, *Inorg. Chem.*, 1971, **10**, 893.

[5] A. B. Burg and C. D. Good, *J. Inorg. Nuclear Chem.*, 1956, **2**, 237.

[6] S. Akerfeldt, K. Wahlberg, and M. Hellström, *Acta Chem. Scand.*, 1969, **23**, 115.

[7] N. N. Greenwood, E. J. F. Ross, and A. Storr, *J. Chem. Soc.* (*A*), 1966, 706.

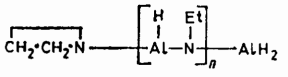
The aziridinyl-compounds are worthy of special attention. A recent communication has reported the structural characterization of the trimer, $[\overline{CH_2\cdot CH_2\cdot N}\cdot GaH_2]_3$.[8] The work involved a single crystal *X*-ray crystallographic study of a sample sublimed in a sealed capillary under low nitrogen pressure. The six membered $[Ga-N]_3$ ring was shown to be in the chair conformation, a configuration earlier predicted to be the most likely, on steric grounds, for other cyclotrigallata-azonianes.[1,2] It is probable that all the trimeric species listed in Table 1 have this same molecular arrangement, although a twist conformation similar to that reported for $[\overline{CH_2\cdot CH_2\cdot N}\cdot AlMe_2]_3$ [9] and $[MeNH\cdot AlMe_2]_3$ [10] cannot be ruled out. It is interesting that the aziridinylgallane and aziridinyldimethylalane trimers have different conformations although the $(M-N)_3$ ring dimensions and angles are virtually identical.[8,9] A plausible explanation might be that unfavourable 1,3,5-triaxial non-bonded interactions between methyl groups in a chair conformation for the aluminium compound are relieved by adopting the twist conformation whereas with the gallium compound the axial hydrogen non-bonded interactions are minimal. In benzene solution, aziridinylgallane exhibits a sharp singlet, for the aziridinyl-methylene protons, in its ^1H n.m.r. spectrum. However, cryoscopic molecular weight determinations in this same solvent give a degree of association of only 2·6. A rapid equilibrium between dimer and trimer may exist in these solutions to give magnetic equivalence for these protons although, surprisingly, no solution concentration effect was observed for the signal, and molecular weight measurements for the compound were not concentration dependent. There is no evidence of aziridine ring-opening which seems to be characteristic of the corresponding aluminium system.

TABLE 1

Analytical data

Compound	Mol H_2 per mol $\overline{CH_2\cdot(CH_2)_x\cdot N}H$	Mol Me_3N per mol $\overline{CH_2\cdot(CH_2)_x\cdot N}H$	*M* Found	Degree of association, *n*	Analysis: Found %: M	Analysis: Found %: Hydrolysable hydrogen	Analysis: $\overline{CH_2\cdot(CH_2)_x\cdot N}\cdot MH_2$ requires %: M	Analysis: $\overline{CH_2\cdot(CH_2)_x\cdot N}\cdot MH_2$ requires %: Hydrolysable hydrogen
$\overline{CH_2\cdot CH_2\cdot N}\cdot GaH_2$	1·01	1·00	296	2·60	62·1	1·76	61·4	1·76
$\overline{CH_2\cdot(CH_2)_2\cdot N}\cdot GaH_2$	0·99	1·00	255	2·00	54·1	1·55	54·5	1·56
$\overline{CH_2\cdot(CH_2)_3\cdot N}\cdot GaH_2$	0·99	0·99	286	1·99	49·0	1·38	49·2	1·41
$\overline{CH_2\cdot(CH_2)_4\cdot N}\cdot GaH_2$	0·99	0·98	295	1·89	43·9	1·26	44·7	1·28
$\overline{CH_2\cdot CH_2\cdot N}\cdot AlH_2$	1·01		223	3·14	38·3	2·90	38·0	2·82
$\overline{CH_2\cdot(CH_2)_2\cdot N}\cdot AlH_2$	1·00		260	3·06	31·6	2·36	31·8	2·36
$\overline{CH_2\cdot(CH_2)_3\cdot N}\cdot AlH_2$	0·99		308	3·10	27·1	2·04	27·3	2·02
$\overline{CH_2\cdot(CH_2)_4\cdot N}\cdot AlH_2$	1·01		266	2·35	24·0	1·74	23·9	1·77
$\overline{CH_2\cdot CH_2\cdot N}\cdot BH_2$			165	3·00	18·8	3·50	19·7	3·65
$\overline{CH_2\cdot(CH_2)_2\cdot N}\cdot BH_2$	0·97		134	1·94	15·5	2·79	15·7	2·80
$\overline{CH_2\cdot(CH_2)_3\cdot N}\cdot BH_2$	1·03		166	2·00	12·8	2·38	13·1	2·42
$\overline{CH_2\cdot(CH_2)_4\cdot N}\cdot BH_2$	1·08		196	2·02	11·0	2·04	11·2	2·06

The aziridinylalane compound has received previous attention. It was first reported as a white solid which was explosive in the absence of solvent [3] and later [11] as a polymeric ring-opened product of the form:



$\overline{CH_2\cdot CH_2\cdot N}-\left[\overset{H}{Al}-\overset{Et}{N}\right]_n-AlH_2$ where $n \simeq 10$

In the present study it was found that only with freshly prepared samples could molecular weights corresponding to a trimer in benzene solution be obtained, together with satisfactory analytical results. Freshly prepared samples exhibit singlets in their ^1H n.m.r. spectra in benzene solution but on standing ring-opening of the type suggested by Ehrlich *et al.*[11] does occur. This is evidenced by the appearance of increasingly strong signals due to NEt groups in the ^1H n.m.r. spectra, and also by higher molecular weight values obtained on the solutions. Eventually polymeric material is deposited from solution and ' aged ' material gives analysis figures for Al : H *ca.* 1 : 1, indicating a high degree of polymerization. The higher reductive power of the Al–H unit over the corresponding Ga–H group is probably responsible for the differences observed in the two compounds. The Al–H bond is predicted to be much more polar

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[8] W. Harrison, A. Storr, and J. Trotter, *Chem. Comm.*, 1971, 1101.

[9] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1970, **92**, 285.

[10] K. Gosling, G. M. McLaughlin, G. A. Sim, and J. D. Smith, *Chem. Comm.*, 1970, 1617.

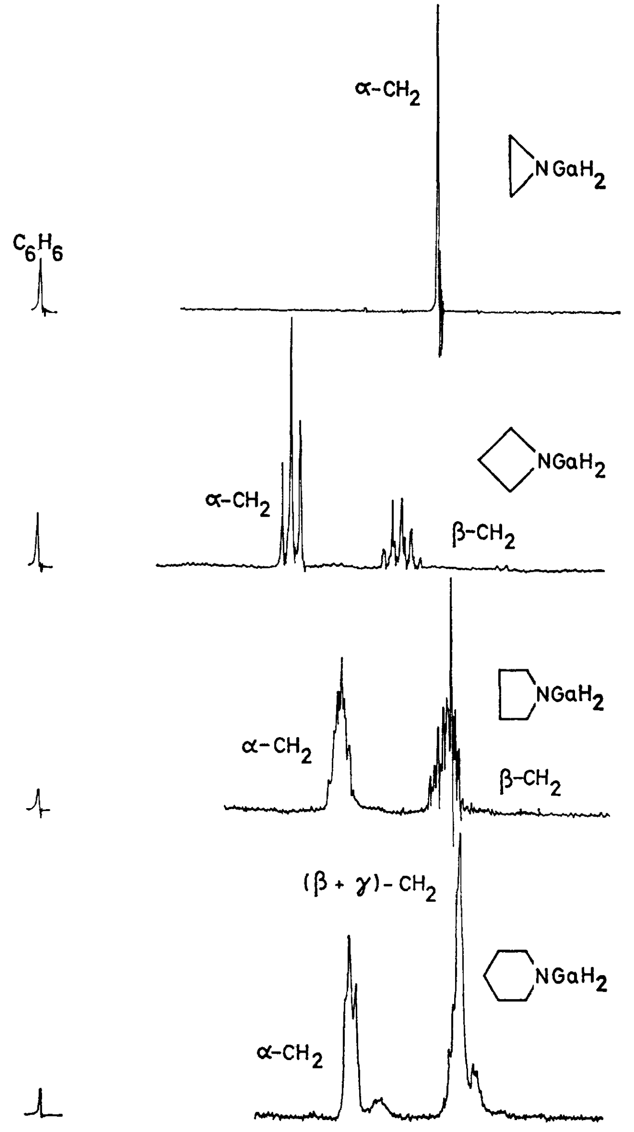
[11] R. Ehrlich, A. R. Young, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, 1964, **3**, 628.

than its gallane counterpart on the basis of electronegativities and this polarity must be sufficient to lead to ring cleavage of the aziridinyl-moiety. In contrast, with the larger (*N*-polymethylene)aluminata-azonianes there is little tendency to open the ring and give polymeric materials. Presumably this difference is due to the reduced angular strain around the nitrogen atoms in the larger heterocycles.

The aziridinylborane derivative has been reported to be trimeric in the gas phase[6] and the present work has demonstrated the same degree of association in benzene solvent for the compound. The preparation of this material, by refluxing the parent adduct, $\overline{\mathrm{CH_2\cdot CH_2\cdot N}}\mathrm{H\cdot}$-$\mathrm{BH_3}$, in benzene inevitably leads to some polymerization and ring-opening as suggested previously,[5] but the compound can be purified quite readily by vacuum sublimation.

It is difficult to rationalize the trimeric nature of the higher (*N*-polymethylene)aluminata-azonianes unless reaction intermediates play a critical role in their formation. The covalent radii of gallium and aluminium are very similar and thus steric requirements should be the same for both the gallata-azonianes and the aluminata-azonianes. However, the formation of the amine–alane trimers may proceed *via* polymeric intermediates involving five-co-ordinate aluminium, as suggested by Beachley and Coates for $[\mathrm{Me_2NAlH_2}]_3$.[12] A similar mechanism involving five-co-ordinate gallium is less likely since compounds of the type $(\mathrm{Me_3N})_2\mathrm{GaH_3}$ are known to be thermally unstable.[13] The series of compounds $(\mathrm{Me_2NMH_2})_n$ (where M = Ga, Al, or B) show the same trend in degree of association as observed in the present study. Thus, as indicated above, dimethylaminoalane is trimeric both in the vapour phase[14] and in benzene solution[15] whereas dimethylaminogallane is dimeric in benzene solvent and is postulated to be monomeric in the vapour phase on the basis of its i.r. spectrum.[7] Dimethylaminoborane can exist as monomer,[16,17] dimer,[16–18] or trimer[19,20] depending on the mode of preparation, which again indicates the major importance of the reaction intermediates in determining the degree of association of the final product.

N.m.r. Spectra.—The ^{1}H n.m.r. spectra for the three series of compounds are summarized in Table 2 and illustrative spectra, for the gallane series, are shown in the Figure. The singlets observed for the aziridinyl-compounds are consistent with a rapid inversion at room temperature of cyclohexane-type chair $[\mathrm{M{-}N}]_3$ rings leading to magnetic equivalence for the methylene protons of the aziridinyl-moieties. In the case of the gallium compound (n = 2·6) a fast equilibrium between dimer and trimer may exist in benzene solution. The azetidinyl-compounds also give simple spectra which for the trimeric aluminium species can again be rationalized in terms of a rapidly inverting cyclohexane-type chair configuration and for the borane and gallane derivatives can be explained in terms of planar four-membered $[\mathrm{M{-}N}]_2$ ring formation. The pyrrolidinyl- and piperidinyl-derivatives give spectra which involve more complex spin–spin interactions but which are



^{1}H N.m.r. spectra of (*N*-polymethylene)cyclogallata-azonianes in benzene solution at 60 MHz

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[12] O. T. Beachley and G. E. Coates, *J. Chem. Soc.*, 1965, 3241.

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

[14] D. Y. Yee and R. Ehrlich, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2681.

[15] J. K. Ruff and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1960, **82**, 2141.

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[17] G. W. Schaeffer and E. R. Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.

[18] O. T. Beachley, *Inorg. Chem.*, 1967, **6**, 870.

[19] A. B. Burg and J. S. Sandhu, *J. Amer. Chem. Soc.*, 1967, **89**, 1626.

[20] L. M. Trefonas, F. S. Mathews, and W. N. Lipscomb, *Acta Cryst.*, 1961, **14**, 273.

again consistent with the above formulations for dimers or trimers. The pyrrolidinyl- and piperidinyl-alane spectra are in agreement with those recently published.[4]

TABLE 2

^{1}H N.m.r. data in benzene solution

Compound	$\tau_{\alpha-\mathrm{CH_2}}$	$\tau_{\beta-\mathrm{CH_2}}$ ($\tau_{\gamma-\mathrm{CH_2}}$)
$\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}N}}\mathrm{{\cdot}GaH_2}$	8·46s	
$\overline{\mathrm{CH_2{\cdot}(CH_2)_2{\cdot}N}}\mathrm{{\cdot}GaH_2}$	6·41t	7·97q
$\overline{\mathrm{CH_2{\cdot}(CH_2)_3{\cdot}N}}\mathrm{{\cdot}GaH_2}$	7·14m	8·54m
$\overline{\mathrm{CH_2{\cdot}(CH_2)_4{\cdot}N}}\mathrm{{\cdot}GaH_2}$	7·21m	8·77 (8·77)
$\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}N}}\mathrm{{\cdot}AlH_2}$	8·37s	
$\overline{\mathrm{CH_2{\cdot}(CH_2)_2{\cdot}N}}\mathrm{{\cdot}AlH_2}$	6·38t	8·05q
$\overline{\mathrm{CH_2{\cdot}(CH_2)_3{\cdot}N}}\mathrm{{\cdot}AlH_2}$	6·94m	8·47m
$\overline{\mathrm{CH_2{\cdot}(CH_2)_4{\cdot}N}}\mathrm{{\cdot}AlH_2}$	7·26m	8·74 (8·74)m
$\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}N}}\mathrm{{\cdot}BH_2}$	8·57s	
$\overline{\mathrm{CH_2{\cdot}(CH_2)_2{\cdot}N}}\mathrm{{\cdot}BH_2}$	6·57t	8·36q
$\overline{\mathrm{CH_2{\cdot}(CH_2)_3{\cdot}N}}\mathrm{{\cdot}BH_2}$	7·26m	8·57m
$\overline{\mathrm{CH_2{\cdot}(CH_2)_4{\cdot}N}}\mathrm{{\cdot}BH_2}$	7·41m	8·67 (8·67)m

s = Singlet, t = triplet, q = quintet, m = multiplet.

The gallium proton signals were not observed principally because of low concentration but also perhaps because of nuclear quadrupole broadening.[7]

I.r. Spectra.—The M–H stretching vibrations for the compounds $[\overline{\mathrm{CH_2{\cdot}(CH_2)}_x\mathrm{{\cdot}N}}\mathrm{{\cdot}MH_2}]_n$ are listed in Table 3.

TABLE 3

M–H Stretching frequencies for $[\overline{\mathrm{CH_2{\cdot}(CH_2)}_x\mathrm{{\cdot}N}}\mathrm{{\cdot}MH_2}]_n$

Compound	$\nu_{\mathrm{M-H}}$
$\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}N}}\mathrm{{\cdot}GaH_2}$	1885vs,sh; 1855vs; 1800vs,sh
$\overline{\mathrm{CH_2{\cdot}(CH_2)_2{\cdot}N}}\mathrm{{\cdot}GaH_2}$	1850vs,br; 1800vs,sh
$\overline{\mathrm{CH_2{\cdot}(CH_2)_3{\cdot}N}}\mathrm{{\cdot}GaH_2}$	1865vs,br; 1800vs,sh
$\overline{\mathrm{CH_2{\cdot}(CH_2)_4{\cdot}N}}\mathrm{{\cdot}GaH_2}$	1870vs,br; 1800s
$\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}N}}\mathrm{{\cdot}AlH_2}$	1835s; 1775vs
$\overline{\mathrm{CH_2{\cdot}(CH_2){\cdot}_2N}}\mathrm{{\cdot}AlH_2}$	1835vs; 1775vs
$\overline{\mathrm{CH_2{\cdot}(CH_2)_3{\cdot}N}}\mathrm{AlH_2}$	1835vs; 1780vs
$\overline{\mathrm{CH_2{\cdot}(CH_2)_4{\cdot}N}}\mathrm{{\cdot}AlH_2}$	1835vs; 1800s,sh
$\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}N}}\mathrm{{\cdot}BH_3}$	2430vs; 2390vs; 2320s; 2260s; 2210m
$\overline{\mathrm{CH_2{\cdot}(CH_2)_2{\cdot}N}}\mathrm{{\cdot}BH_2}$	2395vs; 2330s; 2200m
$\overline{\mathrm{CH_2{\cdot}(CH_2)_3{\cdot}N}}\mathrm{{\cdot}BH_2}$	2400vs; 2330s; 2220m
$\overline{\mathrm{CH_2{\cdot}(CH_2)_4{\cdot}N}}\mathrm{{\cdot}BH_2}$	(2430s,sh?); 2410vs; 2350s; 2240m

The $\nu_{\mathrm{Ga-H}}$ bands are characteristically broad in the benzene solutions but partial resolution into symmetric and asymmetric vibrations is observed. The three bands observed in the spectrum of aziridinylgallane may arise from a dimer–trimer mixture in benzene solution. Similarly, in contrast to an earlier report on two of the compounds,[4] the $\nu_{\mathrm{Al-H}}$ modes for the alane derivatives are also resolved into symmetric and asymmetric stretching vibrations. This resolution is also noted in the Nujol mull spectra of the compounds. The borane spectra are more complicated. The aziridinylborane spectrum is in agreement with published results,[21] the complexity in the BH_2 stretching region arising possibly from a coupling between the three BH_2 groups, or from steric interactions of the type proposed to explain the i.r. spectrum of $[Me_2NBH_2]_3$.[19] With the dimeric boranes a repetitive pattern of three $\nu_{\mathrm{B-H}}$ vibrations is observed and again some type of coupling is probable between the BH_2 groups.

EXPERIMENTAL

Materials were handled in a conventional high-vacuum line or in a glove-box under an atmosphere of oxygen-free dry nitrogen. Benzene was thoroughly dried by being heated under reflux over potassium; it was distilled before use. Azetidine was prepared by a modification of the method reported by Burg and Good [5] and the other amines were commercial samples which were dried over calcium hydride and distilled under reduced pressure before use. All gas volumes are quoted at s.t.p.

Trimethylamine–gallane was prepared as described previously.[13] Trimethylamine–alane was synthesized by a published procedure [15] and converted into the bistrimethylamine–alane adduct by treatment with excess trimethylamine. Commercially available diborane (K and K Laboratories) was used in the preparation of the borane compounds. The parent borane adducts were prepared as previously described [5] and pyrolysed in sealed bulbs to yield the cycloborazanes. The one exception in this series was aziridinylborane which was synthesized by the method of Akerfeldt *et al.*[6] by heating a solution in benzene of the parent adduct.

The procedure for the preparation of the cyclogallataazonianes and the analogous aluminium compounds is standard throughout the respective series and therefore the preparations of the azetidinyl-derivatives only are given as illustrative examples.

Azetidinylgallane.—This was prepared by condensing azetidine (50·7 ml, 2·264 mmol) onto trimethylamine–gallane (0·298 g, 2·264 mmol) at −196 °C and allowing the mixture to warm up to room temperature. After *ca.* 1 h the flask was cooled to −196 °C and the volume of evolved hydrogen was measured. The mixture was again brought to room temperature for *ca.* 1 h and the hydrogen measured as before. The process was repeated until hydrogen evolution had ceased. The total volume of hydrogen was obtained (Found: 50·2 ml. Calc.: 50·7 ml). The mixture was again brought to room temperature and the volume of trimethylamine measured (Found: 50·7 ml. Calc.: 50·7 ml) and its purity checked by its gas phase i.r. spectrum. The product, a white solid at room temperature, gave colourless crystals on vacuum sublimation. It was analysed for hydrolysable hydrogen and gallium and subjected to physical measurements (see Tables 1—3).

Azetidinylalane.—This new compound was synthesized by condensing azetidine (37·2 ml, 1·660 mmol) onto bistrimethylamine–alane (0·246 g, 1·660 mmol) in benzene (20 ml) and warming the mixture to room temperature. Hydrogen was rapidly evolved (Found: 37·2 ml. Calc.: 37·2 ml). Benzene and trimethylamine were removed at

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[21] R. L. Williams, *Acta Chem. Scand.*, 1969, **23**, 149.

−30 °C and the desired product was separated from a small amount of insoluble material by benzene extraction and centrifuging. The white solid obtained after removal of solvent from the clear solution was analysed and its physical properties measured (see Tables 1—3).

Analytical Methods.—The gallane and alane samples were analysed for hydrolysable hydrogen and metal as previously described for gallium hydride compounds.[13] The metals were determined gravimetrically as their 8-hydroxyquinolates. The borane compounds were analysed for hydrolysable hydrogen by sealing off a sample with hydrochloric acid in a break-seal bulb followed by digestion at *ca.* 130 °C for 48 h. The hydrogen liberated was then measured and the boron in solution determined by standard titrimetric analysis. Cryoscopic molecular weight determinations were carried out in benzene solution under strictly anhydrous conditions in a nitrogen-blanketed system.[22] Solutions were prepared and introduced into the apparatus in the glove-box. The freezing points of the solutions (and pure solvent) were measured using a Beckman thermometer. The molecular weights were found to be essentially not concentration dependent over the range of concentrations investigated [0·1—0·25M based on the empirical formula $\overline{CH_2\cdot(CH_2)_x\cdot N}\cdot MH_2$]. Molecular weight determinations for aziridinylgallane were carried out on six solutions of different concentrations and although the value of *n* varied slightly ($n = 2\cdot55$—$2\cdot60$) no regular pattern of *n vs.* concentration became apparent. The results were constant considering the experimental accuracy of the determinations ($\Delta T = \pm 0\cdot005°$).

Spectra.—N.m.r. measurements were obtained on Varian HA-100 and T-60 instruments. The benzene solutions were prepared in the glove-box and the sample tubes were sealed off to avoid atmospheric interference. The concentrations of the solutions were all higher (*ca.* 1M) than those employed for molecular weight measurements but on dilution of the solutions identical spectra were observed but with less favourable signal to noise ratios. All τ values are referred to benzene, 2·84 (τ for $SiMe_4$, 10·00).

Definitive i.r. spectra were recorded on a Perkin-Elmer model 457 spectrometer (4000—250 cm^{-1}).

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