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THE HUNTING OF THE GALLIUM HYDRIDES

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> *They sought it with thimbles, they sought it with care;*
> *They pursued it with forks and hope;*
> *They threatened its life with a railway-share;*
> *They charmed it with smiles and soap.*
> Lewis Caroll, "The Hunting of the Snark"

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I. Introduction

Boron dwarfs the other members of Group 13 in the richness of its hydride chemistry (*1–9*). At a recent count (*9*) about 100 binary borane species are now known, typically as discrete molecules remarkable for their stoicheiometries and structures, which have done much to shape our understanding of chemical bonding at large. By contrast, there is known only one binary hydride of aluminium stable under normal conditions, and that is a polymeric solid, the α-form being isostructural with AlF_3 and featuring six-coordinate aluminium atoms (*10–13*). There is no doubt that the vapors of a Group 13 metal, M, react with hydrogen, under appropriate conditions of excitation, to give transient hydride molecules like MH [M = Al (*14*), Ga (*14–16*), In (*14, 15, 17*), or Tl (*14, 15*)] or MH_3 (M = Al, Ga, or In) (*18*). The MH molecules have appreciable bond dissociation energies, ranging from 294 for M = Al to 190 kJ mol^{-1} for M = Tl, but the heats of atomization of the elements M and H_2 are such that the monohydrides are highly unstable with respect to the elements at normal temperatures. The transients GaH and GaH_3 apart, the uncoordinated binary hydride of gallium, $[GaH_3]_n$, has been for many years something like the fabulous Snark of Lewis Carroll's fertile imagination (*19*), with its existence befogged by both claimants and counterclaimants. Given the history of the compound, it is not surprising that one authoritative view delivered in 1988 (*20*) was that "$[GaH_3]_n$ is questionable."

In this account we shall be concerned with establishing the true credentials of gallane and its derivatives. After a brief outline of earlier searches for gallane, including the characterization of coordinatively saturated gallanes like GaH_4^- and $Me_3N{\cdot}GaH_3$, we shall describe the sort of procedures that it has been necessary to devise in order to hunt not only gallane itself, but also compounds like gallaborane, $[GaBH_6]_n$, and the tetraborane(10) derivative, 2-GaB_3H_{10}, which are little or no less reactive and only slightly more robust with regard to thermal decomposition. Of the instruments used to pursue the Snark, only care and hope have played a major part in our pursuit of the gallium hydrides; more prosaically we dwell on the physical methods that have enabled us to know the "warranted genuine" compounds. How the base-free gallium hydrides have ultimately been tracked down is then revealed, with due note of the pivotal role of monochlorogallane, $[H_2GaCl]_2$, itself the recent fruit of pure serendipity. Such physical properties of the compounds as have been ascertained so far are recorded. Although these are still early days, our account will aim also to give some idea of the potential for new chemistry that the compounds hold. In this prospect alone there is much to relish. Whether there is any moral to the tale is for the reader to judge.

Only two decades ago the hydrides of the heavier Group 13 metals might have appeared as no more than scientific curiosities, although the preparation of ether-free aluminium hydride was classified under U.S. Air Force contracts in the early energy-hungry 1960s. Such a perception has changed out of all recognition with the technological rise of III–V (13–15) compounds (*10*) and the need to form thin films of these or of the metals, e.g., for the growth of GaAlAs and the "metallization" of semiconductor devices. Chemical vapor deposition (CVD) implicating organometallic precursors in reactions such as

$$Me_3Ga(g) + AsH_3(g) \longrightarrow GaAs(s) + 3CH_4(g) \qquad (1)$$

is of primary importance in this connection, although the success of such methods demands close control of the conditions and, even then, cannot always be guaranteed to deliver deposits with the desired purity or physical properties. Volatility and thermal instability, allied to the relative cleanness of the decomposition reactions, confer on hydrides significant advantages over organometallic sources of the Group 13 metals, notably in the formation of carbon-free deposits. For example, trimethylamine alane, $Me_3N{\cdot}AlH_3$, has been found to offer considerable attractions as a precursor to pure aluminium films (*21–26*). Compounds as volatile and thermally frail as the elusive gallane, $[GaH_3]_n$, are therefore of more than passing interest, not only as a means of vapor transport of the metal at low temperatures, but also as a source of solid metal or metal-bearing films. In addition, compounds like gallane may be either active intermediates or parents to such intermediates in the thermolysis reactions associated with useful CVD processes and our current knowledge of which owes more to speculation than to well-substantiated fact.

II. History and Chemical Background

A. The Search for Free Gallane

Earlier searches starting with elemental gallium having been to no avail, the first substantive claim to the synthesis of gallium hydride was staked out just over 50 years ago. It depended on more than one route, viz. (*27–30*)

$$\mathrm{GaCl_3} \xrightarrow{\mathrm{LiGaH_4,\,Et_2O}} \frac{1}{n}\,[\mathrm{GaH_3}]_n \tag{2}$$

$$\mathrm{Me_3Ga} + \mathrm{H_2} \xrightarrow[\text{discharge}]{\text{electric}} \frac{1}{2}\,[\mathrm{Me_2GaH}]_2 \xrightarrow{\mathrm{Et_3N}} \mathrm{Et_3N{\cdot}GaMe_3} + \mathrm{Ga_2H_6}. \tag{3}$$

With the benefit of hindsight, it seems odd that the use of ether as a reaction medium should yield not a complex like $Et_2O{\cdot}GaH_3$ but the base-free hydride $[GaH_3]_n$. That a deficiency of triethylamine should favor ligand redistribution in dimethylgallane with the formation of free gallane and the complex $Et_3N{\cdot}GaMe_3$ is perhaps less surprising if we suppose that the propensity to associate makes gallane a weaker Lewis acid than Me_3Ga. Altogether more surprising were the reports that free gallane is stable at temperatures up to 130°C.

Doubts about the authenticity of some of these claims were raised about 20 years later by the failure of attempts to reproduce the experiments (*31, 32*). On the other hand, analytical and spectroscopic evidence was presented (*32, 33*) to support the low-temperature displacement reaction

$$\mathrm{Me_3N{\cdot}GaH_3(c)} + \mathrm{BF_3(g)} \xrightarrow{258\ \mathrm{K}} \frac{1}{n}\,[\mathrm{GaH_3}]_n(\mathrm{l}) + \mathrm{Me_3N{\cdot}BF_3(c)}, \tag{4}$$

which for more than two decades was widely accepted as a route to uncoordinated gallane (*8, 32*). The compound was described as a viscous oil unstable at room temperature. The vapor exhibited infrared absorptions centered near 1980 and 700 cm^{-1}, attributable to $Ga{-}H_t$ stretching and bending modes, respectively (H_t, terminal hydrogen atom). The physical properties clearly pointed to an oligomeric or polymeric product and so it was curious that the infrared spectrum betrayed no sign of features attributable to motions of $Ga{-}H_b{-}Ga$ units (H_b, bridging hydrogen atom). Yet, on the evidence of mass-spectrometric and matrix-isolation studies (*34, 35*), the vapor species derived from the interaction of $Me_3N{\cdot}GaH_3$ with BF_3 include B_2H_6 and BH_nF_{3-n} species in proportions implying that *halide-hydride exchange,* and not displacement, is the predominant reaction pathway. A product answering to the description of the material alleged to be uncoordinated gallane has been prepared, but the signs are that it is a mixture of fluorogallanes of the type $[H_xGaF_{3-x}]_n$, probably incorporating coordinated Me_3N (x = 1 or 2 and $n > 2$) (*35–37*).

All these vicissitudes must, we feel, call in question the preparation of anything approaching pure gallane in the period before 1989. Monosubstituted derivatives of gallane, $[H_2GaX]_n$, have been no less elusive. The displacement reaction

$$\mathrm{Me_3N{\cdot}GaH_2Cl(c) + BF_3(g) \longrightarrow \frac{1}{\mathit{n}}[H_2GaCl]_{\mathit{n}}(l) + Me_3N{\cdot}BF_3(c)} \qquad (5)$$

was reported to afford a thermally unstable oil, believed to be monochlorogallane, $[H_2GaCl]_n$ (*38*). Little headway was made, however, with the characterization of the product, and, in the light of the doubts cast on the analogous preparation of gallane itself and of more recent studies (to be described) (*36, 37, 39, 40*), this claim too must be treated with caution. By contrast, the same period had witnessed the convincing authentication of several disubstituted derivatives of gallane. These included compounds of the type $[HGaX_2]_2$, where X = Cl or Br, prepared by metathesis (*41, 42*):

$$\mathrm{2Me_3SiH + Ga_2X_6 \xrightarrow{253\ K} [HGaX_2]_2 + 2Me_3SiX.} \qquad (6)$$

The chloride forms white crystals that melt at 29°C with decomposition and, when heated to 150°C, decompose quantitatively into gallium "dichloride," $Ga[GaCl_4]$, and hydrogen. Several diorganogallanes were also described. Among these were $[Et_2GaH]_n$ (*43–45*) and $[Bu^i_2GaH]_n$ (*46*) prepared, for example, by reactions such as (7) and (8):

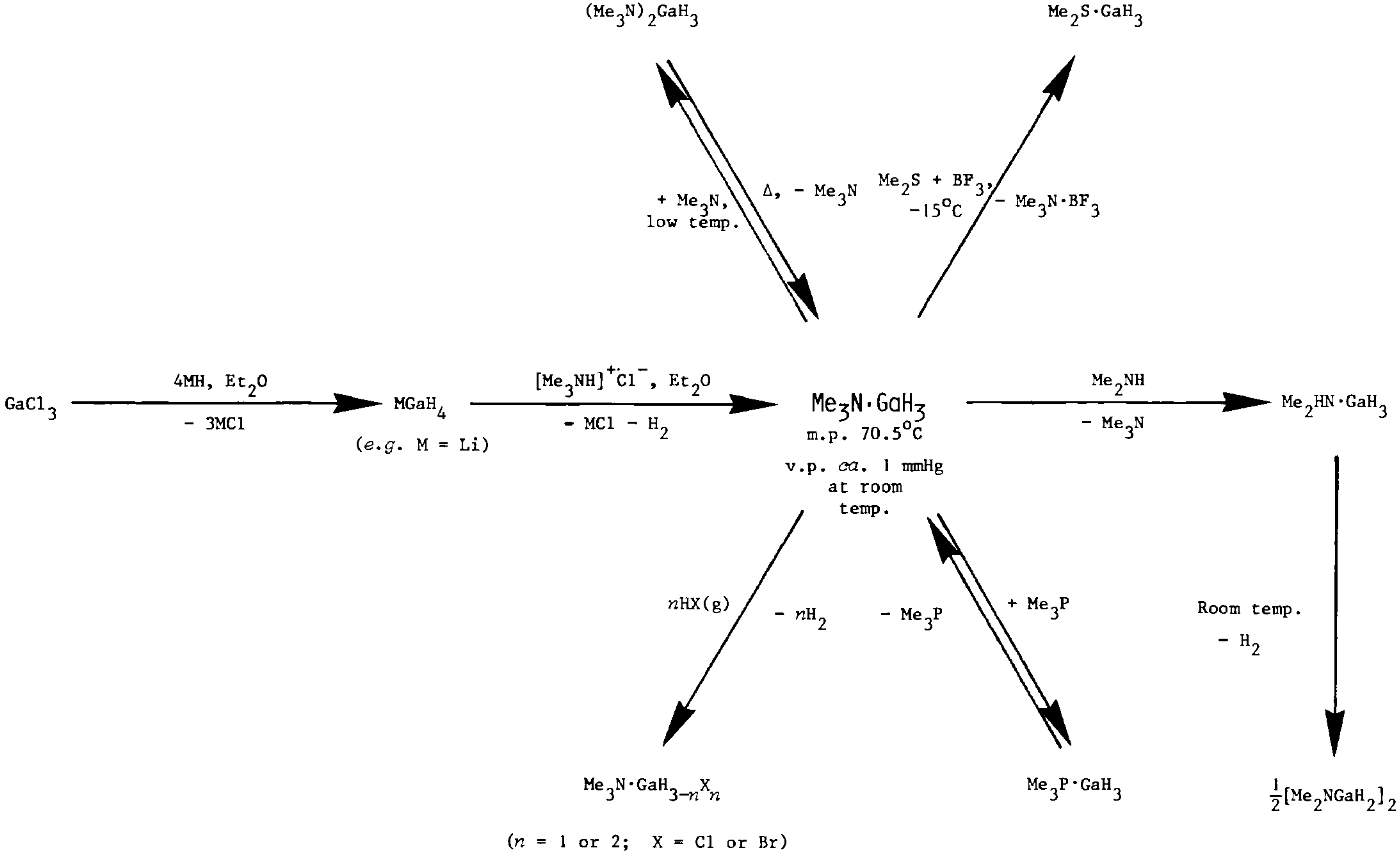
$$\mathrm{Et_3Ga + NaGaH_4 \xrightarrow{70^\circ C} \frac{1}{\mathit{n}}[Et_2GaH]_{\mathit{n}} + NaGaH_3Et} \qquad (7)$$

$$\mathrm{\frac{1}{2}[Bu^i_2GaCl]_2 + LiH \xrightarrow{Et_2O,\ 40\text{–}45^\circ C} \frac{1}{\mathit{n}}[Bu^i_2GaH]_{\mathit{n}} + LiCl.} \qquad (8)$$

Only recently, however, with the isolation and more detailed interrogation of the compounds $[Me_2GaH]_n$ (*47*) and $HGa(BH_4)_2$ (*48–50*), has it been possible to discover with any sureness the properties—including the structures—of such compounds. Insofar as these properties have a bearing on the hunting of other gallium hydrides, it will be better that we elaborate on them in due course (in Section IV).

B. COMPLEXES OF GALLANE

The confusion besetting the status of gallane itself has certainly not extended to coordinated derivatives, usually of the type $L{\cdot}GaH_3$, where



SCHEME 1. Preparation and representative reactions of some complexes of gallane (*12, 32*).

L is a basic species like Me_3N or H^- (*12, 32*). Prepared by methods along the lines indicated in Scheme 1, many of these have been known for some years, in several cases as compounds long-lived at ambient temperatures. Numerous neutral 1:1 complexes have been prepared with stabilities varying in the sequences $Me_2NH > Me_3N > C_5H_5N > Et_3N > PhNMe_2 \gg Ph_3N$; $Me_3N \approx Me_3P > Me_2PH$; and $R_3N > R_2O$ or R_2S. More or less tetrahedral coordination of the gallium center is the norm, as illustrated in Fig. 1 for the gaseous molecules $Me_3N{\cdot}GaH_3$ (*51*) and $[Me_2NGaH_2]_2$ (*52*), whose structures have been determined by electron diffraction. Measuring about 150 pm, the $Ga{-}H_t$ bonds are somewhat shorter here than in the monohydride GaH [$r_e = 166.21$ pm (*16*)], but comparable with $Ge^{IV}{-}H$ and $As^{III}{-}H$ bonds. The $Ga{-}H_t$ stretching modes of $L{\cdot}GaH_3$ moieties have wave numbers that vary with the nature of L (and with the medium) in the range 1720–1880 cm^{-1} (*32, 53–55*). Partial replacement of the hydrogen by more electronegative substituents like chlorine shifts $\nu(Ga{-}H_t)$ to higher energy, as exemplified by the mean wave numbers (in cm^{-1}) in the following series: $Me_3N{\cdot}GaH_3$, 1836; $Me_3N{\cdot}GaH_2Cl$, 1902; and $Me_3N{\cdot}GaHCl_2$, 1959.

III. Conduct of the Hunt: Practical Methods of Attack

A. HANDLING

The gallium hydrides known prior to 1989 are, without exception, unusually susceptible to attack by air or moisture. None of them is thermally robust and some evidently decompose at subambient temperatures. Of necessity, therefore, the compounds are nearly always handled *in vacuo*. However, because they tend to dissolve in, or react with, vacuum greases, it is usually a minimum requirement that they be handled in apparatus incorporating greaseless valves and unions with vacuum seals made in a material like Teflon. Yet even these measures are inadequate sometimes to guard against decomposition or reaction with impurities adsorbed on the surfaces of the apparatus. To succeed with the synthesis and manipulation of such hydrides has demanded scrupulous attention to practical techniques, including the development of special procedures (*37, 56*). There follows a brief outline indicating some of the practical and strategic considerations.

1. *Vapor Transfer and Sampling*

In the pursuit of gallane and related hypersensitive compounds, we have found that operations must be carried out at pressures $<10^{-4}$ mm

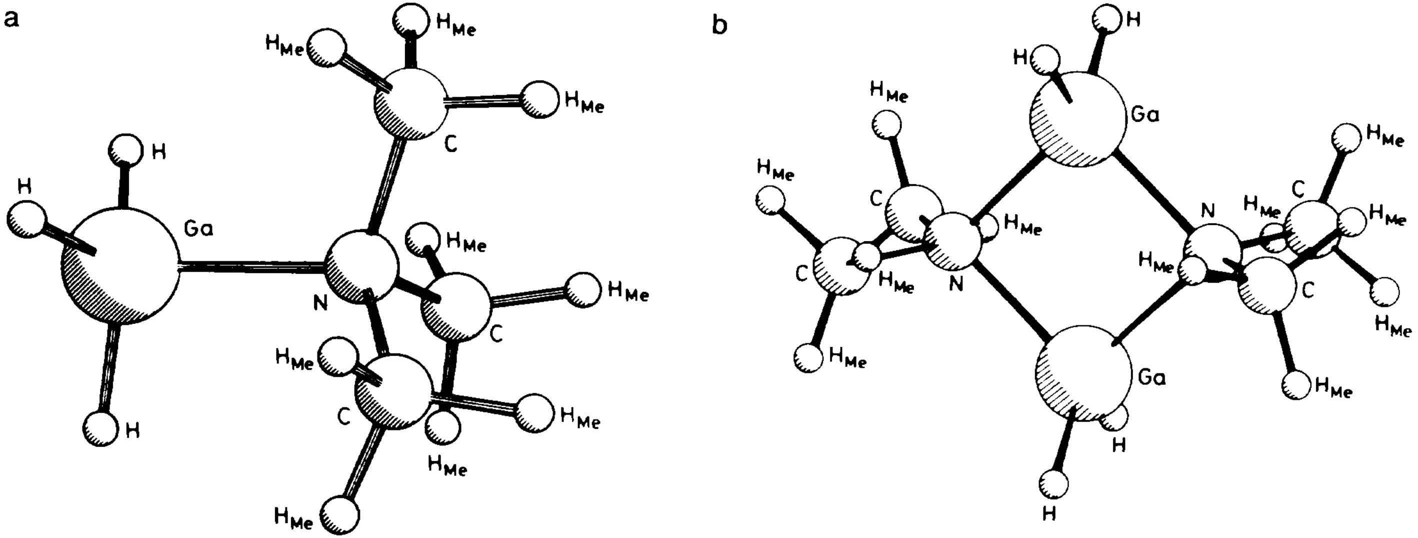


FIG. 1. Molecular structures of the gallane derivatives (a) $Me_3N{\cdot}GaH_3$ and (b) $[Me_2NGaH_2]_2$ as deduced from the electron-diffraction patterns of the vapors (reproduced with permission from Refs. *51* and *52*).

Hg *in all-glass apparatus* individually constructed and incorporating appropriately sited break-seals and constrictions (*37, 56*). Figure 2a illustrates a typical assembly. Such apparatus possesses two crucial advantages. In the first place, cooling of all parts can be effected by blowing a stream of cold gas over the exposed surfaces. Second, the apparatus can be rigorously preconditioned by heating under continuous pumping to eliminate volatile impurities adsorbed on the inner walls. Distillation trains are kept short, each trap normally being equipped (a) with constrictions to permit isolation of a sample by sealing under vacuum and (b) with a break-seal permitting access to the contents to be regained under equally rigorous conditions. Even so, the properties of some gallium hydrides impose severe limitations on what

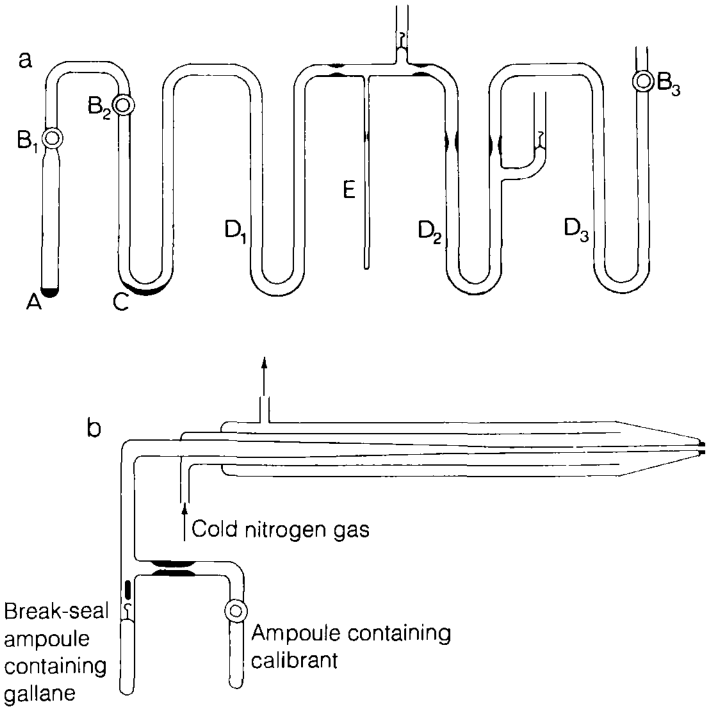


FIG. 2. Pyrex glass apparatus used (a) for the synthesis and sampling of a base-free gallane and (b) for the admission of the gallane vapor to the chamber of the electron-diffraction apparatus. In (a) A is a sample of $[H_2GaCl]_2$; B_1, B_2, and B_3 are greaseless valves; C is freshly prepared $LiGaH_4$, $LiBH_4$, or $[Bu^n{}_4N][B_3H_8]$; D_1, D_2, and D_3 are U-tube traps for fractionation of the volatile components of the reaction mixture; and E is an NMR tube (reproduced with permission from Ref. *56*; copyright 1991, American Chemical Society).

can be realistically achieved by way of physical and chemical characterization. Thus, the proclivity to decompose means that vapor pressures must be kept low and this tends to thwart a variety of potentially informative studies involving, for example, the use of Raman or NMR spectroscopy to investigate the vapor. The problems are less acute with more sensitive techniques, like modern FTIR spectroscopy offering sampling times in the order of 1–2 min, and the lifetime of the vapor sample can be extended by going to lower pressures with a compensating increase in path length (as in a multiple-reflection cell) (*37, 56*). There is also scope, as yet unexploited, for introducing the molecules into a supersonic jet and investigating their microwave, rovibrational spectra, or both, taking advantage of the enhanced signal strength and spectroscopic resolution made possible by the internal cooling induced under these conditions (*57–59*). Without rigorous sampling techniques, however, there is the risk of confusion caused by reactions of the hydride with adventitious impurities; such is the case, for example, with conventional mass spectrometric analysis. Accordingly, for electron-diffraction measurements it has been necessary to construct a special all-glass inlet assembly (*37, 56*). As illustrated in Fig. 2b, this provides for the direct injection of the gallium hydride vapor from a storage ampoule into the chamber of the diffraction apparatus via a glass channel that can be suitably passivated and then cooled to whatever temperature may be needed to forestall thermal decomposition. But problems, like sorrows, "come not single spies." The strongly reducing vapor of the gallium hydride is liable to react with the emulsion of the photographic plates used to record the electron-diffraction patterns; the resulting fogging effects can be alleviated, but not eliminated, by various measures (*37, 56*).

2. *Trapping Experiments*

Such is the thermal instability of the gallium hydrides that meaningful studies of the condensed phases are largely confined to samples at low temperatures. In these circumstances, the tracking and identification of the compounds have called for trapping. This may be achieved *physically* by quenching the vapor on a cold surface either alone or with an excess of a suitable diluent [as in matrix isolation (*60*)]; questions of identity and likely structure are then addressed by reference to the infrared or Raman spectrum of the deposit, the attribution of the features being checked by examining the effects of isotopic enrichment of the sample. Alternatively the experimenter may resort to *chemical* trapping of the hydride by treating it with a compound likely to undergo a *fast* and quantitative reaction, yielding a known product. Trimethylamine is such a compound and the discovery that the addition reactions (9) and (10) take place cleanly at 178 K has provided irresistible proof of the identities of the relevant gallanes:

$$\frac{1}{2}[H_2GaCl]_2 + m\mathrm{NMe}_3 \xrightarrow{178\ \mathrm{K}} H_2ClGa(\mathrm{NMe}_3)_m \ (\mathit{36, 39, 40}) \qquad (9)$$

$$\frac{1}{n}[GaH_3]_n + m\mathrm{NMe}_3 \xrightarrow[(m = 1 \text{ or } 2)]{178\ \mathrm{K}} H_3Ga(\mathrm{NMe}_3)_m \ (\mathit{37, 56, 61}). \qquad (10)$$

3. *Chemical Analysis*

To determine the composition of a compound that is more or less short-lived at normal temperatures, it is necessary to devise a method of chemical analysis that can be carried out on site, that is, with the aid of a glass vacuum line. The prime desideratum is to find a suitable reaction of the compound that can be engineered to proceed quantitatively in an evacuated, preconditioned glass ampoule to deliver stable products that are amenable to direct assay, for example, by weighing, tensimetric measurements, or elemental analysis. A good illustration is provided by hydridogallium *bis*(tetrahydroborate) (see Section IV.A), which decomposes at or just above room temperature in accordance with Eq. (11) (*48–50*):

$$HGa(BH_4)_2(l) \longrightarrow Ga(s) + B_2H_6(g) + \frac{3}{2}H_2(g). \qquad (11)$$

In this case a Toepler pump can be used to remove the volatile products derived from a known mass of the gallane, and an efficient trap cooled to 77 K to separate the condensable B_2H_6 from the noncondensable H_2; the two fractions are then assayed tensimetrically. The mass balance is completed simply by weighing the residue of elemental gallium. Similar measures can be adopted to determine the stoicheiometry of a reaction engaging a gallane with another compound, e.g., NH_3, NMe_3, or HCl.

B. Physical Methods of Detection and Analysis

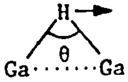
It will be evident from the preceding account that not all physical methods lend themselves equally well to the detection and specification of the gallium hydrides. There are, for example, obvious difficulties in trying to grow single crystals of a low-melting, thermally unstable compound, and, although the case of hypofluorous acid (*62*) shows what can be achieved ultimately, X-ray methods do not obviously commend themselves at the first sighting of the molecular quarry. In any case, there is ample circumstantial evidence that aggregation is a primary motif in gallium hydride chemistry and that the form of the compound may well vary from one phase to another. Three methods have in the event formed the spearhead of the present hunt, namely,

(a) vibrational spectroscopy;
(b) NMR spectroscopy; and
(c) electron diffraction of the vapor.

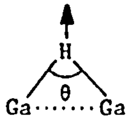
Some of the more robust molecules, like $HGa(BH_4)_2$ (*48–50*) and $H_2GaB_3H_8$ (*63*), can be identified by their mass spectra, and UV photoelectron spectroscopy has also been turned to account in studies of gaseous tetrahydroborate molecules like $Al(BH_4)_3$ (*64*) and $HGa(BH_4)_2$ (*50*), notably for the light it sheds on the mode of coordination of the BH_4 ligand. Compared with the three primary methods, however, such sources of supplementary information are barely in the running.

1. *Vibrational Spectroscopy*

Identification of a gallium hydride sample has been accomplished in the first place more often than not by reference to its infrared spectrum, supported sometimes by its Raman spectrum. To test and elaborate upon the inferences drawn from such a spectrum, we can appeal to various particulars; most informative of these are (i) signs of rotational fine structure associated with the infrared absorptions of the vapor, (ii) the response to isotopic changes, and (iii) analogies with the vibrational properties of related, authenticated molecules. As with the characterization of metal carbonyls, it is the stretching vibrations that by their energies and intensities offer the most telling commentary on the molecular identity. Where ν(C–O) modes differentiate terminal from bridging carbonyl functions, so ν(M–H) modes differentiate terminal from bridging M–H functions in hydride derivatives of a Group 13 metal, M. Studies carried out in Oxford supplement earlier measurements in establishing, for example, that the stretching modes of terminal Ga–H bonds give rise to strong infrared absorptions in the range 1720–2050 cm^{-1} (Refs. *32, 37, 38, 41, 42, 48–50, 54–56, 63,* and *65,* for example). This contrasts with bridging Ga–H–Ga units for which ν(Ga–H) occurs with variable intensity in the range 900–1720 cm^{-1} (*37, 47, 56, 66, 67*). A similar distinction can be drawn between terminal Al–H and bridging Al–H–Al moieties (*12, 47, 68, 69*), just as the number, energies, and intensity patterns of ν(B–H) modes are familiar signatures for the BH_4 ligand in different types of coordination (*70, 71*). For an M–H–M bridge there are two stretching vibrations depicted



(1a)



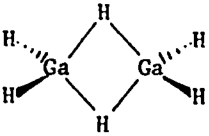
(1b)

schematically in **1a** and **1b**, which may be described as antisymmetric (ν_{as}) and symmetric (ν_s), respectively. The wave numbers of these two vibrations are linked via the simple relationship (12) to the M–H–M bond angle θ:

$$\nu_{as}/\nu_s = \tan(\theta/2). \tag{12}$$

The relation is subject to certain approximations, namely (a) that the mass of M is effectively infinite compared with that of hydrogen; (b) that the angle-bending force constant, k_θ, is much smaller than the bond-stretching force constant, k_r, and that neither ν_s nor ν_{as} experiences significant mixing with any other motion of the molecule at large; and (c) that the stretch–stretch interaction constant, k_{rr}, is negligible (*72*). As θ approaches 90°, so, according to Eq. (12), the ratio ν_{as}/ν_s approaches unity; i.e., the separation between ν_{as} and ν_s tends to zero, and, as θ approaches 180°, the ratio and frequency separation increase. There is a concomitant change in the relative intensities of the two infrared absorptions corresponding to these modes, such that the ratio I_{as}/I_s runs from near unity to infinity as θ ranges from 90 to 180°. Such considerations have been invaluable in the first sighting of hydrogen-bridged molecules like dimethylgallane, $[Me_2GaH]_n$ (*47*), and gallane itself, $[GaH_3]_n$ (*56*).

At the same time, a relatively simple molecule like Ga_2H_6 (*37, 56*) or $GaBH_6$ (*37, 65*) may be expected to betray its presence in the gas phase by infrared absorptions modulated by rotational structure. Scrutiny of this structure, preferably at high resolution, opens up the prospect of determining the symmetry properties of the associated vibrational transitions and of securing at least a rough estimate of one or more of the rotational constants. Thus, Ga_2H_6 with a diborane-like structure (**2**) featuring two massive gallium atoms on a common symmetry axis



(2)

has a momental ellipsoid approximating to that of a highly prolate symmetric top with $I_A \ll I_B \approx I_C$. Such a molecule may be expected to show infrared absorptions of two kinds according to whether the dipole change associated with the vibrational transition is *parallel* or *perpendicular* to the Ga···Ga axis. A parallel-type band should be dominated by more or less structured P- and R-branches flanking a single, very narrow Q-branch, whereas a perpendicular-type band should be dominated *not* by the P- and R-branches, which form an unresolved or only partially resolved background, but by a regular series of Q-subbranches with a spacing approximating to $2(A' - \tilde{B}')$ (where the rotational constants A' and $\tilde{B}'$ refer to the $v = 1$ vibrational state and $\tilde{B}'$ is the average of the two constants B' and C'). Under modest resolution a parallel-type feature is expected to show a P–R branch separation, $\Delta\nu_{PR}$, to which we may appeal, through another approximate relation, viz. Eq. (13), for an estimate of the mean rotational constant $\tilde{B}$:

$$\Delta\nu_{PR} = \sqrt{\frac{8kT\tilde{B}}{hc}}. \tag{13}$$

Because the magnitude of $\tilde{B}$ is governed mainly by the Ga···Ga distance, it is thus possible to gauge this distance to a useful approximation. A similar approach was used to arrive at the first estimate of the Xe–F bond length in the linear molecule XeF_2 (*73*). How the results of such studies in practice point irresistibly to the fugitive species Ga_2H_6 is more aptly treated later (Section V.B.2).

2. *NMR Spectroscopy*

The normal edge that NMR measurements enjoy in so many matters of detection and characterization has been somewhat blunted where gallium hydrides are involved. The studies carried out to date have been concerned exclusively with hydrocarbon solutions of the compounds, sometimes at room temperature, more often at low temperatures (down to 190 K). One immediate problem is whether the compound has the same form under these conditions as in the vapor at low pressure or in the solid phase. The signs are that aggregation becomes a serious issue in solution where a given gallium hydride often exists in more than one oligomeric form. Further problems stem from the quadrupolar character of the two naturally occurring gallium isotopes, ^{69}Ga (60.108%, $I = \frac{3}{2}$) and ^{71}Ga (39.892%, $I = \frac{3}{2}$) (*10*), which causes marked broadening of the ^1H resonances originating in hydrogen atoms bound to gallium. The ^1H signals do sharpen when the solution is cooled, but the spectra hold relatively little structural information, beyond the finding that terminal hydrogen atoms have chemical shifts in the range δ 4.0–5.5, whereas bridging hydrogen atoms resonate at lower frequency (δ 1–3.1) (*32, 36, 37*). The ^{71}Ga nucleus (which is superior in its receptivity and width factor to the more abundant ^{69}Ga) has featured in numerous NMR experiments (*74, 75*), but the line widths associated with gallium atoms in less than symmetrical environments make it relatively unattractive as a marker for a gallium hydride.

Rather more instructive are the NMR spectra of mixed gallium boron hydrides like $GaBH_6$ and GaB_3H_{10}, with which ^{11}B measurements help to build up a fuller picture. Yet further complications are in store. First, there is the susceptibility of any hydrogen-bridged framework to undergo facile exchange. Fluxionality is a familiar phenomenon in metal tetrahydroborates, most investigations implying magnetic equivalence of the four protons of each BH_4 ligand irrespective of its coordination mode and of the temperature (*71, 76*). Compounds containing a metal coordinated to an octahydrotriborate group, B_3H_8, show a wider repertoire of properties, ranging from the essentially rigid behavior of $Mn(B_3H_8)(CO)_4$ to the rapid exchange of boron and hydrogen atoms in $Be(B_3H_8)(C_5H_5)$ and $M^+[B_3H_8]^-$ salts (*63, 77–78*). A rigid system involving bidentate ligation of the B_3H_8 group, with the adoption of a B_4H_{10}-like structure, gives a distinctive ^{11}B NMR spectrum featuring two resonances with intensities in the ratio 2:1 and that exhibit characteristic chemical shifts. On the other hand, coupling patterns frequently belie the simplicity of their appearance, being invariably subject to second-order effects. Another potential source of confusion comes from relaxation phemomena. This problem is exemplified by the effects of cooling a metal tetrahydroborate sample, resulting typically in the collapse of the multiplet structures of the ^1H and ^{11}B resonances. Such a change reflects the decrease in the spin-lattice relaxation time T_1 brought about by the increased viscosity of the sample at low temperatures; the accelerated interconversion between nuclear spin states can lead ultimately to decoupling of the ^1H and ^{11}B nuclei, a phenomenon referred to as "thermal" or "correlation-time" decoupling (*71*).

3. *Electron Diffraction*

Electron diffraction needs no introduction as a relatively simple and direct tool for determining the interatomic distances within a molecule in the vapor state, in which it is free from the constraints and perturbations of the condensed phases (*79, 80*). In an ideal situation, the method is capable of defining quite precisely the positions of hydrogen atoms because the electron scattering, unlike X-ray scattering, originates from close to the nuclei and the intensity is determined by the *product* of scattering factors for the components of a given atom pair. There is scope to determine the structures of quite complicated molecules, always provided that the inherent shortcomings of the method are recognized.

One problem arises from the low resolution of electron-diffraction measurements. The experimental results, after various preliminary manipulations, can be presented as a plot of scattering intensity against scattering angle, which contains one-dimensional information only. Fourier transformation of the complex wave form gives, as in Fig. 3, a radial distribution curve that contains one peak for each distance in the molecule. If two or more of these distances are similar, the corresponding peaks will overlap and it may be impossible to resolve them. In these circumstances the geometric and vibrational parameters used to specify the molecular model tend to act in concert or to be subject to correlation, and, unless one or more of the parameters can be constrained on the basis of additional, independent information, there must be a degree of uncertainty about the structure analysis. The problem is clearly exacerbated for a relatively weakly scattering atom pair (like Ga–H), which has a separation more or less coincident with that of a more strongly scattering pair (like Ga–N), to the detriment of the accuracy with which the separation of the first pair can be determined. Sometimes, too, the scattering pattern may fail to distinguish clearly between different model structures for a particular compound. This has proved to be the case, for example, with gaseous $Be(BH_4)_2$, the nature of which has still to be resolved (*79, 80*). The fortunes of $Be(BH_4)_2$ illustrate *inter alia* the potential mischief that impurities may cause, particularly if the impurity molecules carry interatomic distances similar to those in the sample molecule. Understandably, therefore, it is imperative that pure samples be used and that steps be taken to prevent decomposition or contamination of the sample en route to the diffraction chamber.

Another problem arises from the fact that each distance determined by electron diffraction is averaged over the vibrations of the molecule. The effect is most acute for a molecule undergoing one or more vibrations of large amplitude, as with the bending vibration of linear Cl–Hg–Cl or the out-of-plane puckering vibration of the central four-membered ring of $Cl_2Ga(\mu\text{-}Cl)_2GaCl_2$; certain nonbonded distances then appear on average to be appreciably shorter than expected. Unless a correction is made for the so-called "shrinkage" effect (ideally through calculations requiring a detailed knowledge of the vibrational proper-

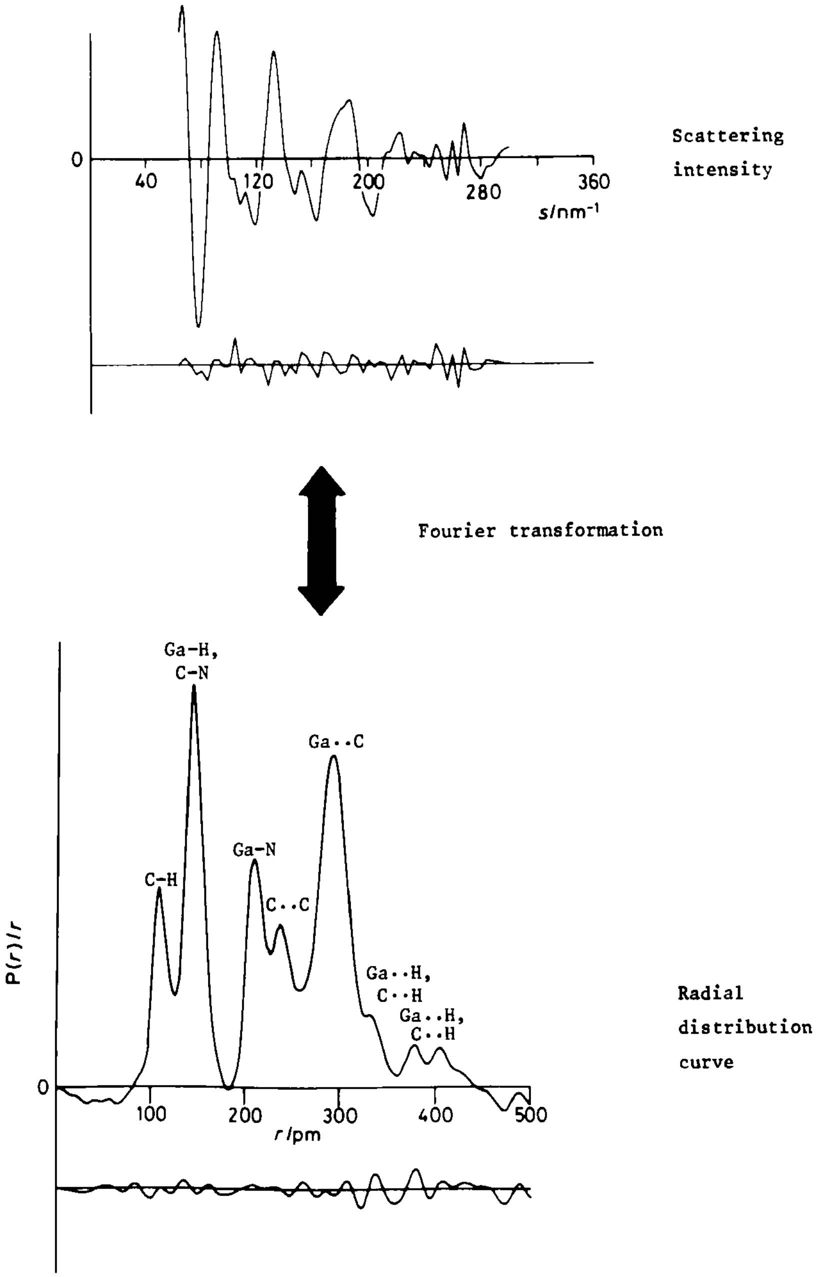


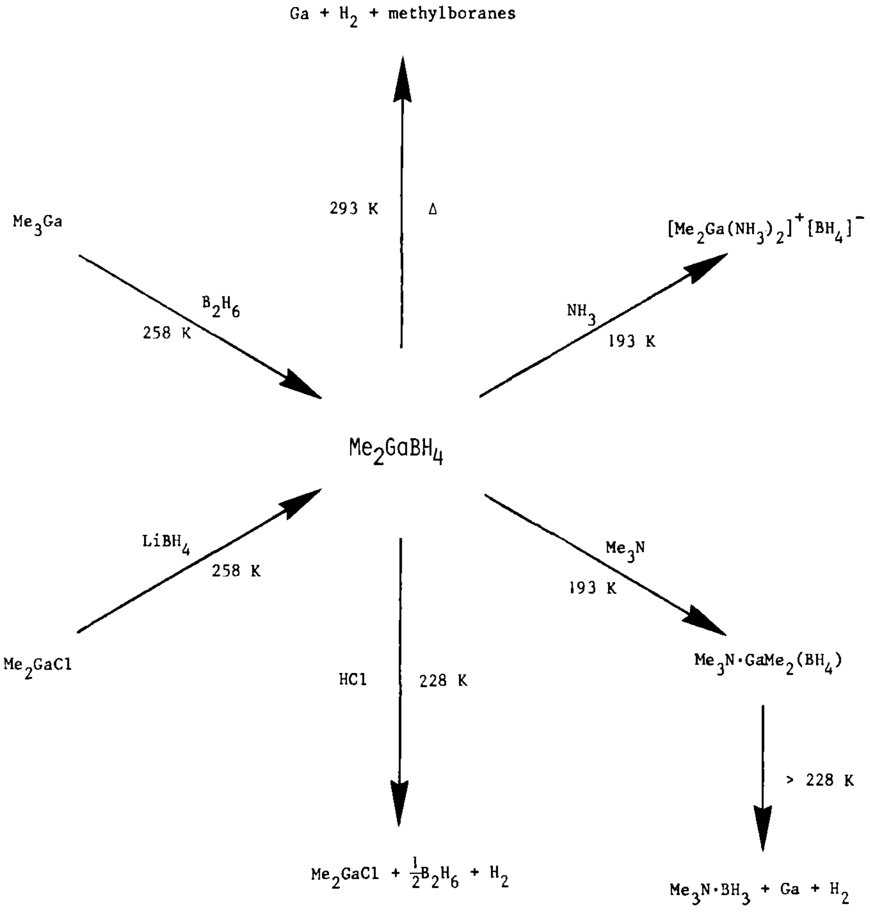
FIG. 3. The molecular scattering intensity pattern for the $Me_3N{\cdot}GaH_3$ molecule related by Fourier transformation to the corresponding radial distribution curve. The difference between the observed and calculated radial distribution curves is also shown (adapted from Ref. *51*).

ties of the molecule), the analysis may give one to believe that a linear molecule is bent or that a planar one is nonplanar. Shrinkage need not be a problem with a molecule whose vibrational properties are well characterized or when there is independent evidence from some other source affording a realistic estimate of the magnitude of the effect. Otherwise, though, there is no escaping the uncertainty implicit in the vibrational-averaging of interatomic distances.

IV. Toward Gallane: Preparations for the Hunt

A. DIMETHYLGALLIUM TETRAHYDROBORATE

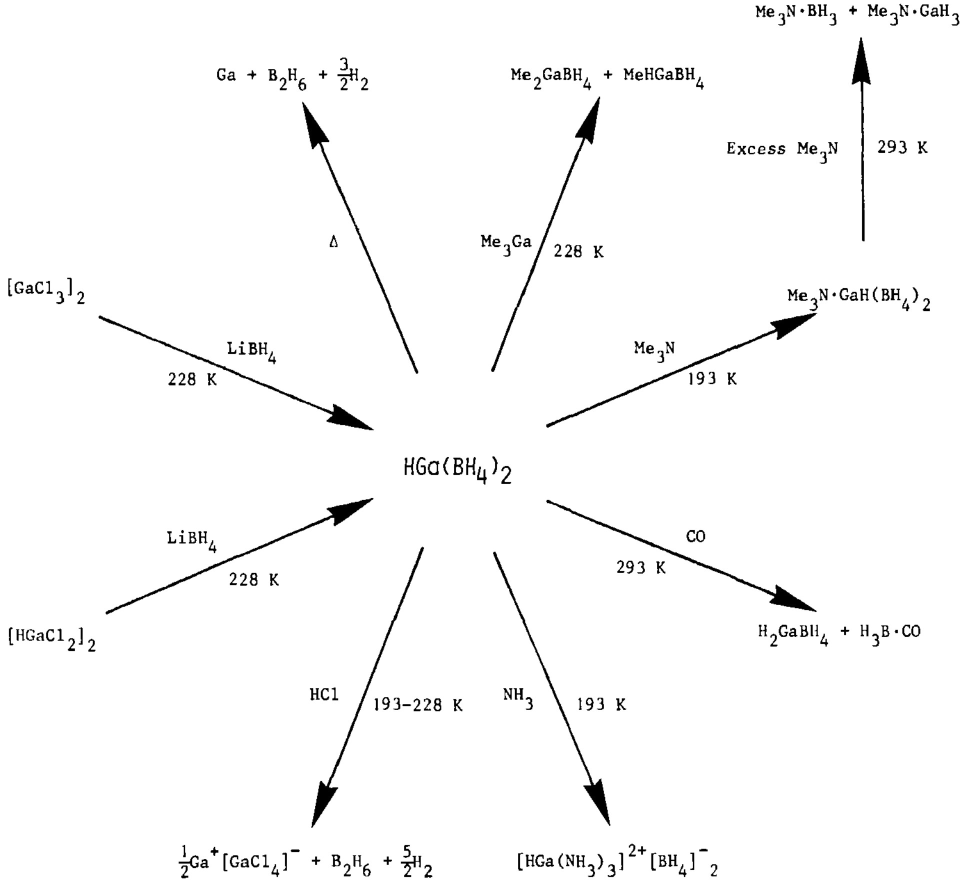
One of the first compounds containing a Ga–H bond to receive detailed attention was the mixed gallium boron hydride Me_2GaBH_4. First reported in 1943 as the product of the interaction of Me_3Ga with B_2H_6 (*81*), the compound is more satisfactorily prepared by the reaction of Me_2GaCl with freshly recrystallized lithium tetrahydroborate in the absence of a solvent at 258 K (see Scheme 2) (*82*). The preferred method is significant in pointing the way to what has generally proved to be the most productive and dependable strategy for the synthesis of hydrides of the heavier Group 13 elements. Avoidance of a solvent is dictated by the need to minimize the risks of contamination of the free hydride. Nevertheless, a relatively efficient reaction can be engineered, with yields depending chiefly on the precise state and purity of the solid reagents. A similar approach has been adopted previously for making volatile tetrahydroborates of other metals, e.g., $Al(BH_4)_3$ (*83*) and $Zr(BH_4)_4$ (*84*). Dimethylgallium tetrahydroborate melts at ca. 274 K and has a vapor pressure of 13–14 mm Hg at 273 K. It decomposes at ambient temperatures; at a pressure of 10 mm Hg the vapor has a half-life in the order of 3 hr, decomposing to give elemental gallium and hydrogen together with a mixture of methylated boranes. The vapor is composed of the diborane-like molecules $Me_2Ga(\mu\text{-}H)_2BH_2$, in which fourfold coordination of the gallium is completed by bidentate ligation of the BH_4 group (*82, 85*). The resemblance to diborane is underlined by the response to nitrogen bases. Thus, ammonia induces heterolytic cleavage of the $Me_2Ga(\mu\text{-}H)_2BH_2$ skeleton with the formation of the salt-like product $[Me_2Ga(NH_3)_2]^+BH_4^-$. By contrast, trimethylamine forms a molecular adduct $Me_3N{\cdot}GaMe_2(BH_4)$ at low temperatures and this appears to undergo homolytic cleavage at temperatures above 228 K to give $Me_3N{\cdot}BH_3$ with gallium metal and dihydrogen, as well as traces of an unstable intermediate containing Ga–H bonds.



SCHEME 2. Formation and some reactions of dimethylgallium tetrahydroborate, Me_2GaBH_4 (*82*).

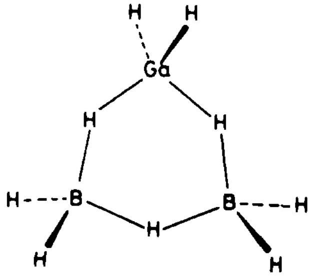
B. HYDRIDOGALLIUM *bis*(TETRAHYDROBORATE)

The reaction with Me_2GaCl suggests that lithium tetrahydroborate should also undergo metathesis with gallium(III) chloride, as it does with aluminium(III) chloride (*83*), to give the *tris*(tetrahydroborate) derivative of the Group 13 metal. In fact, it was found in 1976 that the powdered solids react at ca. 228 K to afford *not* $Ga(BH_4)_3$ but the *hydrido*gallium compound $HGa(BH_4)_2$ (*48*); the same product is formed when dichlorogallane, $[HGaCl_2]_2$ (*41, 42*), is substituted for the trichloride (Scheme 3). Hydridogallium *bis*(tetrahydroborate) melts at about



SCHEME 3. Preparation and some reactions of hydridogallium *bis*(tetrahydroborate), $HGa(BH_4)_2$ *(48–50)*.

200 K to give a colorless, relatively mobile liquid that has a vapor pressure of ca. 10 mm Hg at 228 K. It decomposes to gallium metal, dihydrogen, and B_2H_6 at room temperature [see Eq. (11)]; at a pressure of ca. 10 mm Hg the vapor has a half-life on the order of 10 min. The compound is a rare example of an M_3H_9 species involving one or more Group 13 elements, M, and for which theoretical studies predict a cyclic structure (**3**) with the three M atoms linked in pairs through single hydrogen bridges (*86*). On the evidence of the density, mass and vibrational spectra, and electron-diffraction pattern, however, the vapor consists of molecules in the form not of **3** but of $HGa[(\mu\text{-}H)_2BH_2]_2$, with a single terminal Ga–H bond and two bidentate BH_4 groups making



(3)

up a five-coordinated gallium center (see Fig. 4 and Table I) (*48–50*). On the other hand, the physical properties of the compound imply that the monomer is subject to loose aggregation in the condensed phases; in particular, the ^{1}H and ^{11}B NMR spectra of $C_6D_5CD_3$ solutions at temperatures in the range 190–270 K suggest that the monomer and an oligomer $[HGa(BH_4)_2]_n$ (where $n = 2$ in all probability) coexist in equilibrium. Noteworthy chemical features revealed in Scheme 3 include the behaviors of bases as varied as CO, NMe_3, and NH_3, which bring about homolytic or heterolytic fission of the $Ga(\mu\text{-}H)_2BH_2$ fragments. The reaction with CO provides a link with the thermally less

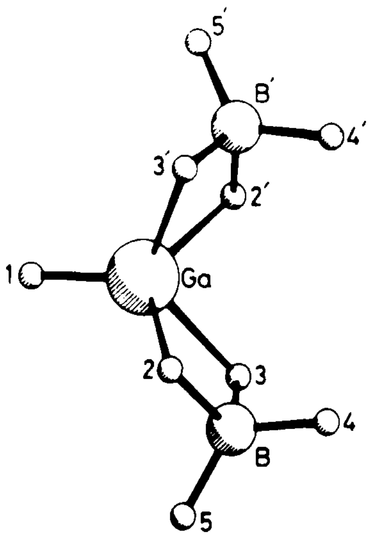
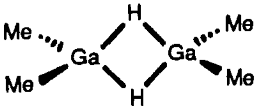


FIG. 4. Structure of the gaseous molecule $HGa(BH_4)_2$ as determined by electron diffraction. H atoms are numbered 1, 2, 2′, 3, 3′, 4, 4′, 5, and 5′ (*48–50*).

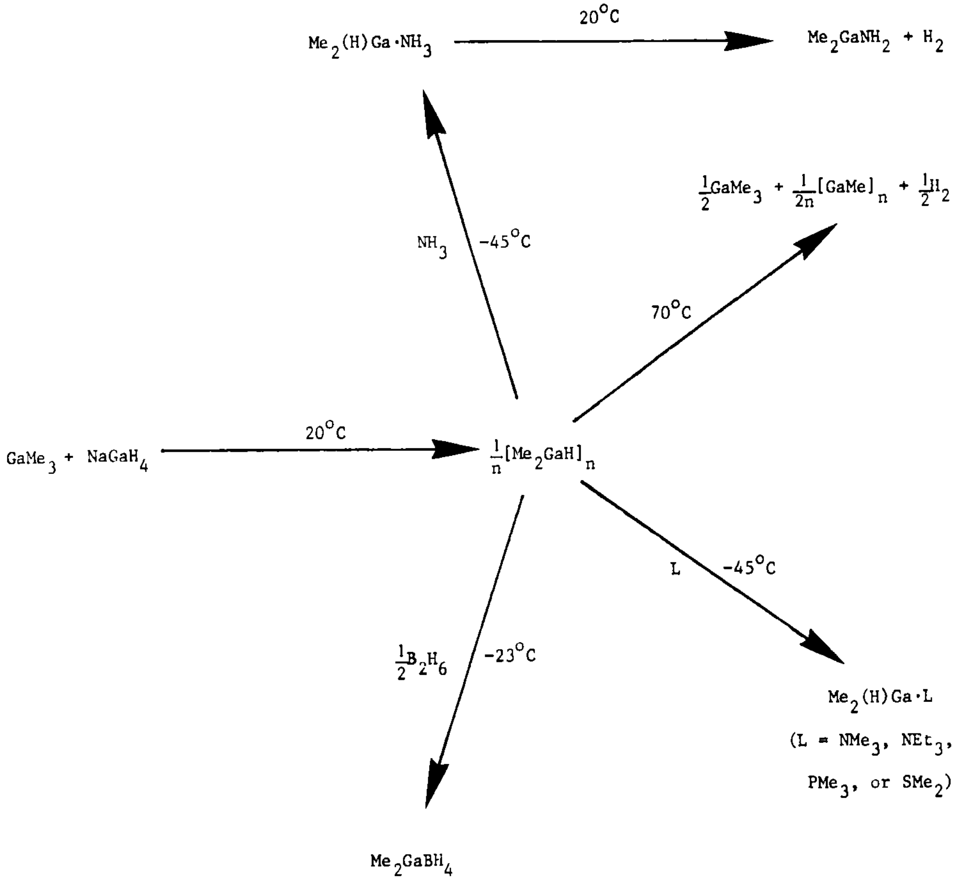
stable gallaborane, H_2GaBH_4, whose detailed characterization postdates that of $HGa(BH_4)_2$ by some 14 years (see Section VI.A). Of $Ga(BH_4)_3$, however, there is still no vestige, even at low temperatures. These findings appear to emphasize the comparative reluctance of gallium, compared with aluminium, to rise to coordination numbers greater than four (*10*).

C. DIMETHYLGALLANE

After earlier sightings of what was probably the impure compound, dimethylgallane, $[Me_2GaH]_n$, was prepared relatively efficiently in 1984–1986 by way of the exchange reaction between trimethylgallium and freshly prepared lithium or sodium tetrahydrogallate (Scheme 4) (*47*). Careful fractionation *in vacuo* gives a viscous liquid (m.p., ca. 273 K; v.p. at 293 K, ca. 1 mm Hg) that decomposes in a matter of days at room temperature. The compound resembles physically the product reported some 40 years previously (*27–30*) as having been isolated from the discharge reaction between Me_3Ga and H_2 [Eq. (3)]. It resembles too the corresponding aluminium compound, $[Me_2AlH]_n$, which exists in the vapor and solution phases as a mixture of oligomers with $n = 2$ and, probably, 4 (*35, 69, 87–89*). On the evidence of its mass and infrared spectra and electron-diffraction pattern (*47*), the vapor of dimethylgallane at low pressures and near-ambient temperatures consists predominantly of the dimeric molecule (4) (see Fig. 3 and Table I). This represented, therefore, the first gallium hydride to be shown positively to contain a $Ga(\mu\text{-}H)_2Ga$ bridging unit in a structure closely resembling that of the corresponding alane, $[Me_2AlH]_2$ (*87–89*). At 261.0 pm, the Ga···Ga separation is comparable with the shorter Ga···Ga distances (247–307 pm) displayed by elemental gallium in its different guises (*10*), and the Ga–H bond, measuring 170.8 pm, is notable for being about 20 pm longer than the terminal Ga–H bonds of molecules like $Me_3N{\cdot}GaH_3$ (*51*) and $HGa(BH_4)_2$ (*49, 50*). The infrared spectrum of the vapor includes, in addition to the bands associated with internal motions of the Me_2Ga groups, two conspicuous features at 1290 and 1185 cm^{-1}, which shift to 971 and 893 cm^{-1}, respectively, when the hydrogen bound to gallium is replaced by deuterium. These must repre-

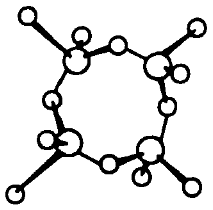


(4)



SCHEME 4. Preparation and some reactions of dimethylgallane, $[Me_2GaH]_n$ (reproduced with permission from Ref. *47*).

sent to a fair approximation the antisymmetric (**1a**; ν_{as}, 1290/971 cm^{-1}) and symmetric (**1b**; ν_s, 1185/893 cm^{-1}) stretching vibrations of the central $Ga(\mu\text{-}H/D)_2Ga$ moiety of **4**. The Ga–H–Ga bond angle, θ, is estimated on the basis of Eq. (12) to be ca. 95°; the electron-diffraction measurements imply a value of 99.6° ± 1.4°. Condensation of the dimethylgallane at low temperatures gives a solid with a significantly different pattern of infrared absorptions attributable to ν_{as} and ν_s; ν_{as} now gives rise to an intense, broad band centered near 1700/1250 cm^{-1} and ν_s to a much weaker feature near 965/850 cm^{-1}. The obvious inference is that the degree of aggregation has increased on condensation with the formation, possibly, of a trimer akin to **3** or, more likely, the

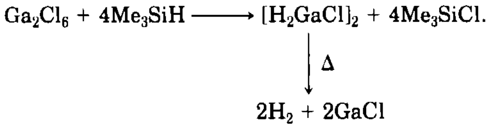


(5)

tetramer (**5**) akin to $[Me_2AlH]_4$ (*89*). In either case the Ga–H–Ga bridge angle has opened out to at least 120°. As we shall see shortly, dimethylgallane foreshadows in its structural and spectroscopic properties the most distinctive features of gallane itself, $[GaH_3]_n$.

D. MONOCHLOROGALLANE

The next step involves not so much a logical progression as a stroke of luck. We have noted already that dichlorogallane, $[HGaCl_2]_2$, is produced by metathesis between gallium(III) chloride and trimethylsilane, in accordance with Eq. (6) (*41, 42*). In an experiment designed to prepare dichlorogallane by this route, an excess of trimethylsilane was inadvertently taken. Exchange between the neat reagents took place, as expected, at 250–258 K, but fractional condensation of the volatile products *in vacuo* gave not a white solid, which dichlorogallane is known to be (*41, 42*), but a viscous, colorless liquid freezing at ca. 183 K and with a vapor pressure at ambient temperatures on the order of 0.5 mm Hg (*36, 39, 40*). The compound was found to decompose over a period of days at room temperature with the quantitative formation of equimolar proportions of H_2 and an involatile white solid having the composition GaCl. Hence exchange with an excess of the silane has given rise to *mono*chlorogallane, which, on the evidence of its infrared and Raman spectra, exists as the dimer $[H_2GaCl]_2$ in both the condensed and vapor phases:



$$\begin{tikzcd} Ga_2Cl_6 + 4Me_3SiH \arrow[r] & {[H_2GaCl]_2 + 4Me_3SiCl.} \arrow[d, "\Delta"] \\ & 2H_2 + 2GaCl \end{tikzcd} \tag{14}$$

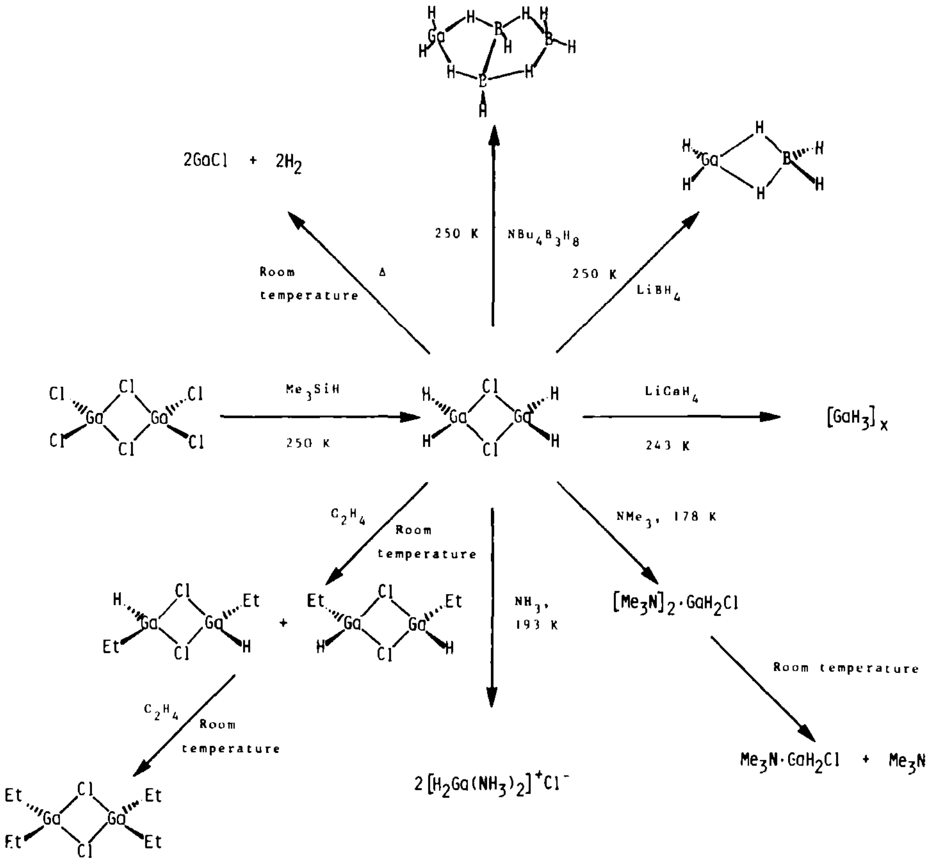
The electron-diffraction pattern of the vapor can be satisfactorily interpreted, like the vibrational properties, on the basis of a molecule $H_2Ga(\mu\text{-}Cl)_2GaH_2$ with D_{2h} symmetry, as illustrated in Fig. 3. Here the Ga–H distance is back to the 150-pm mark that typifies terminal Ga–H bonds and the central Ga(μ-Cl)$_2$Ga unit is comparable in its dimensions to those in [Me_2GaCl]$_2$ (*47*) and Ga_2Cl_6 (*90*). Quantum mechanical methods confirm that chlorine-bridging takes precedence over hydrogen-bridging and predict dimensions and vibrational properties in keeping with the experimental findings (*91, 92*).

More recently the monomeric molecules $HGaCl_2$ (*93*) and H_2GaCl (*94*) have both been prepared by quite a different approach. This involves the photolytically induced addition of HCl or H_2 to molecular GaCl isolated in an argon matrix:

$$\mathrm{GaCl} + \mathrm{HX} \xrightarrow[\text{Ar matrix}]{h\nu} \mathrm{HXGaCl} \quad (\mathrm{X} = \mathrm{Cl\ or\ H}). \tag{15}$$

Identification rests firmly on the infrared spectra of the natural and deuteriated molecules, the results being borne out by *ab initio* calculations. Whether this method would lend itself to the synthesis of monochlorogallane on the larger scale remains to be seen.

With the unearthing of monochlorogallane good fortune has delivered into the stalkers' hands the most important agent yet in the pursuit of hydrogen-rich gallanes. Scheme 5 illustrates some of its more important reactions (*36, 37, 39, 40*). Its decomposition is intriguing in offering a low-temperature route to what appears to be metastable gallium(I) chloride (*10*). Independent studies have shown that GaCl, maintained in a mixed toluene/diethyl ether solvent at subambient temperatures, can be used as a source of other gallium(I) compounds, e.g., C_5H_5Ga (*95, 96*), and the decomposition of a monosubstituted gallane opens up further synthetic possibilities. Predictably bases cleave the Ga(μ-Cl)$_2$Ga skeleton of monochlorogallane. For example, trimethylamine forms the 2 : 1 adduct $(Me_3N)_2GaH_2Cl$ at low temperatures; this dissociates at room temperature to the 1 : 1 adduct $Me_3N{\cdot}GaH_2Cl$ (*38*) and free NMe_3. Ammonia, by contrast, brings about heterolytic cleavage with the generation of the salt-like product $[H_2Ga(NH_3)_2]^+Cl^-$. The ability of Ga–H bonds to add to the double bonds of alkenes has also been shown to extend from dichlorogallane (*41, 42*) to monochlorogallane, ethene reacting in stages to give first *cis*- and *trans*-[EtHGaCl]$_2$ and then [Et_2GaCl]$_2$. Most compelling of all, though, is the role of monochlorogallane as a precursor to other derivatives of the type $[H_2GaX]_n$, typically through the interaction with a salt of the X^- anion under solvent-free conditions. From this point the hunt for gallane itself is truly entered.



SCHEME 5. Preparation and reactions of $[H_2GaCl]_2$ (reproduced with permission from Ref. *10*).

V. Gallane at Last!

A. PRELIMINARIES

Earlier attempts to prepare gallane in the Oxford laboratory (*35, 36*) compassed a variety of potential routes, viz., (a) displacement reactions involving an adduct of GaH_3, e.g., $Me_3N{\cdot}GaH_3$ or $MGaH_4$ (M = Li or Na), and an acid, e.g., BF_3 or HCl; (b) gas-phase pyrolysis or matrix photolysis of an adduct of GaH_3; and (c) the interaction of a tetrahydrogallate $MGaH_4$ with a gallium compound, e.g., Ga_2Cl_6. The only one of these to give any encouragement was the interaction of gallium(III) chloride with a tetrahydrogallate, the solid mixture yielding under solvent-free conditions at ambient temperatures small amounts (in the order of 1–2 mg or less) of a volatile, thermally unstable product, in addition to substantial quantities of elemental gallium and hydrogen. The condensate formed by quenching the vapor of the product on a CsI window held at 77 K was typically characterized by the infrared spectrum reproduced in Fig. 5, with three main absorptions at 1978 (s), 1705 (s,br), and 550 cm^{-1} (s,vbr) (*97*). The spectrum differs significantly from the one reported by Greenwood and Wallbridge (*33*) for the product they identified as free gallane for it includes a prominent, broad absorption near 1700 cm^{-1}, as well as the much sharper feature near 1980 cm^{-1}. The vibrational properties of known gallium hydrides, as outlined in earlier sections, prompt the bands at 1978 and 1705 cm^{-1} most plausibly to be identified with $\nu(Ga{-}H_t)$ and $\nu(Ga{-}H_b{-}Ga)$ fundamentals, respectively, in an aggregate with a comparatively wide $Ga{-}H_b{-}Ga$ bridge angle [cf. $[Me_2GaH]_n$ (*47*). Irrespective of the conditions of the experiment, however, it proved impossible to isolate a product that was entirely free from chloride. Thus, chemical analysis showed the proportion Ga : Cl to be typically 5 : 1, and the ^1H NMR spectrum of $C_6D_5CD_3$ solutions at low temperatures confirmed that

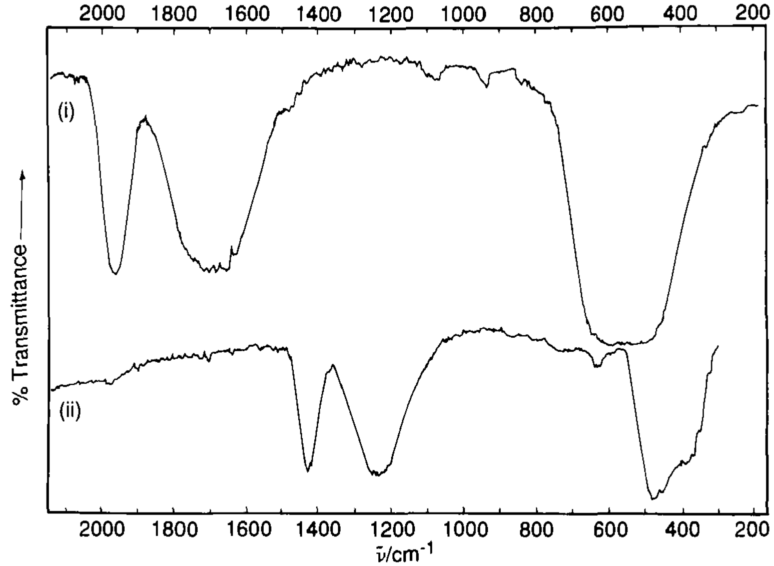


FIG. 5. The IR spectrum of the annealed solid film formed by condensing the volatile products of the reaction between solid gallium(III) chloride and (i) $NaGaH_4$ or (ii) $NaGaD_4$ on a CsI window held at 77 K (reproduced with permission from Ref. *56*; copyright 1991, American Chemical Society).

the product contained more than one gallium hydride derivative. It appears, therefore, that a hydride-rich product including species like $[GaH_3]_n$ is formed through the interaction of neat gallium(III) chloride and a tetrahydrogallate, but only in very low yields (<1%) and with little prospect for the isolation of pure gallane.

Altogether superior to gallium(III) chloride as a precursor to gallane, however, is the newly discovered monochlorogallane, $[H_2GaCl]_2$. Not only has hydride/chloride exchange already gone two-thirds of the way to completion, but monochlorogallane is also a liquid even at quite low temperatures and therefore susceptible to more efficient mixing with a hydride ion source like $LiGaH_4$.

B. SYNTHESIS AND CHARACTERIZATION

1. *Synthesis*

Monochlorogallane has indeed been the turning point in the hunt for gallane and its derivatives. For it reacts *in vacuo* with lithium tetrahydrogallate at 243–250 K to give not only substantial quantities of elemental gallium and hydrogen but also gallane in yields up to 50%, based on Eq. (15) (*37, 56, 61*):

$$\frac{1}{2}[H_2GaCl]_2 + LiGaH_4 \xrightarrow{243\text{–}250\ K} \frac{1}{n}[GaH_3]_n + LiGaH_3Cl. \qquad (15)$$

The identity of the volatile, thermally perishable product has been established unequivocally by chemical analysis, by its vibrational and ^{1}H NMR spectra, and by chemical trapping with trimethylamine to give the known molecular adduct $(Me_3N)_2GaH_3$ as the sole product at 178 K. The reaction affording gallane is carried out between freshly prepared reagents under solvent-free conditions. The choice of hydride ion source is dictated by its activity and by the need, at least in the first place, to avoid the formation of mixed hydride derivatives. Thus, lithium tetrahydroaluminate is less efficient in this role than the tetrahydrogallate, and lithium tetrahydroborate gives high yields of gallaborane, $[GaBH_6]_n$ (see Section VI.A) (*37, 65*). The volatile products of the reaction are removed under continuous pumping and essentially pure gallane can be isolated by fractional condensation. Here it is imperative that operations be carried out at pressures less than 10^{-4} mm Hg in preconditioned all-glass apparatus of the sort described previously (see Section III.A.1). In addition, the thermal frailty of gallane requires that all apparatus to which it has access must be maintained at temperatures less than 263 K; without such cooling the fate of the gallane is signaled by the formation of gray deposits of elemental gallium on the walls of the apparatus.

Efforts to improve the yield of gallane by using a solvent to give better control over the metathesis reaction have so far met with only limited success. The choice of medium is obviously restricted by the need to minimize both the basic properties and the susceptibility to reduction of the would-be solvent. Thus, the mildly basic properties characterizing an ether, say, may enhance its ability to dissolve the reagents, but only at the expense of producing a sample of the gallane that can be freed from the solvent, if at all, only with difficulty. On the other hand, such a solution may be perfectly suitable if the gallane is needed merely as a synthetic intermediate or for the growth of gallium-containing films. Just such an approach has been used with signal success, for example, to open up the synthetic chemistry of AlCl (*98–102*) and GaCl (*95, 96*). Preliminary studies of reaction media show that *n*-octane and methylcyclohexane offer no advantage in the yields of gallane they afford; some improvement may be achieved by the use of toluene, but fractional condensation gives only small quantities of pure gallane, the bulk of the product remaining with the solvent-rich fraction.

2. *Physical Properties and Chemical Analysis*

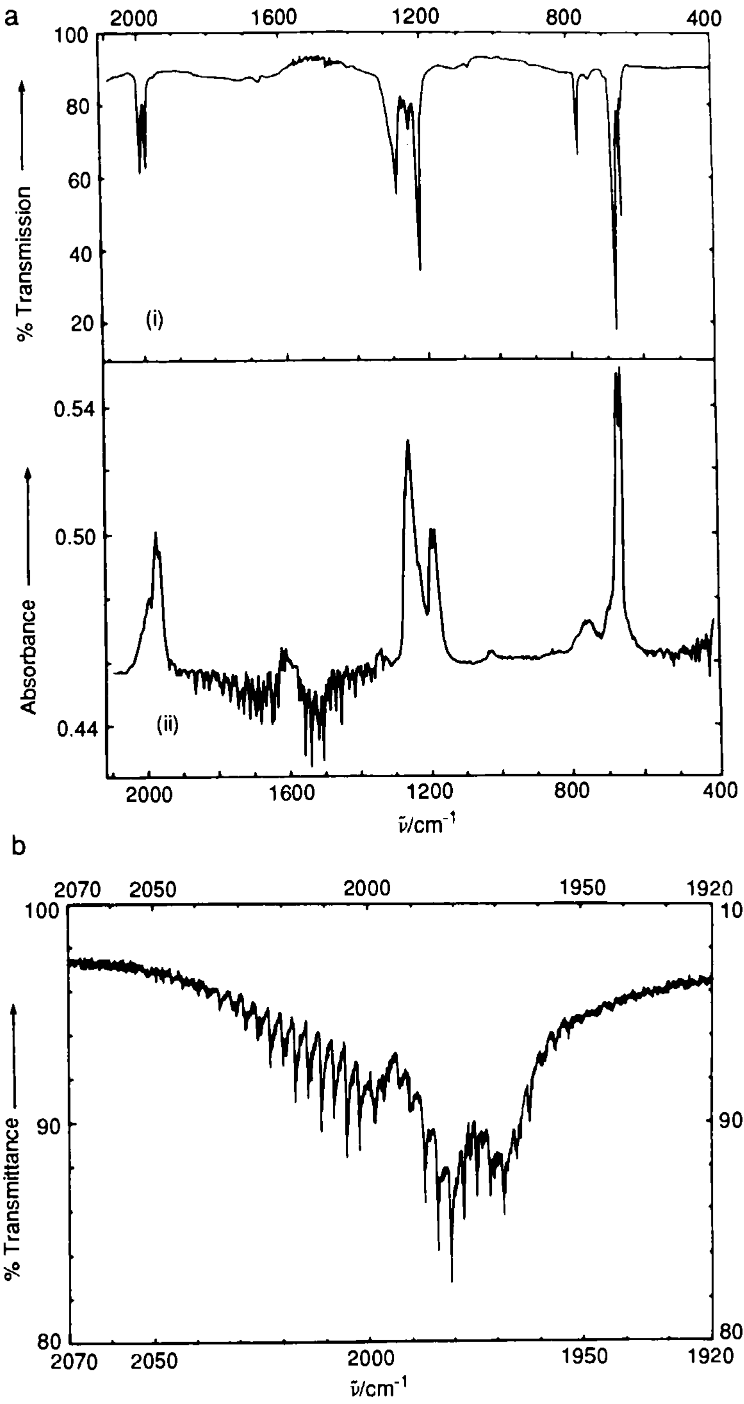
Gallane condenses at low temperatures as a white solid that melts at ca. 223 K to form a colorless, viscous liquid. The rate of vaporization of the solid at 210 K is consistent with a vapor pressure on the order of 1 mm Hg. Samples of the material in the condensed phase (liquid or solution) decompose to the elements at temperatures in excess of 243 K. At a pressure of 10 mm Hg the vapor has a half-life of about 2 min at ambient temperatures.

Decomposition to the elements in accordance with Eq. (16),

$$\frac{1}{n}[\mathrm{GaH_3}]_n \longrightarrow \mathrm{Ga(s)} + \frac{3}{2}\mathrm{H_2(g)}, \tag{16}$$

furnishes a method of chemical analysis for the gallane, albeit one which is rendered less than ideal for small amounts of the material by competition from side reactions with traces of adsorbed moisture or other hydroxylic impurities. A superior method of quantitative assay exploits the reaction with an excess of anhydrous hydrogen chloride at much lower temperatures (178 K):

$$\frac{1}{n}[\mathrm{GaH_3}]_n + 3\mathrm{HCl} \longrightarrow \frac{1}{2}\mathrm{Ga_2Cl_6} + 3\mathrm{H_2}. \tag{17}$$


a
2000
1600
1200
800
400
100
80
60
40
20
% Transmission
(i)
0.54
0.50
0.44
Absorbance
(ii)
2000
1600
1200
800
400
ṽ/cm⁻¹
b
2070
2050
2000
1950
1920
100
90
80
% Transmittance
2070
2050
2000
1950
1920
ṽ/cm⁻¹

Qualitative and quantitative analysis for chlorine confirms, moreover, that the compound can be made free from contamination by chlorogallanes.

3. *Vibrational Spectra*

A film of the annealed solid compound at 77 K displays an infrared spectrum resembling that of the condensate formed by the vapors derived from the reaction of an excess of metal tetrahydrogallate with gallium(III) chloride (see Fig. 4) (*35–37, 56, 61*). Hence it appears that small amounts of impure gallane are indeed generated by chloride–hydride exchange starting from gallium(III) chloride. The three main absorptions at 1978, 1705, and 550 cm^{-1} are observed to shift to 1422, 1200, and 400 cm^{-1}, respectively, for the perdeuteriated compound. The corresponding Raman spectrum of the solid also includes just three significant features, namely, at 1979 (s), 700 (w), and 520 cm^{-1} (w) (*97*), which shift to 1412, 500, and 375 cm^{-1}, respectively, upon deuteriation.

Very different infrared spectra are exhibited by the vapor or by solid matrices formed by codepositing the vapor with an excess of a suitable inert gas at ca. 20 K (see Fig. 6). Here the pattern and energies of the absorptions, and particularly the rotational structure of individual absorptions of the vapor, testify to the presence of a relatively simple molecule with a momental ellipsoid in which at least one of the principal moments of inertia is unusually small for a gallium derivative. Three aspects of the spectra turn out to be critical to the unambiguous identification of the gaseous molecule.

(*i*) The infrared spectrum of gallane vapor includes four distinct absorptions attributable to ν(Ga–H) [or ν(Ga–D)] fundamentals. Of these two occur at high energy—near 1980 (1430) cm^{-1}—in the region diagnostic of the stretching motions of *terminal* Ga–H bonds in a neutral gallium hydride (see Section III.B.1). The other two occur at substantially lower energy, namely, 1180–1300 (840–950) cm^{-1}. So closely does gallane match dimethylgallane (see Section 4.3) in this region of the spectrum that it is hard to resist a similar interpretation, the two absorptions being most plausibly identified with the stretching

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FIG. 6. (a) The IR spectrum of gallane vapor (i) trapped in a solid nitrogen matrix at ca. 20 K and (ii) at a pressure of ca. 5 mm Hg and temperature near 270 K (contained in a cell fitted with CsI windows and having a path length of 10 cm). (b) Part of the IR spectrum of gallane vapor at a pressure of ca. 0.05 mm Hg contained in a multiple-reflection cell set to a path length of 6.5 m and maintained at ca. 290 K (reproduced with permission from Ref. *56*; copyright 1991, American Chemical Society).

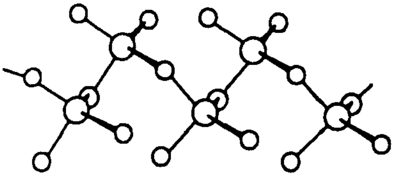
vibrations of one or more Ga–H–Ga bridges. In that case, Eq. (12) leads to an estimate of ca. 93° for the Ga–H–Ga bond angle, θ, in gallane, thereby adducing strong circumstantial evidence that the absorber is in fact Ga_2H_6 with a diborane-like structure (**2**).

(*ii*) Most of the bands in the infrared spectrum of gallane vapor carry unmistakable signs of rotational structure; no better example is provided than that of the two absorptions near 1980 cm^{-1}, the appearance of which, as measured at moderately high resolution with the aid of a multiple reflection cell, is illustrated in Fig. 5. There are, it appears, two types of band. One type, exemplified by the band at 1976 cm^{-1}, displays all the features characteristic of a *parallel* band of a highly prolate symmetric top molecule (see Section III.B.1). The other type has the attributes of a *perpendicular* band of such a molecule (as witness the band at 1993 cm^{-1} in Fig. 5).

Under modest resolution, the parallel-type features assume envelopes with an average P–R branch separation of 10.3 ± 0.5 cm^{-1}. According to Eq. (13), this implies a mean rotational constant $\tilde{B}$ of about 0.066 cm^{-1}; with reasonable allowance for the small contribution made to the $\tilde{B}$ value by the hydrogen atoms, a molecule with the structure of **2** is then estimated to have a Ga···Ga distance on the order of 260 pm. A result so tantalizingly close to the corresponding distance in the dimethylgallane dimer, $Me_2Ga(\mu\text{-}H)_2GaMe_2$ [261 pm as measured by electron diffraction (*47*)] may not be wholly beyond the reach of blind chance, but the odds must be stacked heavily in favor of $H_2Ga(\mu\text{-}H)_2GaH_2$ as the principal component of gallane vapor.

Detailed elucidation of the rotational structure associated with the observed vibrational transitions must await the services of an infrared spectrometer having a resolving power compatible with the $\tilde{B}$ value of the molecule and so with the capacity to resolve the closely spaced rotational lines forming the P- and R-branches of the parallel-type bands. This will inevitably be challenging work, but some idea of the potential rewards may be gained from a preliminary analysis of the Q-branch pattern so conspicuous in the perpendicular-type band at 1993 cm^{-1}. Hence comes an estimate of 1.5095 ± 0.0010 cm^{-1} for $A''\text{–}\tilde{B}''$, the difference between the appropriate rotational constants of the absorber molecule in its vibrational ground state (*37*). Even this morsel of information carries significant weight, as will be evident shortly in relation to what can be learned about the dimensions of the molecule by experiment.

(*iii*) In the pattern and wave numbers of the vibrational transitions observed in infrared absorption, there is no change of consequence when the vapor species are trapped in a solid inert matrix at low temperatures. What is remarkable, however, is that annealing of the matrix (at temperatures no higher than 35 K for an argon matrix) causes the bands associated with the vapor species to decay with the simultaneous appearance and growth of bands akin to those of solid gallane (*q.v.*). Facile aggregation of Ga_2H_6 molecules appears therefore to be the rule in the condensed phases, giving, at least in the first instance, a discrete oligomer; the infrared spectrum argues that this must involve a change in the mode of hydrogen bridging while retaining terminal Ga–H bonds [cf. α-AlH_3 (*13*)]. One possible formulation of the oligomer is the tetramer $[GaH_3]_4$ with a cyclic configuration such as **5**. Such a structure is certainly consistent with the energies and relative intensities of the infrared absorptions associated with the stretching vibrations of bridging Ga–H functions, and which imply that, as with dimethylgallane, the Ga–H–Ga angle, θ, has now opened out to at least 120°. The physical properties of solid gallane—its volatility and solubility in solvents like toluene—favor the belief that it too consists of discrete oligomers like $[GaH_3]_4$, rather than an extended one-dimensional polymer along the lines of **6**.



(**6**)

Although the full interpretation of the vapor spectrum of normal and perdeuteriated gallane is far from straightforard, the main features can be successfully analyzed in terms of the vibrational properties to be expected of the molecules Ga_2H_6 and Ga_2D_6, with the structure (**2**) belonging, like B_2H_6, to the D_{2h} point group. The relevant assignments, given in Table II, rest on six principal criteria: (a) the selection rules expected to govern the activity of vibrational transitions in infrared absorption; (b) the effect of deuteriation on the energy of a given transition (with due appeals to product-rule calculations, etc.); (c) the rotational fine structure modulating individual vibrational bands; (d) analogies with the vibrational properties of related molecules, notably $[H_2GaCl]_2$ (*36, 37, 39, 40, 103*), $[Me_2GaH]_2$ (*47*), $H_2Ga(\mu\text{-}H)_2BH_2$ (*37*), $Me_3N{\cdot}GaH_3$ (*54*), and B_2H_6 (*104*); (e) the harmonic frequencies and infrared intensities calculated for the molecules on the basis of *ab initio* MO techniques (*86, 105–109*); and (f) the results of normal coordinate

TABLE I

DIMENSIONS OF SOME GASEOUS GALLIUM HYDRIDES AS DETERMINED BY ELECTRON DIFFRACTION[a]

Molecule	$r(\mathrm{Ga—H_t})$ (pm)	$r(\mathrm{Ga—H_b})$ (pm)	$r(\mathrm{Ga\cdots X})$ (pm)	Other parameters	Refer
$\mathrm{H_2Ga(\mu\text{-}H)_2GaH_2}$	151.9 (3.5)	171.0 (3.8)	X = Ga, 258.0 (0.2)	$\angle$(Ga—H$_\mathrm{b}$—Ga 97.9 (3.2)°	*37,*
$\mathrm{H_2Ga(\mu\text{-}H)_2BH_2}$	158.6 (0.8)	182.6 (0.8)	X = B, 217.9 (0.2)	r(B—H$_\mathrm{b}$) 133.4 (0.8), r(B—H$_\mathrm{t}$) 123.4 (0.8) pm; $\angle$(H$_\mathrm{b}$—Ga—H$_\mathrm{b}$ 75.3 (1.2)°, $\angle$(H$_\mathrm{b}$—B—H$_\mathrm{b}$ 113.4 (2.7)°	*37,*
$\mathrm{Me_2Ga(\mu\text{-}H)_2BH_2}$	—	179.1 (3.0)	X = B, 216.3 (0.8)	r(Ga—C) 194.4 (0.4), r(B—H$_\mathrm{b}$) 121.7 (1.9), r(B—H$_\mathrm{t}$) 119.2 (1.9) pm; $\angle$(H$_\mathrm{b}$—Ga—H$_\mathrm{b}$ 68.4 (4.6)°	*8*
$\mathrm{H_2Ga(\mu\text{-}Cl)_2GaH_2}$	155.9 (1.9)	—	X = Ga, 324.1 (0.7)	r(Ga—Cl$_\mathrm{b}$) 234.9 (0.3) pm; $\angle$(Cl$_\mathrm{b}$—Ga—Cl$_\mathrm{b}$ 92.8 (0.8)°	*39,*
$\mathrm{Me_2Ga(\mu\text{-}H)_2GaMe_2}$	—	170.8 (1.4)	X = Ga, 261.0 (0.5)	r(Ga—C) 195.4 (0.4) pm; $\angle$(Ga—H$_\mathrm{b}$—Ga 99.6 (1.4)°	*4*
$\mathrm{H_2GaB_3H_8}$	144.2 (1.1)	176.0 (2.8)	X = B, 231.2 (0.1)	r[B(1,3)-B(4)] 185.2 (1.3), r(B—H$_\mathrm{b}$) 126.4 (0.7) pm; dihedral angle 114.4 (0.6)°	*37,*
$\mathrm{H_3Ga{\cdot}NMe_3}$	149.7 (1.5)	—	X = N, 212.4 (0.7)	r(N—C) 148.2 (0.5) pm; $\angle$(Ga—N—C 109.9 (0.5)°	*5*
$\mathrm{[H_2GaNMe_2]_2}$	148.7 (3.6)	—	X = N, 202.7 (0.4)	r(N—C) 146.3 (1.3) pm; $\angle$(Ga—N—Ga 90.6 (0.8)°	*5*

[a] Estimated standard deviations are given in parentheses.

analysis calculations. Most of the fundamentals active in infrared absorption have thus been accounted for; only the b_{1u} deformation mode ν_{14} (dominated by the $\mathrm{GaH_2}$ wagging motion) has not been pinned down as positively as the others, and the b_{2u} ring-puckering mode, expected to occur near 200 cm^{-1}(*105–109*), has so far escaped detection.

4. *Electron Diffraction of the Vapor*

With cooling of the specially constructed inlet system described in Section III.A to temperatures between 253 and 258 K, it has been feasible to record an electron diffraction pattern for gallane vapor (*37, 56*). For reasons that will by now be self-evident, the results are not of the highest quality. Nevertheless, the pattern is wholly consistent with the inferences drawn from the infrared spectrum of the vapor, and its analysis gives access to the first experimentally determined dimensions of the $\mathrm{Ga_2H_6}$ molecule. Figure 7 depicts the experimental radial-distributon curve, which, like that of $\mathrm{B_2H_6}$ (*110*), is distinguished by just two prominent peaks corresponding to scattering from M–H and M···M atom pairs (M = B or Ga). That atom pairs separated by more than 300 pm do not contribute appreciably to the scattering endorses $\mathrm{Ga_2H_6}$ as the predominant vapor species under the prevailing

TABLE II

OBSERVED AND CALCULATED VIBRATIONAL PROPERTIES OF THE Ga_2H_6 AND Ga_2D_6 MOLECULES (*56, 105, 109*)[a]

			Ga_2H_6		Ga_2D_6	
Symmetry class[b]	Number and approximate description of mode[b]		Harmonic vibrational frequency (cm^{-1}) calc.[c,d]	Observed (anharmonic) vibrational frequency (cm^{-1}) in IR absorption[e]	Harmonic vibrational frequency (cm^{-1}) calc.[c]	Observed (anharmonic) vibrational frequency (cm^{-1}) in IR absorption[e]
a_g	ν_1	$\nu(\text{Ga—H}_t)$	2099	ia	1488	ia
	ν_2	$\nu(\text{Ga—H}_b)$	1577	ia	1116	ia
	ν_3	$\delta(\text{H}_t\text{—Ga—H}_t)$	782	ia	558	ia
	ν_4	$\nu(\text{Ga}\cdots\text{Ga})$	241	ia	237	ia
a_u	ν_5	Twist	473	ia	335	ia
b_{2g}	ν_6	$\nu(\text{Ga—H}_b)$	1356	ia	960	ia
	ν_7	$\text{H}_t\text{—Ga—H}_t$ wag	406	ia	297	ia
b_{2u}	ν_8	$\nu(\text{Ga—H}_t)$	2101 (353)	1993 m	1502	1439 m
	ν_9	$\rho(\text{H}_t\text{—Ga—H}_t)$	837 (178)	760 w	598	555 w
	ν_{10}	Ring pucker	225 (7)	no	159	no
b_{1g}	ν_{11}	$\nu(\text{Ga—H}_t)$	2096	ia	1498	ia
	ν_{12}	$\rho(\text{H}_t\text{—Ga—H}_t)$	493	ia	359	ia
b_{1u}	ν_{13}	$\nu(\text{Ga—H}_b)$	1294 (291)	1202 s	924	860 s
	ν_{14}	$\text{H}_t\text{—Ga—H}_t$ wag	682 (165)	ca. 650 m	487	439 mw
b_{3g}	ν_{15}	Twist	808	ia	572	ia
b_{3u}	ν_{16}	$\nu(\text{Ga—H}_t)$	2093 (120)	1976 m	1482	1416 m
	ν_{17}	$\nu(\text{Ga—H}_b)$	1412 (1229)	1273 s	1004	923 s
	ν_{18}	$\delta(\text{H}_t\text{—Ga—H}_t)$	722 (607)	671 vs	518	484 vs

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; ia, inactive in infrared absorption; no, not observed.

[b] Numbering and classification of the modes conform to those given for B_2H_6 and B_2D_6 in Ref. *104*.

[c] Results based on configuration interaction methods with single and double excitations (CISD) with double-zeta plus polarization basis sets (see Refs. *105* and *109*). Computed frequencies are typically some 5% higher than ω_e values determined experimentally, which are in turn larger than observed, anharmonic frequencies, by up to ca. 60 cm^{-1} for vibrations like ν(Ga—H) with large amplitudes. The frequencies have been calculated for the molecules $^{69}Ga_2H_6$ and $^{69}Ga_2D_6$.

[d] Calculated infrared intensities given in parentheses; values in km mol^{-1}.

[e] Frequencies are those for Ga_2H_6 and Ga_2D_6 molecules with gallium of natural isotopic composition.

conditions (pressure, ca. 1 mm Hg; temperature, ca. 256 K); heavier oligomers like $[GaH_3]_4$ (*q.v.*) would surely include Ga···Ga atom pairs with separations exceeding 300 pm. Within the limits of experimental uncertainty, a Ga_2H_6 molecule having the structure of **2** is found satisfactorily to account for the measured scattering. The two independent distances $r(\text{Ga}\cdots\text{Ga})$ and $r(\text{Ga–H})_{\text{mean}}$ are well determined, but correlation between the parameters specifying the bridging and terminal Ga–H distances obviates an exact differentiation between these distances. The $\text{H}_t\text{–Ga–H}_t$ angle, which is specified by the dimensions of the GaGaH_t triangle, is correspondingly ill-determined. Irrespective of the precise basis set adopted, all the *ab initio* calculations reported so

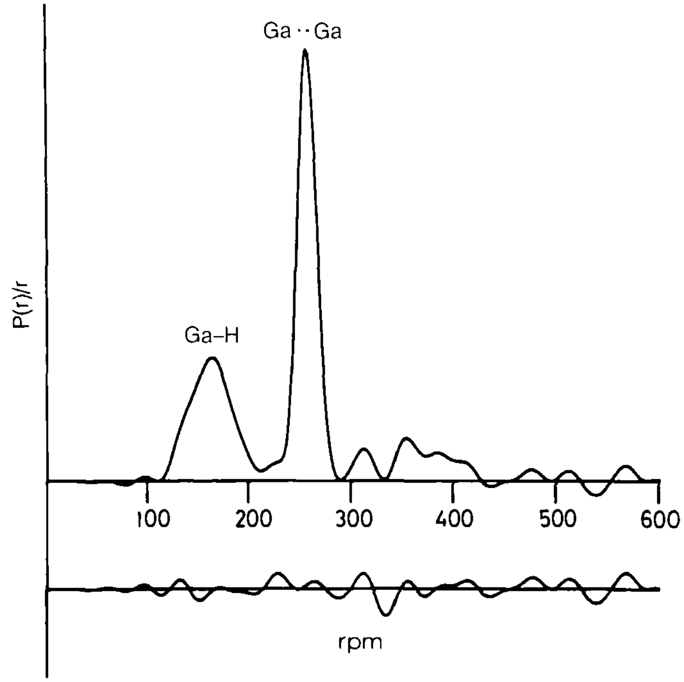


FIG. 7. Observed and difference radial distribution curves, $P(r)/r$ versus r, for digallane vapor; before Fourier transformation the data were multiplied by $s\cdot\exp[(-0.000\,020\,s^2)/(Z_{Ga} - f_{Ga})^2]$ (reproduced with permission from Ref. *56*; copyright 1991, American Chemical Society).

far (*86, 105–109*) seem to converge on a value near 130° for this angle; indeed, according to other theoretical calculations involving the molecules $H_2Ga(\mu\text{-}H)_2BH_2$ (*111, 112*) and $H_2Ga(\mu\text{-}Cl)_2GaH_2$ (*91, 92*), such a value seems to be endemic to the $H_2Ga(\mu\text{-}X)_2$ moiety (X = H or Cl). According to the results of the diffraction study, the mean B-value, $\tilde{B}''$, is ca. 0.0676 ± 0.001 cm^{-1} (pleasingly close to the first rough estimate elicited from the P–R branch separations of the parallel-type infrared bands). The rotational analysis of the infrared-active fundamental ν_8 having already delivered a value of $A''\text{–}\tilde{B}''$, it follows that $A'' = 1.5771 \pm 0.002$ cm^{-1}. Because A'' depends only on the positions of the light hydrogen atoms with respect to the Ga···Ga axis, it provides an independent means of appraising the H_t–Ga–H_t angle. A value near 138° is thus deduced. Uncertainty necessarily persists while we lack a realistic audit of the effects of vibrational averaging (implicit in the electron-diffraction input to this calculation). Such an audit, together with more precise information about the rotational constants of natural and isotopically enriched Ga_2H_6, will be needed before a more complete and exact picture of the molecular structure can be secured. Suffice it to say that the best estimates at present available give dimensions in keeping not only with those of related molecules, e.g., $Me_2Ga(\mu\text{-}H)_2GaMe_2$ (*47*), $H_2Ga(\mu\text{-}Cl)_2GaH_2$ (*37, 39, 40*), and $Me_3N \cdot GaH_3$ (*51*), but also with the predictions of recent theoretical calculations (*105–109*).

5. ^1H NMR Spectrum

The ^1H NMR spectrum of gallane dissolved in $[^2H_8]$toluene at 208 K consists of two singlets at δ 4.41 and 1.11, with relative intensities in the ratio 2 : 1 (see Fig. 8); both show the broad line widths typical of protons directly bound to gallium atoms (*32*). The gallane is relatively volatile under these conditions and so it is tempting to infer the presence of Ga_2H_6 molecules having the structure of **2**. Such an interpretation appears questionable, however, in the light of the ready aggregation of Ga_2H_6 revealed by the matrix experiments. In fact, the spectrum does not differentiate between Ga_2H_6 and any other oligomer, like

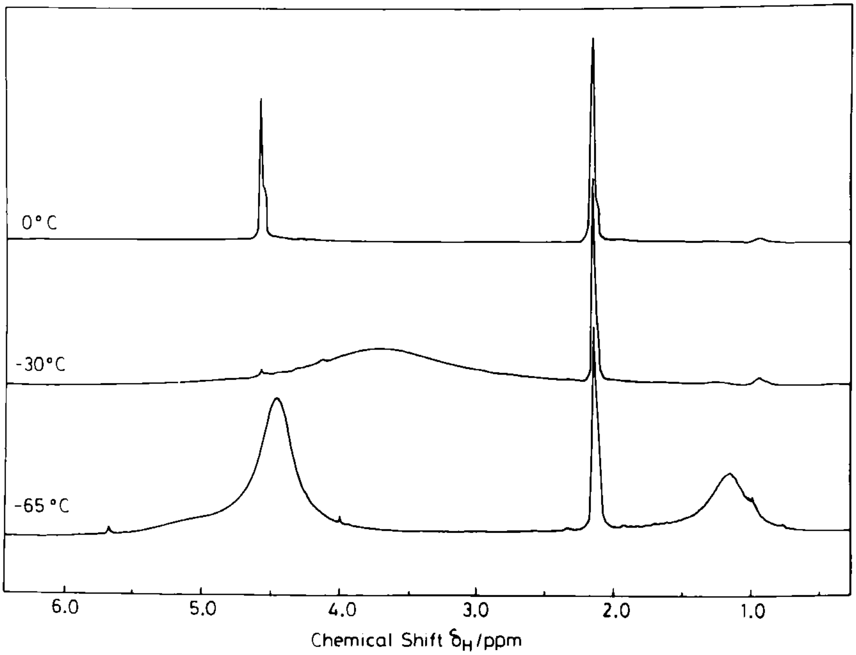


FIG. 8. The ^1H NMR spectrum of a $C_6D_5CD_3$ solution of gallane recorded with the sample held successively at −65, −30, and 0°C. The resonance near δ_H 2.0 is due to residual C_7D_7H in the solvent (reproduced with permission from Ref. *56*; copyright 1991, American Chemical Society).

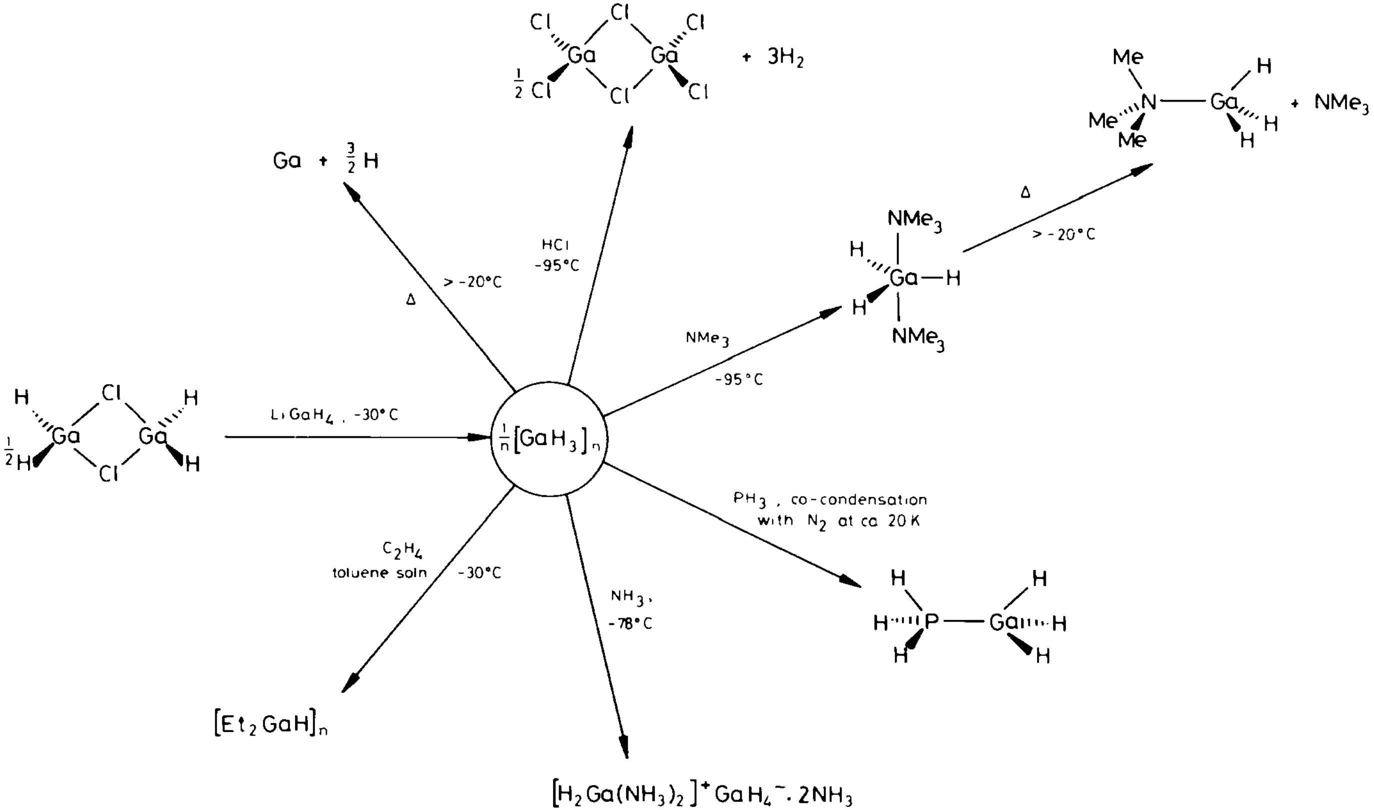
$[GaH_3]_4$, containing terminal and bridging hydrogen atoms in the proportion 2:1. Warming the sample to 243 K results in broadening and coalescence of the two resonances, indicating rapid exchange between bridging and terminal proton sites. The single broad resonance that the sample now displays occurs at δ 3.7, a chemical shift appreciably different from the weighted mean (δ 3.31) of the shifts characterizing the separate resonances observed with the sample at lower temperatures. In all probability, therefore, more than one molecule is implicated in the exchange process. Further warming to 273 K results in rapid decomposition of the sample. Studies of the decomposition have failed as yet to pick up any scent of gallium hydride intermediates formed en route to the ultimate products, namely, elemental gallium and hydrogen. It is possible, however, that polygallane intermediates like Ga_4H_{10} enter into the decomposition [compare, for example, the thermolysis of diborane (*1–8*)] and that they will prove to be amenable to physical or chemical trapping.

C. CHEMICAL PROPERTIES

Some of the chemical properties of gallane have now been charted, with the results summarized in Scheme 6. The reactions appear mostly to parallel those of diborane (*1–8*). Thus, symmetrical cleavage of the Ga_2H_6 moiety occurs, at least formally, with trimethylamine or phosphine to give the corresponding molecular adduct L_nGaH_3 [$L = Me_3N$, $n = 1$ or 2; $L = PH_3$, $n = 1$ (*37, 56, 113*)]. The phosphine derivative $H_3P\cdot GaH_3$ is a frail vessel, even by the standards of gallane chemistry. That it is formed, however, on cocondensation of gallane with an excess of nitrogen doped with phosphine at ca. 20 K is signaled by the infrared spectrum of the resulting matrix (*56, 113*); natural and deuteriated versions of the molecule $H_3P\cdot GaH_3$ have thus been characterized in some detail. By contrast, ammonia causes unsymmetrical cleavage of the Ga–H–Ga bridges of gallane at 178 K, with the formation of a salt-like product most aptly formulated as $[H_2Ga(NH_3)_4]^+[GaH_4]^-$. Stepwise insertion into the Ga–H bonds is the path taken by the reaction with ethene, affording mainly diethylgallane, $[Et_2GaH]_n$.

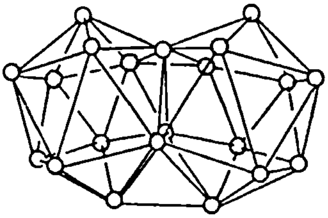
D. SUMMARY

The experiments described in the preceding sections leave little room for doubt that the base-free trihydride of gallium has at last been run to earth. It can be prepared in amounts up to 500 mg. While decomposing to the elements at ambient temperatures, gallane vaporizes at low



SCHEME 6. Preparation and reactions of gallane (reproduced with permission from Ref. *56*; copyright 1991, American Chemical Society).

pressures as the diborane-like molecule $H_2Ga(\mu\text{-}H)_2GaH_2$, the main dimensions of which have been deduced from the electron-diffraction pattern of the vapor. Despite this progress, there is much still to be done. For example, the nature of the compound in the condensed phases has still to be unraveled. Growing a single crystal will be a tall order indeed, but neutron-diffraction studies on crystalline powder samples of the wholly or partially deuteriated gallane at 4.5 K are already in train (*114*). Preliminary analysis of the results suggests a body-centered tetragonal unit cell with $a = 1262.8$ and $c = 499.6$ pm; more detailed analysis may expose the molecular form of the solid to give a definitive explanation of such properties as its volatility and the apparent retention of terminal as well as bridging Ga–H bonds. Extending our chemical knowledge is never going to be easy with a compound so predisposed to decomposition. On the evidence of the reaction with phosphine, however, dissociation of $[GaH_3]_n$ aggregates appears to be no less facile than aggregation, and there is clearly scope for further cocondensation experiments, for example to afford a glimpse of the arsine adduct $H_3As \cdot GaH_3$, the stable existence of which receives support both from the recent matrix isolation of the complex $H_3As \cdot GaMe_3$ (*115*) and from the diagnosis of *ab initio* calculations (*116*). Such a molecule is of more than esoteric interest, as testified by very recent spectroscopic studies of the adsorption of hydrogen atoms on the (1 × 6) reconstruction of GaAs(100) (*117, 118*); unmistakable evidence has thus been found for the formation of gallium hydride species with both terminal and bridging Ga–H functions. Another facet inviting exploration is the possibility of forming open or closed cages in gallium species analogous to $B_{10}H_{14}$ and $B_{12}H_{12}^{2-}$, with the potential for kinetic and thermodynamic stabilization of the Ga–H bonds that may thus be achieved. Gallium clusters are already known in intermetallic compounds (*10*). Typically they are not discrete but interlinked, as with the Ga_{21} unit found in the phase $Rb_{0.6}Na_{6.25}Ga_{20.02}$ (*119*); consisting of a pair of confacially linked Ga_{12} icosahedra, **7** is joined by its vertices to other such units as well as to single Ga_{12} icosahedra. Added encour-



(**7**)

agement to the search for polygallane derivatives comes too from the icosahedral anion $[Al_{12}Bu^{i}_{12}]^{2-}$, which has just seen the light of day as its potassium salt (*120*).

VI. Hydrogen-Rich Derivatives of Gallane

A. INTRODUCTION

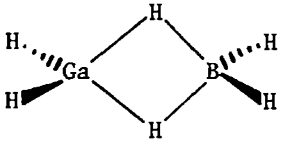
Monochlorogallane has been of crucial importance in the entrée it has given to gallane. It is also the obvious precursor to other monosubstituted gallanes of the type $[H_2GaX]_n$, typically through its interaction with a salt of the X^- anion *in vacuo* and under solvent-free conditions (see Scheme 5). Hence it has been possible to achieve 80–90% conversion of the monochlorogallane to the simple mixed hydride $GaBH_6$ (*37, 65*) or the tetraborane(10) derivative 2-GaB_3H_{10} (*37, 63*). As with the synthesis of gallane, operations need to be carried out in preconditioned, all-glass apparatus along the lines illustrated in Fig. 2a, and the vapors of the volatile product need to be kept at low pressure and exposed to wall temperatures not exceeding 263 or 283 K for $GaBH_6$ or GaB_3H_{10}, respectively. The new compounds have been authenticated by chemical analysis, by their spectroscopic properties, and by electron diffraction of the vapors. In addition, a reconnaissance of their chemistries has been mounted.

B. GALLABORANE, $GaBH_6$ (*37, 65*)

In its synthesis and early characterization, gallaborane has followed closely the precedents set by gallane. Preparation involves the reaction between monochlorogallane and freshly recrystallized lithium tetrahydroborate at 250 K. Fractional condensation *in vacuo* gives a product even more volatile and marginally more robust to thermal decomposition than gallane. The solid condensate registers a vapor pressure on the order of 1 mm Hg at 195 K and melts near 228 K. In the condensed phases gallaborane decomposes at temperatures exceeding 238 K; at a pressure near 100 mm Hg, the vapor enjoys a half-life on the order of 2 min at room temperature. Decomposition results in the quantitative formation of elemental gallium, diborane, and dihydrogen in the stoicheiometric proportions required by Eq. (18) and so provides a means of chemical assay:

$$2GaBH_6(g) \longrightarrow 2Ga(s) + B_2H_6(g) + 3H_2. \tag{18}$$

The infrared spectra of natural and perdeuteriated samples of gallaborane imply the presence of a molecular unit common to the vapor and matrix-isolated states. The results advance strong circumstantial evidence that the molecule is $H_2Ga(\mu\text{-}H)_2BH_2$ (8) with a bidentate BH_4 group and possessing C_{2v} symmetry. This conclusion is strongly endorsed by the well-resolved rotational structure displayed by most of the infrared absorptions of the vapor. For example, as illustrated in Fig. 9, the absorption near 2550 cm^{-1}, associated with a $B\text{–}H_t$ stretching fundamental, clearly shows the P- and R-branches characteristic of a *perpendicular*-type transition of a rotor approximating to a symmetric top. Strongly in evidence are the individual Q-subbranches corresponding to the transitions betwen different K-levels; analysis of these gives a value of 1.7675 ± 0.0010 cm^{-1} for the difference between the rotational constants $A''\text{–}\bar{B}''$ (cf. Section V.B.3). As in the case of digallane, such a large value can be reconciled only with a molecule having a very small moment of inertia about one principal axis, here the $Ga \cdots B$ axis; it therefore implies that only hydrogen atoms lie off this axis. By contrast, the second infrared band originating in a $\nu(B\text{–}H_t)$ fundamental, located near 2480 cm^{-1} (see Fig. 8), displays all the features characteristic of a *parallel*-type transition, the partially resolved rotational structure serving notice of a value of $\bar{B}''$ on the order of 0.25 cm^{-1}. Once again, therefore, we must be dealing with a distinctly prolate symmetric top. In its information relating to the vibrational and rotational properties and dimensions of the $GaBH_6$ molecule, the spectrum will undoubtedly be a happy hunting ground of the future, once the appropriate conditions of resolution can be met. Unlike digallane, the dipolar $GaBH_6$ molecule also invites high-resolution microwave measurements (*79*). By taking account of the rotational structure, the effects of deuteriation, the selection rules expected to govern the activity of vibrational transitions in infrared absorption, and the vibrational properties of related molecules, e.g., $[H_2GaCl]_2$ (*39, 40, 103*), Ga_2H_6 (*37, 56*), B_2H_6 (*104*), and $Me_2Ga(\mu\text{-}H)_2BH_2$ (*82*), it has been possible to identify most of the vibrational fundamentals of the $H_2Ga(\mu\text{-}H)_2BH_2$ molecule. Strong support for the proposed assignment comes from the



(8)

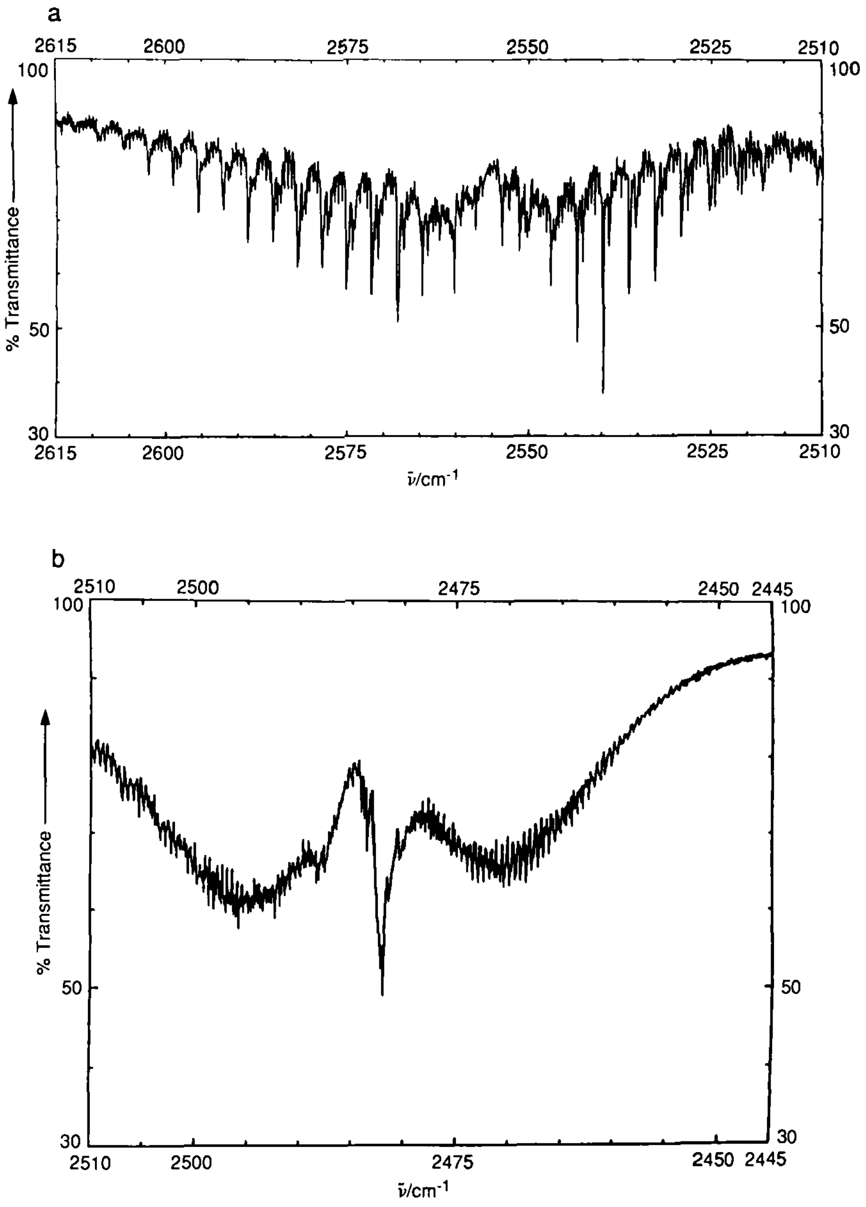


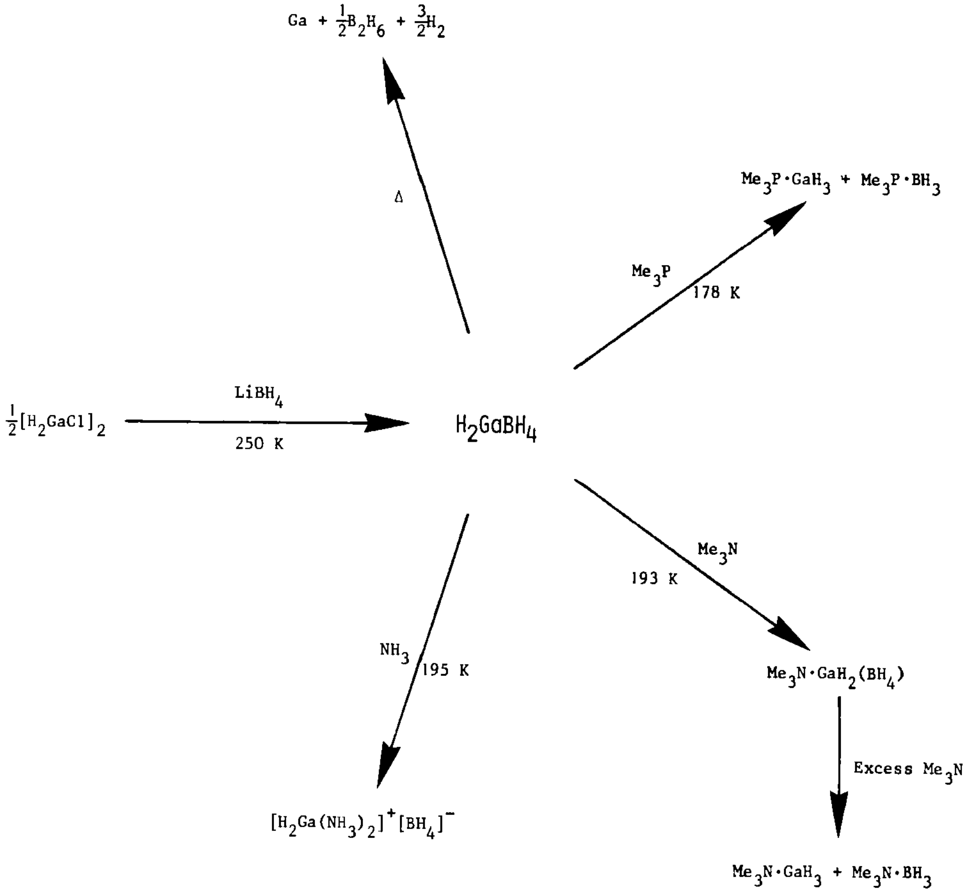
FIG. 9. Portions of the IR spectrum of gallaborane vapor at a pressure of 0.15 mm Hg and maintained at ca. 290 K, showing the two $\nu(B—H_t)$ fundamentals; the vapor is contained in a multiple-reflection cell set to a path length of 3.9 m (*37, 65*).

harmonic frequencies and infrared intensities computed on the basis of *ab initio* procedures (*111, 112*).

Electron-diffraction measurements on the vapor at low pressures (ca. 1 mm Hg) have yet to be completed at more than one camera distance, for technical reasons connected with the reactivity and thermal instability of the compound. According to the preliminary measurements made at a single camera distance, however, the scattering pattern meets all the primary requirements of a simple $GaBH_6$ molecule with the structure of **8**. Neither the infrared spectrum nor the electron-diffraction pattern gives any grounds for believing that any oligomer $[GaBH_6]_n$, with $n = 2, 3$, etc., makes up an appreciable fraction of the vapor. Table I includes the best estimates attainable in present circumstances for the dimensions of the $GaBH_6$ molecule. In that the results come close not only to the corresponding distances and angles in molecules like Ga_2H_6 (*56*), Me_2GaBH_4 (*85*), and $HGa(BH_4)_2$ (*48–50*), but also to the prognoses of detailed quantum mechanical studies (*111, 112*), they are unlikely to be too wide of the mark. There is reassuring substance here to bring to the increasingly lively theoretical speculation excited by this and related discoveries (*86, 91, 92, 105–109, 111, 112*). The Ga–H bond in the central $Ga(\mu\text{-}H)_2B$ bridge is attenuated by some 10 pm compared with its counterpart in the symmetrical $Ga(\mu\text{-}H)_2Ga$ unit of Ga_2H_6; this reflects presumably the greater charge separation between the gallium and hydrogen atoms in the unsymmetrical Ga–H–B bridges, as well as the steric demands imposed by BH_4 as a bidentate ligand with a peculiarly short "bite."

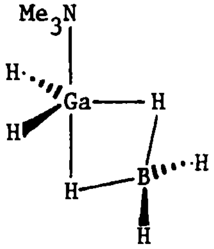
Less clear is the state of gallaborane in the condensed phases, although aggregation appears to be a recurring theme of both the solid and solutions. At temperatures in the range 153–238 K, solutions of the gallane in toluene or methylcyclohexane display (*37, 65*) the ^1H and ^{11}B magnetic resonances characteristic of a "rigid" terminal GaH_2 and a fluxional BH_4 unit (*71*) in a molecule having the empirical formulation H_2GaBH_4. In addition, though, the spectra reveal the coexistence of a second component in dynamic equilibrium with the first. This has ^1H and ^{11}B resonances close to those believed to originate in monomeric H_2GaBH_4, but the $^1H\{^{11}B\}$ spectrum discloses, intriguingly, that, unlike the monomer, it is characterized not by a singlet but by a *doublet* BH_4 resonance with a separation of 8.5 Hz due to spin–spin coupling to a second nucleus. We have still to find a wholly convincing explanation of these findings, but the properties of the second component (including its response to changes of concentration) point to a loosely bound aggregate, possibly a dimer $[H_2GaBH_4]_2$ having a cyclic structure similar to **5** (*89*) with alternating GaH_2 and BH_2 groups linked via single hydrogen bridges. Bidentate coordination of the BH_4 group is retained in solid gallaborane, on the evidence of its infrared and Raman spectra, but as yet there are few other clues to the nature of the solid.

Chemical studies are still only in their infancy, but Scheme 7 summarizes the results of a preliminary survey. Scrutiny of the products of thermal decomposition, engineered under various conditions, has failed so far to spot any clear-cut signs of new gallaborane intermediates, e.g., $Ga_2B_2H_{10}$. Homolytic cleavage of the $Ga(\mu\text{-}H)_2B$ bridge is brought about by the bases Me_3N and Me_3P, which give rise to an equimolar mixture of the adducts $L{\cdot}GaH_3$ and $L{\cdot}BH_3$ ($L = Me_3N$ or Me_3P). At lower temperatures gallaborane and Me_3N appear to unite in a molecu-



SCHEME 7. Synthesis and some reactions of gallaborane (*37*, *65*).

lar adduct, $Me_3N\cdot GaH_2(BH_4)$, in which bidentate ligation of the BH_4 group is preserved, thereby implying a structure such as **9** with fivefold coordination of the gallium center; the infrared spectrum of this product hints at an obvious kinship to another unstable complex, $Me_3N\cdot GaMe_2(BH_4)$ (*121*), as well as the more stable aluminium analogues $Me_3N\cdot AlR_2(BH_4)$ [R = H (*122*) or Me (*121, 123*)]. Ammonia differs from the larger bases Me_3N and Me_3P in promoting heterolytic cleavage of the $GaBH_6$ molecule with the formation of a relatively robust product most aptly formulated as a cationic gallane derivative, $[H_2Ga(NH_3)_2]^+[BH_4]^-$.



(9)

C. 2-GALLA-*ARACHNO*-TETRABORANE(10), 2-GaB_3H_{10} (*37, 63*)

Metathesis with tetra-*n*-butylammonium octahydrotriborate, $[Bu^n{}_4N]^+[B_3H_8]^-$, at temperatures near 243 K converts monochlorogallane into gallatetraborane, GaB_3H_{10}, in yields not far from those implied by

$$\tfrac{1}{2}[H_2GaCl]_2 + [Bu^n{}_4N]^+[B_3H_8]^- \xrightarrow{243-268\text{ K}} GaB_3H_{10} + [Bu^n{}_4N]^+Cl^-. \qquad (19)$$

The product melts at ca. 178 K to give a colorless mobile liquid, the vapor pressure of which reaches 1 mm Hg at temperatures near 210 K. Its thermal stability shows a distinct advance on those of gallane and gallaborane. Although samples of the material in the condensed phase decompose rapidly at temperatures above 283 K, the half-life of the vapor at room temperature and a pressure of ca. 100 mm Hg extends to about 30 min. Handling is also made easier in that the vapor will even survive the passage through a greaseless (Teflon) valve provided that steps are taken to precondition the surfaces of preliminary exposure to a portion of the vapor, which is subsequently pumped to waste. Decomposition of the vapor at ambient temperatures proceeds in accordance with

$$GaB_3H_{10}(g) \longrightarrow GaB_2(s) + \tfrac{1}{2}B_2H_6(g) + \tfrac{7}{2}H_2(g), \qquad (20)$$

and the resulting quantitative assay serves to fix the chemical composition of the gallane. The involatile solid residue answering to the composition GaB_2 may be an authentic example of a rare breed, namely, a gallium boride. The course of decomposition is complicated, however, by the existence of more than one channel. As the local concentration of the gallane increases, for example, with the move to the condensed phases, bimolecular processes compete with the unimolecular one, which is presumed to hold the key to the gas-phase reaction (20). Thus, decomposition of gallatetraborane in toluene solution gives metallic gallium, dihydrogen, and tetraborane(10) as the principal products, as in Eq. (21), although these are accompanied by small amounts of unidentified boranes generated by secondary reactions:

$$4GaB_3H_{10} \longrightarrow 4Ga + 3B_4H_{10} + 5H_2. \qquad (21)$$

Gallatetraborane has been characterized (a) by its mass spectrum, (b) by the vibrational spectra of the vapor (sampled directly at room temperature or trapped in a solid nitrogen matrix at ca. 20 K) and of the annealed solid at 77 K, and (c) by the ^1H and ^{11}B NMR spectra of $[^2H_8]$toluene solutions of the compound. That the vibrational spectra are essentially invariant with phase and temperature points to the presence of a molecular unit common to the vapor and solid states. Comparison with the spectra of compounds known to contain terminal GaH_2 groups (*37, 39, 40, 52, 56, 63*) and bidentate octahydrotriborate groups, $(\mu\text{-}H)_2B_3H_6$ [e.g., $Me_2GaB_3H_8$ (*124, 125*) and B_4H_{10} (*126*)] leaves little doubt that the new compound is a derivative of tetraborane(10), with gallium replacing boron at the 2 position (see Fig. 10). Unequivocal evidence of identity comes in any case from the NMR spectra. At temperatures between 193 and 283 K solutions of the hydride exhibit two ^{11}B resonances with relative intensities of 2 : 1 (see Fig. 11): the triplet resonance at $\delta(^{11}B)$ -12.9 is due to the unique apical boron atom [B(4) in Fig. 10], whereas the resonance with the unusual triplet splitting pattern centered at $\delta(^{11}B)$ -44.0 is due to the "hinge" boron atoms [B(1) and B(3) in Fig. 10]. The details of the ^1H NMR spectrum have been decoded by ^{11}B decoupling, as illustrated in Fig. 11. The broad AB-type signal at δ_H 4.02, 4.56 must be associated with the *exo*- and *endo*-protons of the GaH_2 unit, the corresponding doublet at δ_H 2.09, 2.78 with the apical BH_2 unit; the resonance at δ_H 1.16 is due to the terminal hydrogens of the hinge boron atoms and those at δ_H -0.80 and -1.49 are due to the four bridging hydrogens. The NMR properties echo those of the dimethylgallium derivative $Me_2GaB_3H_8$ (*124*) and related compounds featuring bidentate ligation of the $B_3H_8^-$ anion to a metal center (*77, 78*). Such systems run the whole gamut of fluxional-

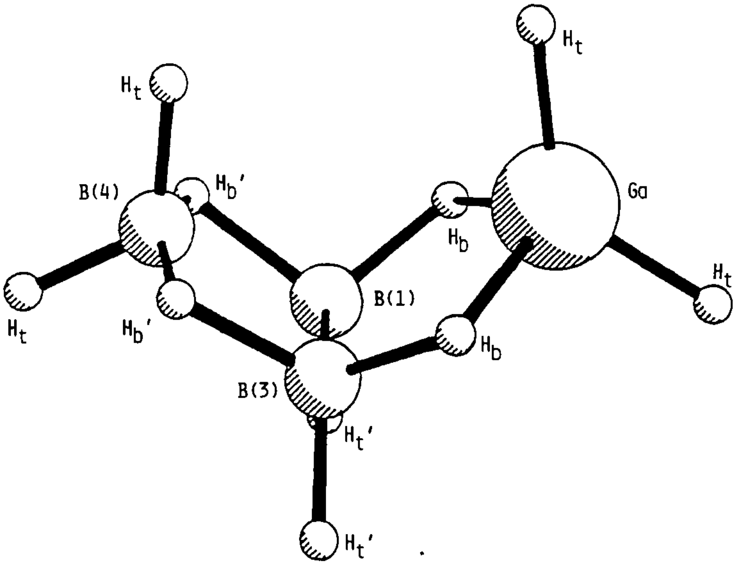


FIG. 10. The structure of the molecule 2-GaB_3H_{10} as deduced from the electron-diffraction pattern of the vapor (reproduced with permission from Ref. *63*).

ity from the essentially static behaviors of $H_2GaB_3H_8$ and $(OC)_4MnB_3H_8$ (*78*) to the rapid exchange of boron and hydrogen atoms that distinguishes $(C_5H_5)BeB_3H_8$ (*78*) and $M^+[B_3H_8]^-$ salts (*127*), even at very low temperatures.

The electron-diffraction pattern of the vapor at ca. 273 K, like the spectroscopic properties, has all the features to be expected of the GaB_3H_{10} molecule with the tetraborane(10)-like structure illustrated in Fig. 10. Such a structure has yielded satisfactorily to refinement, despite some problems of correlation, giving the dimensions detailed in Table I. The measured geometrical parameters hold few surprises, being concordant not only with those of the related species B_4H_{10} (*128*), $Me_2MB_3H_8$ (M = Al or Ga) (*125*), $(Ph_3P)_2CuB_3H_8$ (*129*), and $(\eta^5\text{-}C_5H_5)_2\text{-}NbB_3H_8$ (*130*), but also with some theoretical forecasts (*131*).

The known reactivity of tetraborane(10) (*1–8*) holds out the promise of a varied and potentially fertile chemistry for its 2-gallium-substituted derivative. That promise remains largely untested at present, although gallatetraborane has been shown to react with an excess of ammonia at 195 K, yielding a white solid long-lived at room temperature and that, on the evidence of its infrared spectrum, is another cationic gallium hydride derivative, viz., $[H_2Ga(NH_3)_2]^+[B_3H_8]^-$. It will be interesting to see whether homolytic cleavage of the GaB_3 skeleton is also possible and, if so, whether gallium is eliminated as a complex of the type L·GaH_3 or whether it is retained in a trinuclear GaB_2 cluster, also as a complex L·GaB_2H_7 (e.g., L = a phosphine). Another noteworthy reaction of tetraborane(10) is that with CO, leading to the

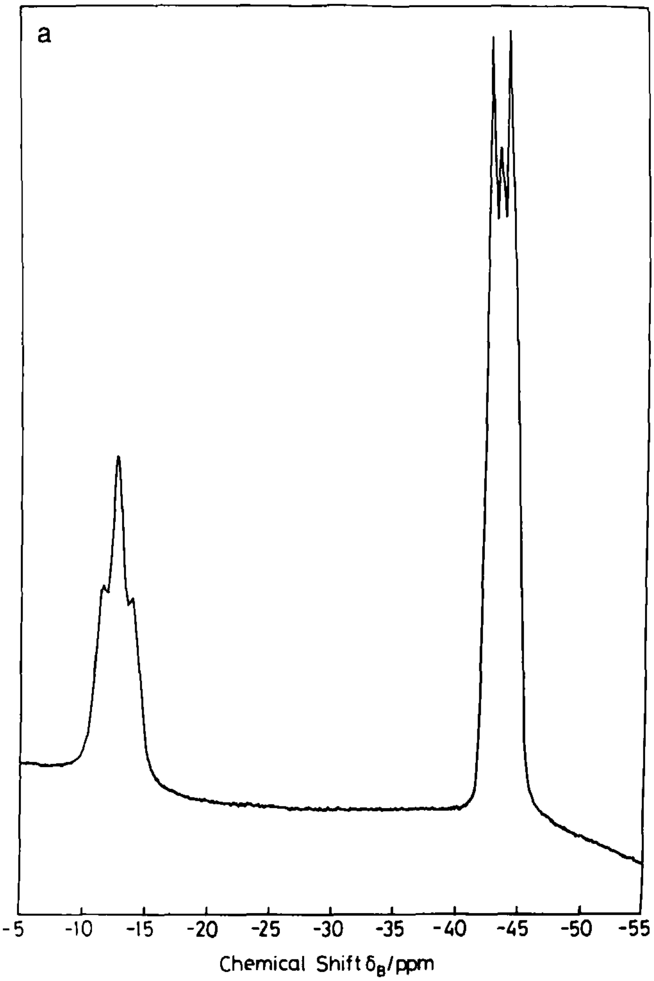


FIG. 11. (a) ^{11}B NMR spectrum of a $C_6D_5CD_3$ solution of 2-GaB_3H_{10} at 233 K (measured at 96.25 MHz). (b) ^1H NMR spectrum of the same solution at 233 K (measured at 300 MHz), showing the effects of broad-band and selective ^{11}B decoupling. The sharp resonance in the ^1H spectrum near δ_H 2.0 is due to the solvent (reproduced with permission from Ref. *63*).

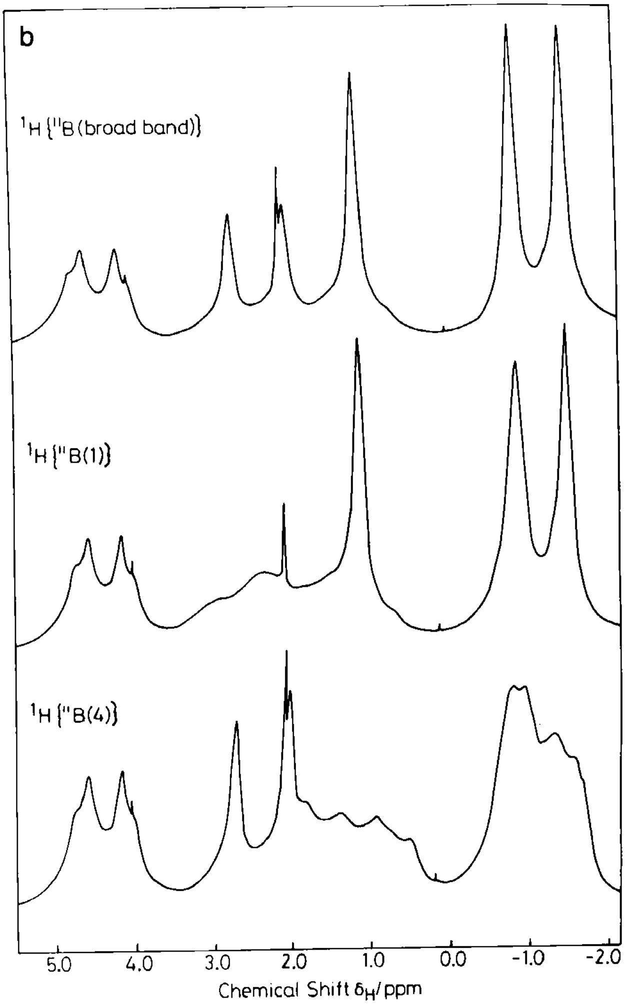


FIG. 11b—*Continued.*

elimination of H_2 and the formation of B_4H_8CO, and so the action of CO on the gallium derivative would surely repay investigation. It remains also to be seen whether controlled, rapid pyrolysis or copyrolysis offers a route to other gallium-substituted boranes.

VII. Hydrides of the Other Group 13 Metals: Preliminaries and Prospects

A. INTRODUCTION

By degrees, a picture of the gallium hydrides is starting to take shape. With the identification and characterization of the thermally fragile but discrete molecules Ga_2H_6, $GaBH_6$, and GaB_3H_{10}, it appears that gallium, in its hydride chemistry, comes closer than aluminum to shadowing the unique behavior of boron (*1–8, 10*). This can be correlated with the valence electrons, which are bound somewhat more tightly in the Ga than in the Al atom, as a result of the imperfect screening of the increased nuclear charge by the additional $3d^{10}$ shell. The tendency for gallium to remain four-coordinate in situations in which aluminum favors sixfold coordination is another sign of the reversion to boron-like properties on the part of gallium. In the light of what we now know, it is reasonable to expect that the chemistry of gallium hydrides is capable of considerable expansion, if not to match that of the boron hydrides, at least to surpass that of aluminum hydrides. It is appropriate, nevertheless, that we should conclude this chapter with a stocktaking of the other Group 13 metals, aluminum, indium, and thallium, to see what, if any, scope there may be for an enlargement of their hydride chemistry.

B. ALUMINUM HYDRIDES (*10*)

Theoretical analysis of the equilibrium molecular structures, vibrational properties, and binding energies of Group 13 hydrides gives no hint of intrinsic instability in the molecules AlH_3, Al_2H_6, and Al_3H_9 (*86, 105–109*). Hence they tend to underline the seemingly anomalous position of aluminum, vis-à-vis boron and gallium, in that aluminum gives an involatile polymeric hydride $[AlH_3]_n$ (*10–13*), but only fleeting signs of *discrete* molecules like Al_2H_6. With hydride as a ligand it seems that aluminum is seldom to be found in four-coordinated environments, and the tendency to polymerize, more than any thermal instability, is the principal barrier to the isolation of tractable aluminum hydrides, although there are exceptions, e.g., diorganoalanes of the type $[R_2AlH]_n$, alane adducts like $(Me_3N)_2AlH_3$, the dimethylamido derivative $[Me_2NAlH_2]_3$ (*68*), and the mixed hydride $Al(BH_4)_3$. Another practical problem is that there are fewer synthetic options for the formation of Al–H bonds. There is, for example, no prospect of being able to prepare mono- or dichloroalane by reactions analogous to (14), once it is appreciated that the reagent Me_3SiH is itself made by chloride–hydride exchange typically initiated by the Al–H bonds of $LiAlH_4$ (*132*). Instead one must look to metathesis reactions involving alkali-metal hydrides or compounds already containing Al–H bonds, e.g., $LiAlH_4$ or $[R_2AlH]_n$.

One possibility is to turn to direct synthesis from the elements. The molecule AlH has certainly been detected spectroscopically as a short-lived species on appropriate activation of gaseous Al/H_2 mixtures (*14*). AlH_3 and Al_2H_6 have also been detected by mass spectrometry when aluminum is evaporated into a hydrogen atmosphere (*18, 133–135*). Indeed, evaporation of aluminum from a hot tungsten filament into a hydrogen atmosphere (e.g., at a pressure of 2–3 mm Hg) yields at 77 K a heterogeneous solid condensate including elemental aluminum and a hydride with the empirical composition AlH_x (*136*). The hydride appears to be formed mainly not in the gas phase but on condensation of the vapors, and the tungsten filament is probably responsible for activating the reaction (by generating H atoms, by the ultraviolet radiation it emits, or both). Circumstantial evidence based on the overall composition of the deposit implies that $x > 1$. Warming the deposit to ambient temperatures results in decomposition of the AlH_x with the regeneration of H_2. As with gallane (*56*), however, this decomposition can be forestalled by chemical trapping with an excess of trimethylamine (*136*); warming then affords the known, relatively stable alane adduct $(Me_3N)_2AlH_3$, identified by its infrared and ^1H and ^{27}Al NMR spectra (*137*). Although AlH_3 may thus be indicated as the hydride precursor, the inhomogeneous nature of the condensate means that disproportionation, as in a reaction such as (22), cannot be ruled out as a pathway to $(Me_3N)_2AlH_3$:

$$3AlH_2 + 4Me_3N \longrightarrow 2(Me_3N)_2AlH_3 + Al. \tag{22}$$

Matrix isolation is a well-tried stratagem (*60*) for exploring more closely the reactions of metal atoms and other unsaturated species at low temperatures. For example, as noted earlier, it has witnessed the formation of the gallane molecules GaH_nCl_{3-n} [$n = 1$ (*93*) or 2 (*94*)] by their infrared spectra. Likewise the binary hydride molecules GaH, Ga_2H_2, and GaH_2 have been identified in cryogenic reactions engaging H_2 and Ga atoms or Ga_2 molecules (*138*). Such studies have also shown that matrix-isolated Al atoms are inserted into H_2 upon selective photoexcitation, with the formation of the species AlH_2 and hence, by thermal or photolytic dissociation, AlH (*139*). Under the action of *broad-band* irradiation and with a noble-gas matrix relatively rich in H_2, it has now been established that planar, monomeric AlH_3 is the major product (*136*). Thus, irradiation of such a matrix for 10–40 min leads, as illustrated in Fig. 12, to the appearance and growth of three new infrared bands. With H_2 in an argon matrix these occur at 1882.7, 783.5, and 697.6 cm^{-1}; with D_2 each of these bands shifts to substantially lower energy, viz., 1882.7 → 1376.5, 783.5 → 568.4, and 697.6 → 513.9 cm^{-1}, thereby evincing large H(D) displacements for the relevant vibrational mode. Experiments with mixtures of H_2 and D_2 show no less than 15 infrared absorptions attributable to different AlH_nD_{3-n} isotopomers. The identification of the product is strongly sanctioned by the results of MP2 *ab initio* calculations (see Table III) (*136*). Hence it is possible to account for the doublet structure of the absorption near 1880 cm^{-1} and the three absorptions occurring in the region 1350–1380 cm^{-1} in the spectrum of a photolysed matrix containing both H_2 and D_2; even more telling are the prediction and observation of just 10 distinct vibrational fundamentals in the region 500–800 cm^{-1}. The

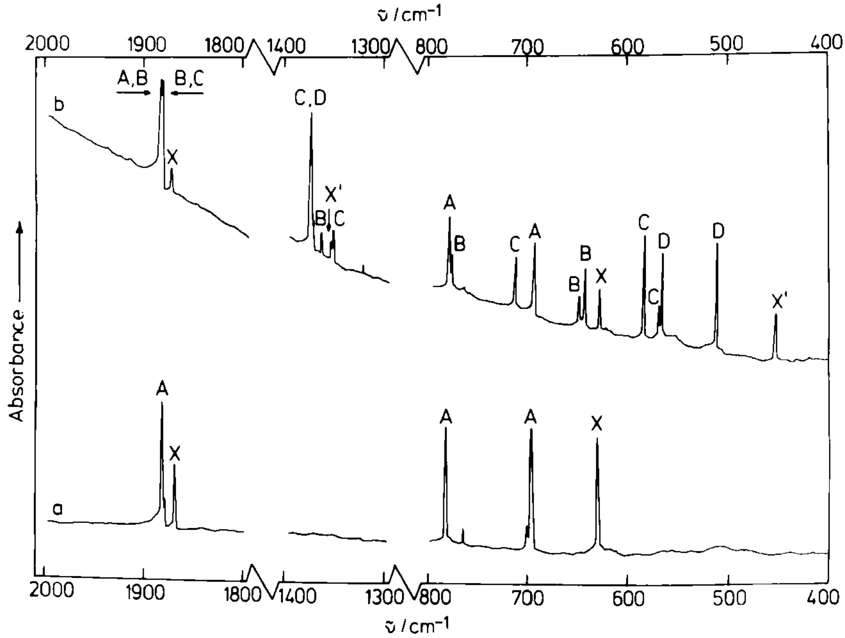


FIG. 12. IR spectra of argon matrices containing Al atoms and H_2 or $H_2 + D_2$, showing the effects of broad-band photolysis: (a) Al with H_2 after photolysis for 20 min; (b) Al with $H_2 + D_2$ in 1:1 proportions after photolysis for 40 min. The species A, B, C, and D correspond to AlH_3, AlH_2D, $AlHD_2$, and AlD_3, respectively. X corresponds to a hydride and X′ to the related deuteride impurity (reproduced with permission from Ref. *136*).

TABLE III

VIBRATIONAL FREQUENCIES ($\tilde{\nu}$ in $\mathrm{cm^{-1}}$) FOR $\mathrm{AlH_3}$ (A), $\mathrm{AlH_2D}$ (B), $\mathrm{AlHD_2}$ (C), AND $\mathrm{AlD_3}$ (D) (a) OBSERVED FOR THE MOLECULES ISOLATED IN Ar MATRICES, (b) CALCULATED BY THE MP2 *AB INITIO* METHOD, AND (c) CALCULATED BY NORMAL COORDINATE ANALYSIS (n.c.a.) (*136*)

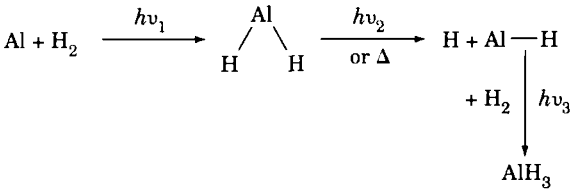
			Calculated	
Species	Experiment, Ar matrix	Assignment	MP2 *ab initio* method (intensity)[a]	n.c.a.
$\mathrm{AlH_3}$, **A**	1882.7	$\nu_{\mathrm{as}}(\mathrm{AlH_2})$ (e')	2024.2 (268)	1881.4
	n.o.[b]	$\nu_{\mathrm{s}}(\mathrm{AlH_3})$ (a_1')	2021.0 (0)	1880.6
	783.5	$\delta(\mathrm{AlH_2})$ (e')	830.7 (249)	782.5
	697.6	$\gamma(\mathrm{AlH_3})$ (a_2'')	737.6 (394)	697.8[c]
$\mathrm{AlH_2D}$, **B**	1882.7	$\nu_{\mathrm{as}}(\mathrm{AlH_2})$ (b_2)	2024.1 (271)	1881.3
	1881.2	$\nu_{\mathrm{s}}(\mathrm{AlH_2})$ (a_1)	2022.1 (93)	1880.9
	1367.3	$\nu(\mathrm{AlD})$ (a_1)	1455.6 (99)	1366.8
	780.6	$\delta(\mathrm{AlH_2})$ (a_1)	830.4 (246)	782.2
	651.8	$\rho(\mathrm{AlD})$ (b_2)	687.0 (170)	649.3
	645.6	$\gamma(\mathrm{AlH_2D})$ (b_1)	680.2 (335)	643.4[c]
$\mathrm{AlHD_2}$, **C**	1881.2	$\nu(\mathrm{AlH})$ (a_1)	2023.0 (186)	1881.0
	1377.9	$\nu_{\mathrm{as}}(\mathrm{AlD_2})$ (b_2)	1468.4 (155)	1378.0
	1355.2	$\nu_{\mathrm{s}}(\mathrm{AlD_2})$ (a_1)	1442.6 (49)	1355.6
	716.4	$\rho(\mathrm{AlH})$ (b_2)	761.6 (206)	717.4
	586.7	$\gamma(\mathrm{AlHD_2})$ (b_1)	617.4 (276)	584.0[c]
	570.8	$\delta(\mathrm{AlD_2})$ (a_1)	601.9 (130)	570.1
$\mathrm{AlD_3}$, **D**	1376.5	$\nu_{\mathrm{as}}(\mathrm{AlD_2})$ (e')	1468.4 (155)	1378.0
	n.o.[b]	$\nu_{\mathrm{s}}(\mathrm{AlD_3})$ (a_1')	1429.7 (0)	1344.4
	568.4	$\delta(\mathrm{AlD_2})$ (e')	601.2 (128)	569.5
	513.9	$\gamma(\mathrm{AlD_3})$ (a_2'')	547.4 (217)	517.8[c]

[a] Intensities in km $\mathrm{mol^{-1}}$, as obtained from the frequency calculation. For direct comparison with observed intensities (as in Fig. 12, for example), these values need to be scaled according to the probabilities of formation of the different $\mathrm{AlH_nD_{3-n}}$ isotopomers in matrices containing both H_2 and D_2.

[b] n.o., not observed. Fundamental is silent in IR absorption for an $\mathrm{AlH_3}$ or $\mathrm{AlD_3}$ molecule with D_{3h} symmetry.

[c] Harmonic frequency for the out-of-plane deformation; *anharmonic* frequencies have been estimated for the other fundamentals (*136*).

spectra give us to believe that AlH is an intermediate, and the finding that an equimolar mixture of H_2 and D_2 gives $\mathrm{AlH_3}$, $\mathrm{AlH_2D}$, $\mathrm{AlHD_2}$, and $\mathrm{AlD_3}$ in highly nonstatistical proportions approaching 1 : 1 : 1 : 1 favors the mechanism,



(23)

in which the ultimate step parallels the oxidative addition of H_2 to GaCl (*94*). To date there are no signs of the dimer Al_2H_6. Whether molecular alane has the thermal stability to survive at temperatures appreciably greater than those of a solid noble-gas matrix and, if so, whether this approach is viable as a method of synthesis on the larger scale are other issues still to be settled.

Altogether easier of access, more stable, and more tractable are complexes in which AlH_3 is coordinated by one or more base molecules, e.g., $(Me_3N)_nAlH_3$ ($n = 1$ or 2). These are of interest as hydride sources for hydroalumination of unsaturated substrates (*10, 140*), as precursors to the hydrides of other metals, and, as already noted, in the chemical vapor deposition of aluminum metal in thin-film technology (*21–26*). The 1 : 1 trimethylamine adduct, $Me_3N \cdot AlH_3$, is monomeric in the vapor but, in common with $PhCH_2Me_2N \cdot AlH_3$ and $\overline{CH_2CH{=}CHCH_2CH_2N}Me \cdot AlH_3$, takes the form of a dimer in the solid state (*141*). The dimer, as exemplified by $[PhCH_2Me_2N \cdot AlH_3]_2$ in Fig. 13, consists of an Al_2H_6 unit with highly unsymmetrical Al–H···Al bridges. It can thus be viewed as a derivative of the elusive dialane, Al_2H_6. Polydentate tertiary amine complexes of alane may be polymeric (*142*), or they may incorporate cationic as well as anionic aluminum hydride moieties (*143*). Another recent development of aluminum hydride chemistry has been the preparation of a variety of aluminohydride complexes of transition metals (*144*). Here too a notable feature is the double hydrogen-bridged moiety, $M(\mu\text{-}H)_2Al$, involved in the bonding of pairs of Al atoms or in the attachment of Al to the transition metal center. It remains to be seen whether the heavier Group 13 metals enter into the formation of similar compounds.

C. INDIUM AND THALLIUM HYDRIDES (*10*)

Such is the weakness of In–H and Tl–H bonds that the chemistry of indium and thallium hydrides is unlikely to rival that of the corresponding aluminum and gallium compounds. This is certainly the inference to be drawn from the thermal instability of the known compounds $LiInH_4$ and $LiTlH_4$, both of which decompose rapidly at 273 K (similar

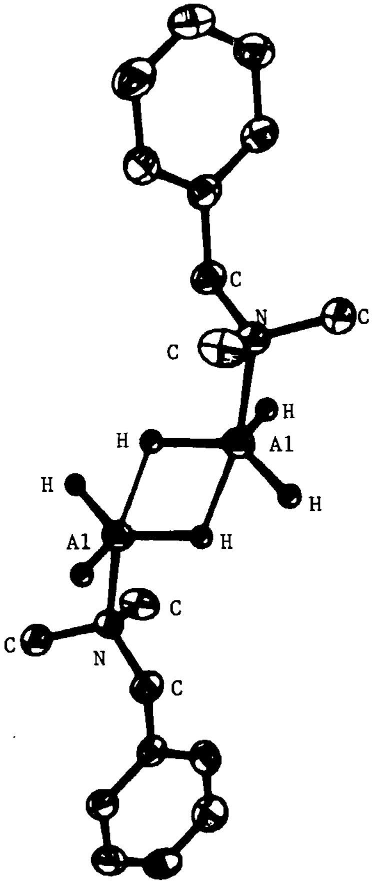
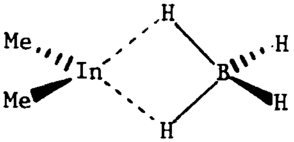


FIG. 13. Projection of $[PhCH_2Me_2N{\cdot}AlH_3]_2$ in the crystalline solid with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms where shown (adapted with permission from Ref. *141*; copyright 1991, American Chemical Society).

decomposition of $LiAlH_4$ and $LiGaH_4$ occurs at ca. 400 and 320 K, respectively). Despite mass spectrometric evidence of InH_3 in the gas phase (*18*), earlier claims to the synthesis of the binary hydrides $[InH_3]_n$ and $[TlH_3]_n$ in the condensed phases have yet to be substantiated.

Until recently the only reasonably well-characterized compounds with In–H bonds were a few thermally unstable alkylindates of the types $M[R_2InH_2]$ and $M[RInH_3]$ (M = alkali metal; R = Me, Et, or Me_3SiCH_2) (*43*). With the aid of the large *tris*(trimethylsilyl)methyl (Tsi) group, however, it has been possible to synthesize an alkylhydroindate that is sufficiently robust to permit characterization in the solid state and in solution (*145*). The crystal structure of the solid complex $[Li(thf)_2][(Tsi)_2In_2H_5]$ (thf, tetrahydrofuran) implies the presence of a complex anion $[(Tsi)H_2In(\mu\text{-}H)InH_2(Tsi)]^-$, the In atoms of which are linked to the Li^+ ion via two of the H atoms. With its single hydrogen bridge the anion has obvious affinities with $[Me_3Al(\mu\text{-}H)AlMe_3]^-$, which is known in the form of its sodium salt (*146*).

Earlier records of indium or thallium tetrahydroborates cite the preparation of an unstable adduct $In(BH_4)_3 \cdot thf$ by the reaction of trimethylindium with diborane in tetrahydrofuran solution. By exploiting solvent-free conditions, we have found that trimethylindium can be made to react with gaseous diborane at ambient temperatures to give a white crystalline solid, Me_2InBH_4, which has been characterized by elemental analysis and by its vibrational and NMR spectra (*147*). The compound is long-lived at room temperature and can be vaporized without decomposition at ca. 350 K. The infrared spectrum of the vapor isolated in a solid nitrogen matrix at ca. 20 K indicates that the predominant species are molecules of the type $Me_2In(\mu\text{-}H)_2BH_2$ (**10**), incorporating a bidentate BH_4 group, and therefore analogous to the corresponding gallium compound (*82, 85*). At the same time the vibrational properties hint at a formulation that comes closer to an ion-pair $Me_2In^+BH_4^-$ than to a molecule with a significant In–H bonding interaction. Studies along these lines are continuing as part of a wider search for tractable indium hydrides. Whatever the odds may be, there is an appealing congruity about this development, for was not Me_2GaBH_4 (see Section IV.A) the first step in the hunting of the gallium hydrides?



(10)

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