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Some Chemical Properties of Monochlorogallane: Decomposition to Gallium(I) Trichlorogallate(III), $Ga^+[GaCl_3H]^-$, and Other Reactions

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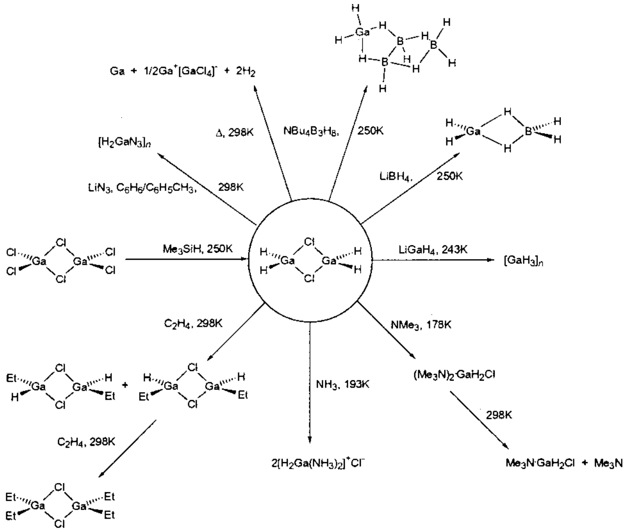
Thermal decomposition of monochlorogallane, $[H_2GaCl]_n$, at ambient temperatures releases H_2 and results in the formation of gallium(I) species, including the new compound $Ga[GaHCl_3]$, which has been characterized crystallographically at 100 K (monoclinic $P2_1/n$, $a = 5.730(1)$, $b = 6.787(1)$, $c = 14.508(1)$ Å, $\beta = 97.902(5)°$) and by its Raman spectrum. The gallane suffers symmetrical cleavage of the $Ga(\mu\text{-}Cl)_2Ga$ bridge in its reaction with NMe_3 but unsymmetrical cleavage, giving $[H_2Ga(NH_3)_2]^+Cl^-$, in its reaction with NH_3. Ethene inserts into the Ga−H bonds to form first $[Et(H)GaCl]_2$ and then $[Et_2GaCl]_2$.

Introduction

Unlike many other base-free monosubstituted derivatives of gallane, $[H_2GaX]_n$, where X is not very bulky or incorporates appropriate donor centers,[1] monochlorogallane is comparatively long-lived and tractable at ambient temperatures.[2−4] In a previous article[2] we have described the synthesis and some of the physical properties of the compound, which is a labile liquid at room temperature and vaporizes to give dimeric molecules, $H_2Ga(\mu\text{-}Cl)_2GaH_2$. Here we report some of its chemical properties including (i) its thermal decomposition to give mixed valence gallium compounds, (ii) selected metathesis reactions which make the compound important as a source of other GaH_2 derivatives, (iii) addition reactions with the nitrogen bases NH_3 and NMe_3, and (iv) the insertion of ethene into the Ga−H bonds.

Scheme 1. Formation, Decomposition, and Some Reactions of Monochlorogallane[5−8,21]



Results and Discussion

The studies we have undertaken have revealed several aspects of the chemistry of monochlorogallane, $[H_2GaCl]_n$, as summarized in Scheme 1. There are four features meriting discussion: (i) the decomposition of the compound with the formation of elemental gallium, hydrogen, and mixed valence gallium derivatives; (ii) metathesis reactions with appropriate nucleophiles X^- at low temperatures to afford other gallanes of the type $[H_2GaX]_n$, e.g., $X^- = GaH_4^-$,[5,6] BH_4^-,[5,7] and $B_3H_8^-$;[5,8] (iii) cleavage of the $Ga(\mu\text{-}Cl)_2Ga$ unit by a nitrogen base either

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"symmetrically" to give a molecular adduct, e.g., $Me_3N{\cdot}GaH_2Cl$, or "unsymmetrically" to give a saltlike product, e.g., $[H_2Ga(NH_3)_2]^+Cl^-$; and (iv) insertion of ethene into the Ga−H bonds in a stepwise manner to form first $[EtGa(H)Cl]_2$ and then $[Et_2GaCl]_2$ in reactions emulating that of ethene with dichlorogallane.[9]

(i) Thermal Decomposition; Characterization of the Intermediate $Ga^+[GaCl_3H]^-$. As noted previously,[2] vaporization of monochlorogallane in vacuo invariably leads to slight decomposition with the deposition of less volatile white solids. During the synthesis of the gallane, moreover, it was noted that the residue was inhomogeneous, typically comprising a clear crystalline material and a white powder. Exactly how the decomposition proceeds is hard to establish since the intermediate products varied significantly with temperature, phase, and other conditions (e.g., according to whether the sample is in a closed system or subject to continuous evacuation with removal of any volatile materials as they are formed).

Raising the temperature of a sample of the liquid in a sealed, evacuated glass ampule to ca. 373 K caused complete decomposition to occur in a matter of hours, with the evolution of dihydrogen and the formation of an involatile, inhomogeneous solid having an overall composition GaCl. The solid consisted of a mixture of finely dispersed elemental gallium (giving a gray coloration, sometimes with metallic flecks) and a white powder identified by its Raman spectrum as $Ga^+[GaCl_4]^-$.[10] Quantitative chemical assay implied that decomposition had occurred in accordance with eq 1, and thereby offered a means of analysis of the monochlorogallane.

$$\frac{4}{n}\,[H_2GaCl]_n \longrightarrow \underbrace{2Ga + Ga^+[GaCl_4]^-}_{\text{Solid residue 4'GaCl'}} + 4H_2 \qquad (1)$$

Numerous experiments in which liquid or gaseous samples of monochlorogallane were heated or left to stand at room temperature invariably witnessed the release of dihydrogen, the deposition of gallium, and the formation of gallium compounds of varying volatility and stability. Only one such intermediate was amenable to isolation and characterization, namely the crystalline solid first noted during the synthesis of monochlorogallane. The maximum yield of this solid was achieved by leaving a sample of monochlorogallane in vacuo at room temperature (283−288 K) for 14 days. A single crystal selected from the reaction mixture was shown to be the new mixed-valence compound gallium(I) trichlorogallate(III), $Ga^+[GaCl_3H]^-$, by X-ray diffraction measurements (see Tables 1 and 2 and Figure 1).

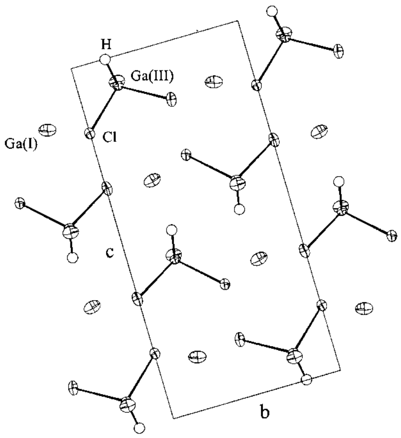

Figure 1. Crystal structure of $Ga[HGaCl_3]$ at 100 K showing the presence of Ga^+ and $[HGaCl_3]^-$ units with 50% thermal ellipsoids.

Table 1. Single Crystal Data for $Ga[GaCl_3H]$

empirical formula	HGa_2Cl_3
fw	246.81
crystal color; dimens, mm	colorless, 0.30 × 0.30 × 0.35
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	5.730(1)
b, Å	6.787(1)
c, Å	14.508(1)
β, deg	97.902(5)
V, Å^3	558.9(3)
Z	4
D_X, g cm^{-3}	2.93
T, K	100
λ(Mo Kα), Å	0.71069
μ, cm^{-1}	109.01
θ_{max}, deg	27
no. of reflns measd	5667
no. of unique reflns	1096
no. of observations with $I > 3\sigma(I)$	888
no. of variables	51
max peak in final diff map, e Å^{-3}	0.54
min peak in final diff map, e Å^{-3}	−0.95
R	0.029
R_w	0.035
S	1.067

Table 2. Selected Distances (Å) and Angles (deg) in $Ga^+[GaCl_3H]^-$

Ga(1)−Cl(1)	2.1985(9)
Ga(1)−Cl(2)	2.212(1)
Ga(1)−Cl(3)	2.2199(8)
Ga(1)−H(1)	1.32(6)
Cl(1)−Ga(1)−Cl(2)	104.24(4)
Cl(1)−Ga(1)−Cl(3)	103.39(4)
Cl(2)−Ga(1)−Cl(3)	104.35(4)
Cl(1)−Ga(1)−H(1)	117.3(24)
Cl(2)−Ga(1)−H(1)	113.4(25)
Cl(3)−Ga(1)−H(1)	112.8(23)

As in the familiar parent compound $Ga^+[GaCl_4]^-$,[11] there are two distinct gallium centers, with the four-coordinated Ga(III) separated from Ga(I) that is at least eight-coordinated by an average distance of 4.13 Å. The novel $[GaCl_3H]^-$ anions closely approximate C_{3v} symmetry, with a mean Ga−Cl bond length of 2.210 Å (cf. 2.172 Å for $[GaCl_4]^-$ in Ga_2Cl_4[11]) and Cl−Ga−Cl angles of 104.0°. The coordination environment of the Ga(I) center is not only more diffuse, but is also distinctly less symmetrical, with eight Ga···Cl contacts at separations ranging from 3.069 to 3.552 Å, a ninth at 3.814 Å, and a Ga···H contact measuring 2.79 Å.

It is of interest to see how the structures of $Ga[GaCl_4]$ and $Ga[GaCl_3H]$ fit into the context of families having the general formula $A[BX_4]$, where BX_4 is tetrahedral and A is eight-coordinated. A starting point is provided by zircon, $Zr[SiO_4]$ (Figure 2a),[12] in which the Zr atoms are eight-coordinated by oxygen atoms, defining a triangulated dodecahedron; this can be considered to be two intersecting tetrahedra which have been

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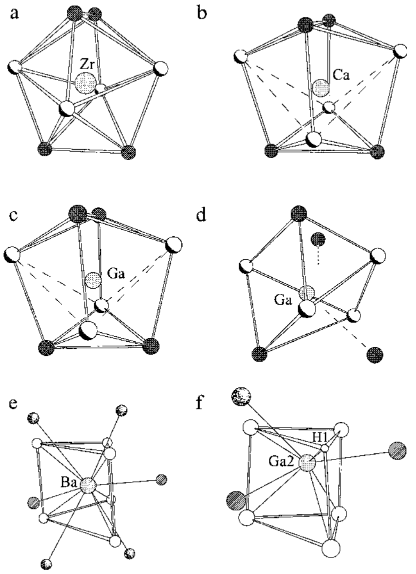

Figure 2. Coordination geometries of the metal atom A in solids with the general formula A[BX_4] where BX_4 is tetrahedral: (a) Zr in zircon, Zr[SiO_4]; (b) Ca in scheelite, Ca[WO_4]; (c) Ga^I in Ga[$GaCl_4$]; (d) Ga^I in Ga[$AlCl_4$]; and (e) Ba in barytes, Ba[SO_4]. (f) For comparison the coordination geometry of Ga^I in Ga[$HGaCl_3$]. The coordination geometries in (a)−(d) can each be considered, in varying degrees, in terms of two intersecting tetrahedra which have been squashed (open circles) or elongated (filled circles) about one diad; the coordination geometries in (e) and (f) can each be related to a trigonal prism capped (filled circles) on two square faces, as well as having longer contacts with additional atoms (open circles).

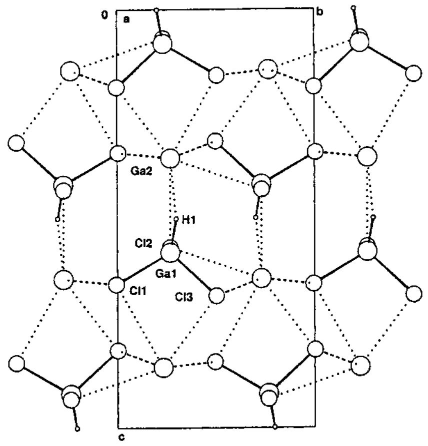

Figure 3. Coordination geometry of Ga^I in Ga[$HGaCl_3$].

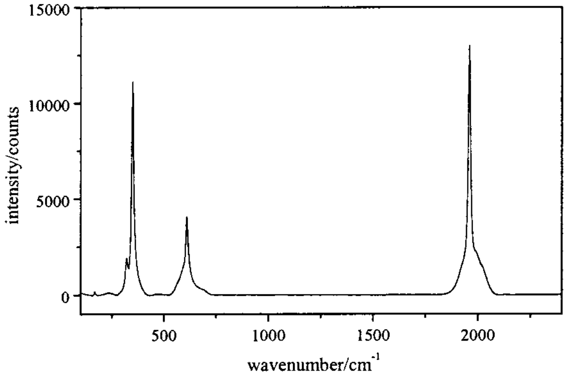

Figure 4. Raman spectrum of a crystal of Ga[$HGaCl_3$] at room temperature.

squashed (open circles) or elongated (filled circles) about one diad (spheroids). Replacement of the spheroids with tetrahedra would yield a cubic array about the central metal atom. A step in this direction is observed in scheelite, Ca[WO_4] (Figure 2b), the coordination polyhedron now being described as a bisdisphenoid. Scheelite is really quite similar to Ga[$GaCl_4$] (Figure 2c);[11] in both structures the Ca···O or Ga···Cl distances fall into two sets of four. While the Ga···Cl contacts in Ga[$GaCl_4$] thus occupy a narrow range (3.17−3.19 Å), those in the related salt Ga[$AlCl_4$] are much more irregular.[13] Here we find six contacts in the range 3.10−3.25 Å forming a trigonal prism that is capped on two "square" faces by Cl atoms. making Ga···Cl contacts of 3.52 Å (Figure 2d). As noted previously,[13] the structure of Ga[$AlCl_4$] is related to that of barytes, Ba[SO_4],[12] where the large Ba^{2+} is 12-coordinated; eight Ba···O contacts of 2.76−2.86 Å form a bicapped trigonal prism about the Ba, and then four longer contacts (3.07−3.32 Å) are made through the edges between the triangular and capped square faces of the prism (Figure 2e). In Ga[$AlCl_4$], the Ga^+ is not large enough to be 12-coordinated and so the four long contacts are lost, leaving the bicapped prismatic array. The coordination sphere of the Ga^+ center in crystalline Ga[$GaCl_3H$], like that in Ga[$AlCl_4$], accommodates a rather broad spread of Ga···Cl contacts within the sum of the van der Waals radii (3.07−3.55 Å) and one Ga···H contact of 2.79 Å. The coordination sphere can again be derived from the barytes structure with a bicapped trigonal prismatic array similar to that observed in Ga[$AlCl_4$] but, instead of being formed by eight Cl atoms, it comprises seven Cl and one H atom (Figure 3). It appears that the small size of the H enables the Ga to take up a higher coordination number than in the aluminum compound, and a ninth (longest) contact is formed through one of the edges between a triangular face and one of the capped square faces, i.e., in the same direction as one of the long contacts in the Ba[SO_4] structure.

To what extent the unsymmetrical hemidirected[14] coordination geometry of the Ga(I) center reflects the role of the $4s^2$ lone pair of electrons, as opposed to the purely steric demands of the Ga^+ and $GaCl_3H^-$ units, is an open question. There are at present insufficient crystallographic data on gallium(I) compounds[15] to warrant the kind of detailed analysis that has recently been undertaken by Glusker et al.[14] for lead(II) compounds.

The air-sensitive intermediate $Ga^+[GaCl_3H]^-$ melts at ca. 303 K and decomposes on further heating with cleavage of the Ga−H bond to form dihydrogen, gallium, and $Ga^+[GaCl_4]^-$. The Raman spectrum of the solid displayed the emissions illustrated in Figure 4 and with the wavenumbers listed in Table 3. It can be satisfactorily interpreted on the basis of the vibrational transitions expected for an $[HGaCl_3]^-$ anion having C_{3v} symmetry with the aid of a quantum chemical model; density functional theory (DFT) calculations employing a 6-311G* basis set were found to give the best account of the observed frequency and intensity pattern (see Table 3). The proposed assignments are also supported by comparisons with the vibrational properties reported not only for the $[GaCl_4]^-$ anion but also for the isoelectronic molecule $HGeCl_3$.[16]

The most prominent feature of the spectrum, occurring at 1960.4 cm^{-1}, is plainly associated with the ν(Ga−H) funda-

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Table 3. Observed and Calculated Raman Frequencies and Intensities for the Vibrational Fundamentals of Solid $Ga^+[HGaCl_3]^-$ and Comparison with $HGeCl_3$

	Ga[HGaCl$_3$]					
	obs		calc^b		$HGeCl_3$	description of mode^c
mode	ν/cm^{-1}	intens^a	ν/cm^{-1}	intens^a	ν/cm^{-1}	
ν_1 (a$_1$)	1960.4	100.0	1996.4	100.0	2155.7	ν(M−H)
ν_2 (a$_1$)	349.5	85.8	344.9	1.7	418.4	sym ν(M−Cl)
ν_3 (a$_1$)	167.9	0.6	163.0	1.1	181.8	sym δ(MCl$_3$)
ν_4 (e)	609.3	20.0	653.6	14.0	708.6	δ(M−H)
ν_5 (e)	320.6	11.6	341.8	2.8	454	antisym ν(M−Cl)
ν_6 (e)	*d*	*d*	124.4	2.8	145.0	ρ(MCl$_3$)
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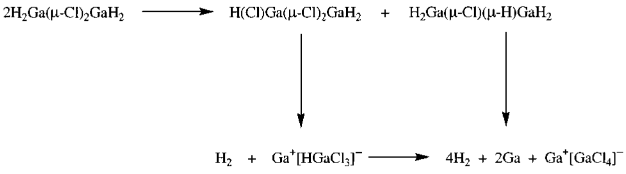
[a] Relative intensities with the strongest band set to 100 arbitrary units. [b] Calculated by DFT methods (B3LYP) with a 6-311G* basis set. [c] M = Ga for $[HGaCl_3]^-$ or M = Ge for $HGeCl_3$. [d] Not observed; outside range of detection.

mental, ν_1 (a$_1$). The frequency is, as expected, somewhat lower than that of the equivalent modes in the neutral molecules $HGeCl_3$ (2155.7 cm^{-1})[16] and $HGaCl_2$ (2015 cm^{-1}),[17] in keeping with the increased polarity of the metal−hydrogen bond induced by the negative charge. On the other hand, replacement of three of the hydrogens of $[GaH_4]^-$ (with a weighted average ν(Ga−H) frequency of 1807 cm^{-1})[18] by more electronegative chlorine substituents clearly results in a strengthening of the surviving Ga−H bond. The symmetric and antisymmetric ν(Ga−Cl) fundamentals, ν_2 (a$_1$) and ν_5 (e), are identified with emissions at 349.5 and 320.6 cm^{-1}, respectively. It is clear from Table 3 that the small differences in the calculated values, both for the positions and intensities of these two features, are of little assistance in deciding their relative ordering. We have been guided, instead, by the observed intensities of the corresponding bands in the Raman spectrum of $HGeCl_3$, where the symmetric M−Cl stretching mode is observed to have approximately 10 times the intensity of the antisymmetric one. There are no such problems in identifying the feature associated with the $\delta(GaCl_3)$ fundamental, ν_3(a$_1$), since here theory anticipates well both the frequency and Raman intensity of this mode, which is assigned to the very weak scattering at 167.9 cm^{-1}. The feature at 609.3 cm^{-1} may be identified with the Ga−H wagging mode, ν_4 (e). This leaves only the $\rho(GaCl_3)$ vibration, ν_6 (e), which is expected to appear near 120 cm^{-1}, and so it would fall outside the range of detection in the present experiments.

Attempts have also been made to investigate the decomposition of monochlorogallane by monitoring the ^{1}H and ^{71}Ga NMR spectra of toluene-d_8 solutions over a range of temperatures. After such a solution had been left to stand for a period of days at room temperature, the broad ^{1}H resonance associated with gallium-bound hydrogen atoms[2] was observed to have shifted from δ_H 5.46 to ca. 6.0; decreasing the temperature to 193 K resolved the signal into two components, the first centered near δ_H 6.4 ($W_{1/2}$ = 48 Hz) and the second near δ_H 5.5 ($W_{1/2}$ = 13 Hz), the latter being attributable to unchanged monochlorogallane and/or other species of the type $[H_mGaCl_{3-m}]_n$ (m = 1 or 2).[19] Continued decomposition with deposition of gallium metal was seen to cause the first resonance to grow at the expense of the second. It proved impossible to prepare a sample of Ga-$[HGaCl_3]$ that was entirely free from monochlorogallane and other decomposition products, but a toluene-d_8 solution of such a sample gave a ^{1}H spectrum similar to that of the decomposed sample of monochlorogallane. At ambient temperatures it showed but one broad resonance at δ_H 5.98 ($W_{1/2}$ = 190 Hz). Decreasing the temperature to 243 K brought about resolution into two main resonances, one at δ_H 6.45 with a shoulder at ca. δ_H 7.2 and the other at δ_H 5.63; further cooling caused the first resonance to develop a broad triplet pattern, with components at δ_H 7.29, 6.67, and 6.23, and the second to split into two sharper lines, at δ_H 5.77 and 5.14. Hence, it was evident that all the solutions of decomposed samples of monochlorogallane contained a mixture of products including some, like the parent compound itself,[2] in different degrees of aggregation. The most plausible interpretation of the results is that resonances at $\delta_H < 6$ arise from uncharged species of the type $[H_mGaCl_{3-m}]_n$ (m = 1 or 2), whereas resonances at $\delta_H > 6$ arise from anions of the type $[H_mGaCl_{4-m}]^-$ (m = 1−4) which are subject to rapid scrambling.

^{71}Ga NMR spectra of these solutions typically revealed a single signal at δ_{Ga} −677 ($W_{1/2}$ = 120 Hz) at ambient temperatures. By virtue of its position,[20] this may be identified with the presence of a Ga(I) species. Decreasing the temperature caused the resonance to shift to lower frequency and to broaden (δ_{Ga} −742 and $W_{1/2}$ = 560 Hz at 230 K) and an additional, substantially weaker feature to appear at a slightly higher frequency (δ_{Ga} −713 at 203 K). A possible explanation is that the more intense signal originates in the ion pair $Ga^+[HGaCl_3]^-$, the weaker one in $Ga^+[GaCl_4]^-$. There was no sign of any feature attributable to a Ga(III) component, which would be expected to resonate near δ_{Ga} +200.[20] This is due in all probability to the pronounced broadening effect of the electric field gradient created by the unsymmetrical environment of the metal atom in a species such as $[HGaCl_3]^-$; as no ^{71}Ga signal has been detected for monochlorogallane itself, the result comes as no particular surprise.

The results of these and other experiments[2] imply that disproportionation precedes the elimination of H_2, and the identification of $Ga^+[HGaCl_3]^-$ as a long-lived intermediate suggests that monochlorogallane decomposes in the liquid phase via stages such as those represented in eq 2. Disproportionation need not be confined to the intermediates given here, but is likely to give rise also to $H(Cl)Ga(\mu\text{-}Cl)_2Ga(Cl)H$[9] and highly labile Ga_2H_6;[6] although this makes no difference to the ultimate decomposition products, the vapor may well be host to these intermediates, as suggested in our analysis of its electron-diffraction pattern.[2]



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(ii) Metathesis Reactions: Preparation of other Gallanes of the Type $[H_2GaX]_n$. Much of the significance of monochlorogallane derives from its potential as a source of other gallanes of the type $[H_2GaX]_n$, where X = H, BH_4, or B_3H_8, through metathesis reactions involving the relevant anion X^- [eq 3]. The reactions, which have been described elsewhere,[5−8,21]

$$\frac{1}{n}[H_2GaCl]_n + M^+X^- \rightarrow \frac{1}{n}[H_2GaX]_n + M^+Cl^- \qquad (3)$$

are normally carried out at low temperatures (e.g., 243−253 K) and in the absence of a solvent, despite any reduction in the

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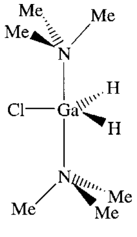
efficiency of the exchange, mainly in order to facilitate the isolation of pure samples of the reactive, thermally frail products $[H_2GaX]_n$.

(iii) Reactions with Nitrogen Bases. Monochlorogallane reacts with an excess of trimethylamine at 178 K. With the mixture warmed to 250 K and the excess of the base recovered, there is but a single product, a white solid identified by mass balance and by its IR and Raman spectra as the known molecular adduct $Me_3N{\cdot}GaH_2Cl$.[22] When the vapor over the adduct is cocondensed with additional NMe_3 at 77 K, the IR spectrum of the deposit shows, besides the bands characteristic of $Me_3N{\cdot}GaH_2Cl$, extra bands attributable to the 2:1 adduct $(Me_3N)_2GaH_2Cl$. Evidence of this second adduct is provided, for example, by the appearance in the IR spectrum of a broad ν(Ga−H) absorption at 1831 cm^{-1} accompanying the absorption at 1909 cm^{-1} due to $Me_3N{\cdot}GaH_2Cl$; the shift of ν(Ga−H) to lower energy with the coordination of a second molecule of NMe_3 is consistent with the formation of a molecule in which NMe_3 ligands are sited above and below a planar GaH_2Cl substrate, **1**, in line with the behaviors of the adducts $Me_3N{\cdot}MH_3$ and $(Me_3N)_2MH_3$ (M = Al[23] or Ga[6]). Annealing the deposit to 250 K under pumping results in the decay and ultimate disappearance of the bands associated with $(Me_3N)_2GaH_2Cl$, which evidently develops an appreciable dissociation pressure under these conditions.



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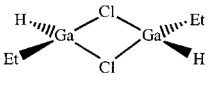
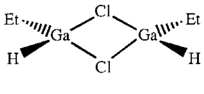
With ammonia at 195 K, monochlorogallane forms a white solid with the composition $H_2GaCl{\cdot}2NH_3$, which is long-lived at room temperature. The IR spectrum of the product is consistent with the presence of the cation $[H_2Ga(NH_3)_2]^+$, showing a distinct resemblance in the pattern and frequencies of its bands to the spectra reported previously for the compound $[H_2Ga(NH_3)_2]^+[GaH_4]^-{\cdot}2NH_3$[6] and also for the isoelectronic species $H_2Ge(CH_3)_2$.[24] Hence, it emerges that the Ga(μ-Cl)$_2$Ga skeleton of the gallane is cleaved unsymmetrically in accordance with eq 4:

$$\frac{1}{n}[H_2GaCl]_n + 2NH_3 \rightarrow [H_2Ga(NH_3)_2]^+\ Cl^- \qquad (4)$$

(iv) Insertion of Ethene into the Ga−H Bonds. Ethene does not react at a measurable rate with neat monochlorogallane at 178 K or with the gallane in isopentane solution at 250 K. A reaction does occur, however, when a benzene solution of the gallane is maintained at room temperature under ethene at an overpressure of ca. 2 atm. After 24 h, 1 mol of $[H_2GaCl]_2$ was found to have consumed 2.4 mol of ethene. Evaporation of the material volatile at 250 K left a colorless, viscous liquid which was a mixture of two components. Warming to 303 K in an all-glass apparatus resulted in the vaporization of a more volatile fraction identified by its IR and ^{1}H NMR spectra as $[Et(H)GaCl]_2$. Thus, the IR spectrum of the solid condensate formed at 77 K showed, in addition to the absorptions characteristic of Et−Ga moieties,[25] prominent bands at 1961 and 708 cm^{-1}, implying the presence of terminal Ga−H bonds.[5,6,22] The ^{1}H NMR spectrum of a toluene-d_8 solution at room temperature pointed to the presence of both trans- **(2a)** and cis-isomers **(2b)** of the $[Et(H)GaCl]_2$ molecule. Raising the temperature of the residue to 333 K led to the vaporization of a second fraction, also a liquid at room temperature but with a Raman spectrum which identified it as $[Et_2GaCl]_2$.[25]



2a



2b

Experimental Section

(a) Synthesis and Manipulation of Monochlorogallane; Chemical Studies and Reagents. The vacuum-line methods used for the preparation and manipulation of monochlorogallane and related compounds have been described elsewhere.[2,5,6] The thermal instability and reactivity of monochlorogallane made it difficult to determine the mass of a sample prior to any chemical reaction. Hence, it was necessary typically to treat the sample with a measured quantity of the reagent, judged to be in excess, under the appropriate conditions, then to separate and identify the components of the reaction mixture (usually on the basis of their vibrational and/or NMR spectra), and, where appropriate, to assay one or more of these components (e.g., by manometric measurements or elemental analysis). The reaction itself was carried out in a sealed, preconditioned all-glass ampule equipped with a break-seal.

The following reagents, from the commercial sources indicated, were purified before use by fractionation in vacuo: NH_3 (B.O.C.) and C_2H_4 (B.O.C.). Toluene-d_8 and benzene, both supplied by Aldrich, were dried and fractionated in vacuo prior to use as solvents. Trimethylamine was prepared by the action of alkali on $[NMe_3H]^+Cl^-$ (Aldrich); fractional condensation in vacuo gave a sample judged to be pure by the criteria of tensimetric and IR measurements.

(b) Spectroscopic Measurements and Analysis. IR Spectra were recorded using one of three spectrometers, a Perkin-Elmer Model 580 dispersive (4000−200 cm^{-1}), a Mattson "Polaris" FT-IR (4000−400 cm^{-1}), or a Mattson "Galaxy" FT-IR instrument (4000−400 cm^{-1}). Raman spectra were excited either at λ = 514.5 nm with a Spectra-Physics Model 165 Ar^+ laser or at 632.8 nm with a He−Ne laser and measured with a Spex Ramalog 5 spectrophotometer operated with a computerized data-handling center or with a Dilor "Labram" system, respectively; the resolution was normally 2 cm^{-1}. Solid deposits of volatile materials were presented for spectroscopic analysis by allowing the vapor to condense on a CsI window (for IR measurements) or a copper block (for Raman measurements) contained in an evacuated glass shroud and maintained at 77 K.

^{1}H NMR measurements on toluene-d_8 solutions at temperatures ranging between 193 and 293 K were made at 250, 300, or 500 MHz using a Bruker Model AM250, a Bruker AM300, or a Varian UNITYplus 500 instrument, respectively. ^{71}Ga NMR measurements over the

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Table 4. Vibrational Frequencies (cm^{-1}) for the Products Formed from the Reaction between Monochlorogallane and Trimethylamine[a]

IR of solid film at 77 K	Raman shift of crystalline solid at room temp.	IR in benzene solution[b]	species	assignment
2980 m	2986 w	2970 sh m	$Me_3N{\cdot}GaH_2Cl$	ν(C−H)
2935 m	2944 w	2936 m		
2913 m	2920 w	2914 m		
2894 m		2883 m		
	2866 w	2864 m		
		2840 w	$Me_3N{\cdot}GaH_2Cl$	overtones and combinations of $\delta(CH_3)$ modes
		2818 w		
	2803 w	2804 w		
		2770 m		
		2729 w		
1909 vs	1911 vs	1905 vs	$Me_3N{\cdot}GaH_2Cl$	ν(Ga−H)
		1899 sh vs		
1831 s			$(Me_3N)_2{\cdot}GaH_2Cl$	ν(Ga−H)
1478 s	1472 m	1447 m	$Me_3N{\cdot}GaH_2Cl$	$\delta_{asym}(CH_3)$
1467 s				
1448 sh	1450 m	1438 sh w		
1407 m	1411 w	1409 m	$Me_3N{\cdot}GaH_2Cl$	$\delta_{sym}(CH_3)$
		1395 sh w		
1252 m	1241 w	1250 m	$Me_3N{\cdot}GaH_2Cl$	$\rho(CH_3)$
1230 sh		1235 w		
1105 w	1110 vw	1105 m		
1205 w			$(Me_3N)_2{\cdot}GaH_2Cl$	$\rho(CH_3)$
1020 m				
1000 s	998 s	996 m	$Me_3N{\cdot}GaH_2Cl$	ν_{asym}(C−N)
828 m	826 s	824 m	$Me_3N{\cdot}GaH_2Cl$	ν_{sym}(C−N)
		819 sh m		
731 vs	734 m	730 vs	$Me_3N{\cdot}GaH_2Cl$	$\delta(GaH_2)$
677 vs	682 m	710 sh s		
610 vw	607 w	603 m	$Me_3N{\cdot}GaH_2Cl$	$\delta(GaH_2)$
515 sh	520 m		$Me_3N{\cdot}GaH_2Cl$	ν(Ga−N)
492 m	494 m	491 s		
335 s	340 s	345 m	$Me_3N{\cdot}GaH_2Cl$	ν(Ga−Cl)

[a] vs very strong; s strong; m medium; w weak; vw very weak; sh shoulder; br broad. [b] Values taken from ref 22.

same temperature range were made at 152.335 MHz using the Varian system; chemical shifts were referenced to $[Ga(OH_2)_6]^{3+}$.[20]

Elemental analyses were performed by the Analytische Laboratorien, Engelskirchen, Germany, or by the analytical services of the Inorganic Chemistry Laboratory at Oxford.

(c) X-ray Crystallography. A crystal of $Ga^+[GaCl_3H]^-$ was immersed in highly viscous perfluoropolyether under argon, very quickly mounted on a glass fiber, and placed in the cold stream of an Oxford Cryosystems low-temperature device[26] attached to an Enraf-Nonius DIP2020 image-plate diffractometer. Measurements were thus made with the crystal at 100 K using graphite-monochromated Mo Kα radiation. Other details are given in Table 1.

(i) Data Collection and Processing. Of the 5667 reflections measured ($1 < \theta < 27°$; $-6 \leq h \leq 6$, $-8 \leq k \leq 8$, $-18 \leq l \leq 18$) 1096 were unique, giving 888 reflections with $I > 3\sigma(I)$. The images were processed with the DENZO and SCALEPACK programs.[27] Corrections for Lorentz and polarization effects and for absorption ("multiscan") were made.

(ii) Structure Solution and Refinement. The crystal structure was solved by direct methods[28] and refined by full-matrix least squares with anisotropic displacement parameters for all non-hydrogen and isotropic displacement parameters for the hydrogen atoms. Fifty-one refined parameters from 888 observations gave an observation: refined parameter ratio of 17:1. Corrections for secondary extinction were applied, and the refinement was completed using a three-term Chebyshev weighting scheme[29] with the coefficients 1.53, 0.641, and 1.16. Refinement on F converged at $R = 0.029$, $R_w = 0.035$, and GOF = 1.067. Despite being surrounded by heavy atoms, the unique hydrogen atom could be reliably located through the combination of good crystal quality, low crystal temperature, and the use of image plate technology for data collection.[30] All calculations made use of the CRYSTALS program package,[31] neutral atom scattering factors being taken from ref 32. The CAMERON program[33] was used to produce Figure 1.

(d) Theoretical Calculations. Density functional theory (DFT) calculations were performed by using the GAUSSIAN98 program package[34] and applying the B3LYP method, which has been shown to give satisfactory results for small group 13 metal compounds.[35]

(e) Chemical Properties of Monochlorogallane. (i) Thermal Decomposition. When heated to 373 K for 4 days to ensure complete

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decomposition, a sample of monochlorogallane (48.5 mg, 0.452 mmol GaH_2Cl) gave 0.41 mmol of H_2 and 47.7 mg of a slightly grayish solid shown by elemental analysis to have the composition GaCl (Found: Ga, 66.0; Cl, 34.0; GaCl requires Ga, 66.3; Cl, 33.7%).

(ii) Reactions with Anionic Hydride Derivatives. Details of these experiments are given elsewhere.[5−8] Essential features are the use of evacuated, rigorously preconditioned, all-glass apparatus; freshly prepared, finely divided solid reagents; and low temperature for all parts of the apparatus, including those accessible by the vapors of the products. The volatile products could be removed under continuous pumping and fractionated; the relevant gallane $[GaH_3]_n$, $[GaBH_6]_n$, or GaB_3H_{10} could thus be isolated in yields up to 80% based on eq 3 and the amount of monochlorogallane taken. Subsequent characterization included chemical and spectroscopic analysis, physical and chemical trapping, and structure determination of the gaseous molecules by electron diffraction.

(iii) Reaction with NMe_3. Monochlorogallane (72 mg, 0.67 mmol GaH_2Cl) reacted with an excess of NMe_3 at 178 K. Evaporation of the material that was volatile at 250 K (unchanged NMe_3) showed that 0.68 mmol of NMe_3 had been consumed, corresponding to a stoichiometry Me_3N:GaH_2Cl of 1.01:1. The white, solid product was characterized by its Raman spectrum (see Table 4). On the other hand, the IR spectrum of the annealed solid film formed by condensing the vapor of this adduct with a small excess of NMe_3 on a CsI window at 77 K showed, in addition to absorptions associated with $Me_3N{\cdot}GaH_2Cl$,[18] extra features attributable to the formation of a second adduct $(Me_3N)_2GaH_2Cl$ at low temperatures (see also Table 4). Raising the temperature of the deposit to 250 K under continuous pumping resulted in the decay of these features.

(iv) Reaction with NH_3. Monochlorogallane (188 mg, 1.75 mmol GaH_2Cl) reacted with an excess of NH_3 at 195 K. After 2 h, the material that was volatile at this temperature (NH_3) was evaporated to leave a white solid found to be stable at room temperature. Hence, it was found that 3.66 mmol of NH_3 had been consumed, corresponding to a stoichiometry NH_3:GaH_2Cl of 2.09:1. Elemental analysis of the solid confirmed the composition $H_2GaCl{\cdot}2NH_3$ (Found: Ga, 48.8; Cl, 24.8; $H_2GaCl{\cdot}2NH_3$ requires Ga, 49.4; Cl, 25.1%). The IR spectrum of the solid showed the following bands in the region 4000−400 cm^{-1} (wavenumbers in cm^{-1}; s strong, m medium, w weak, br broad, sh shoulder): 3280 s, 3166 s, br [ν(N−H)]; 1972 sh, 1915 m [ν(Ga−H)]; 1618 w, br [$\delta_{as}(NH_3)$]; 1407 w [impurity]; 1327/1303 m [$\delta_s(NH_3)$]; 789 m, br [$\rho(NH_3)$]; 734 m [$\delta(GaH_2)$]; 648 w [$\rho(GaH_2)$]; 475/451 w [ν(Ga−N)].

(v) Reaction with C_2H_4. Monochlorogallane reacted neither with neat C_2H_4 at 178 K nor in isopentane solution with an overpressure of C_2H_4 (450 mmHg) at 250 K. However, a benzene solution of the gallane (257 mg, 2.40 mmol GaH_2Cl) reacted with C_2H_4 (overpressure 2 atm) at room temperature. After 24 h, evaporation of the material that was volatile at 250 K (C_2H_4 and C_6H_6) revealed that 2.89 mmol of C_2H_4 had been consumed, corresponding to a stoichiometry C_2H_4:GaH_2Cl of 1.20:1. The residue consisted of a colorless, viscous liquid which gave two fractions on volatilization in vacuo, first at 303 and then at 333 K.

The solid formed by condensing the vapor of the more volatile fraction at 77 K gave an IR spectrum with the following absorptions in the region 4000−400 cm^{-1}: 2959 s, 2930 sh, 2901 s, 2871 s, 2805 w, 2733 w, 1961 s, br [ν(Ga−H)], 1461 m, 1414 m, 1377 w, 1239/1205 w, 1013 m, 962/945 m, 708 m, 672 s, 602 s, br, 551/521 m. The ^1H NMR spectrum of a toluene-d_8 solution at 223 K exhibited two sets of resonances, **A** and **B**, with relative intensities ca. 3:1, the more intense features (**A**) being appreciably broader than the weaker ones (**B**). The resonances comprised (*a*) triplets at δ_H 1.25 (**A**) and 1.14 (**B**) [$GaCH_2CH_3$], (*b*) quartets at δ_H 0.66 (**A**) and 0.46 (**B**) [$GaCH_2CH_3$], and (*c*) broad singlets at δ_H 6.08 (**A**) and 5.53 (**B**) [terminal GaH]. The results are consistent with the presence of trans- and cis-isomers of the dimeric compound $[Et(H)GaCl]_2$ (**2a** and **2b**, respectively), although it is not possible to identify with any confidence which isomer is which. Derivatives containing fewer or more ethyl groups, $Et(H)Ga(\mu\text{-}Cl)_2GaH_2$ and $Et_2Ga(\mu\text{-}Cl)_2Ga(H)Et$, are likely also to be formed at some stage, but the comparative simplicity of both the ν(Ga−H) region of the IR spectrum and the ^1H NMR spectrum argues against their presence as more than minor constituents, at least under the conditions of these experiments.

The less volatile component, vaporizing at ca. 333 K in vacuo, was also a liquid at room temperature. This displayed a Raman spectrum identical in all essential respects with that reported previously for $[Et_2GaCl]_2$,[25] the absence of significant scattering in the region 1600−2000 cm^{-1} appearing to rule out the retention of any Ga−H bonds.

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Supporting Information Available: Full crystallographic data are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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