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Decomposition of Monochlorogallane, $[H_2GaCl]_n$, and Adducts with Amine and Phosphine Bases: Formation of Cationic Gallane Derivatives

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Thermal decomposition of monochlorogallane, $[H_2GaCl]_n$, at ambient temperatures results in the formation of subvalent gallium species. To $Ga[HGaCl_3]$, previously reported, has now been added a second mixed-valence solid, $Ga_4[HGaCl_3]_2[Ga_2Cl_6]$ (**1**), the crystal structure of which at 150 K shows a number of unusual features. Adducts of monochlorogallane, most readily prepared from the hydrochloride of the base and $LiGaH_4$ in appropriate proportions, include not only the 1:1 molecular complex $Me_3P \cdot GaH_2Cl$ (**2**), but also 2:1 amine complexes which prove to be cationic gallane derivatives, $[H_2Ga(NH_2R)_2]^+Cl^-$, where R = ^tBu (**3a**) or ^sBu (**3b**). All three of these complexes have been characterized crystallographically at 150 K.

1. Introduction

The partially chlorinated derivatives of gallane $[H_nGaCl_{3-n}]_m$ ($n = 1$ or 2) are distinctly more robust than the parent compound.[1-4] Nevertheless, the weakness and lability of the Ga−H bond causes them to share with gallane itself both reducing properties and the ability to enter into hydrogallation reactions. Not only does the chlorine act as a ligand to produce Lewis acids stronger than GaH_3 but, by its ability also to support Ga^I and Ga−Ga bonded species, it makes the chlorogallanes potentially useful as sources of subvalent gallium compounds. In this last respect, there is an obvious parallel with halogenated derivatives of indium(III) hydride, which have been shown to act as an entry point to subvalent indium chemistry, as exemplified by the formation of $[In_5Br_8(quin)_4]^-$ (quin = quinuclidine).[5] From the first report in 1965,[6] for example, dichlorogallane has been shown (i) to react with various organic substrates as either a radical mediator, like tributyltin hydride,[7] or to bring about hydrogallation,[8] (ii) to form complexes with a variety of donors, e.g. quinuclidine,[9] substituted pyridines,[10] and PCy_3,[11] (iii) to act via metathesis as a source of other monohydrogallanes, e.g. $[\{^tBuN_2(CH)_2\}GaH]_2$,[12] and (iv) to function via thermal decomposition as a precursor to subvalent gallium compounds, e.g. $Ga[GaCl_4]$ and $[GaCl_2(PEt_3)]_2$.[13] Monochlorogallane is somewhat less robust and more difficult to handle, but since first reported in 1988,[14] it too has found applications, primarily through metathesis as a source of not only gallane itself[1] but also other monosubstituted derivatives of gallane, e.g. H_2GaBH_4,[15] $H_2GaB_3H_8$,[16] and H_2GaN_3.[17] Mo-

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lecular complexes with bases such as NMe_3,[18] quinuclidine,[9] and PCy_3[11] have been described, although the 1:2 complex with NH_3 is believed on the evidence of its IR spectrum to be more aptly formulated as $[H_2Ga(NH_3)_2]^+Cl^-$.[18] That monochlorogallane also provides a route into subvalent gallium chemistry is demonstrated by the finding[18] that thermal decomposition at ambient temperatures releases H_2 and gives rise to a mixture of products that includes the mixed valence compound $Ga[HGaCl_3]$.

Here we report the isolation of a second solid decomposition product of monochlorogallane, formed presumably from $Ga[HGaCl_3]$. This has been shown by X-ray analysis of a single crystal at 150 K to be the mixed-valence compound $Ga_4[HGaCl_3]_2[Ga_2Cl_6]$ (**1**) featuring three distinct Ga^I centers with different coordination environments (including, unusually, a near-square planar arrangement). Complexes of monochlorogallane are more easily prepared not from the isolated compound but by the reaction of the hydrochloride of the base (or the base + HCl) with $LiGaH_4$ in appropriate proportions. Crystallographic characterization at 150 K shows that the 1:1 complex of H_2GaCl with Me_3P is made up of neutral $Me_3P{\cdot}GaH_2Cl$ molecules (**2**), whereas the corresponding 1:2 complexes with primary amines provide the first authenticated examples of cationic gallium hydrides in $[H_2Ga(NH_2R)_2]^+Cl^-$ [R = ^{t}Bu (**3a**) or ^{s}Bu (**3b**)].

2. Results and Discussion

2.1. Decomposition of Monochlorogallane: Characterization of $Ga_4[HGaCl_3]_2[Ga_2Cl_6]$, 1. As reported previously,[14,18,19] monochlorogallane was prepared by the reaction of gallium(III) chloride with an excess of trimethylsilane (eq 1). It is a relatively viscous liquid which decomposes slowly at ambient temperatures and more rapidly at temperatures above 353 K, ultimately with the formation of $Ga[GaCl_4]$, gallium metal, and dihydrogen.[18] The vapor is composed of dimeric $H_2Ga(\mu\text{-}Cl)_2GaH_2$ molecules, with the properties of the liquid and the solid implying a higher degree of aggregation in the condensed phases, although the solid has so far eluded attempts at crystallographic characterization.[19,20]

$$\frac{1}{2}[GaCl_3]_2 + 2Me_3SiH \rightarrow \frac{1}{n}[H_2GaCl]_n + 2Me_3SiCl \quad (1)$$

Earlier studies of the decomposition of monochlorogallane in vacuo at room temperature succeeded in isolating crystals of the mixed-valence intermediate $Ga[HGaCl_3]$, an optimum yield of which was realized in about 14 days.[18] We have enlarged upon these studies by leaving a sample of the compound at 0 °C in an evacuated Pyrex glass ampule for a period of 3 months while checking the progress of any change by reference to the Raman spectrum of the original liquid[21] and of any solid subsequently formed. After 4 weeks, colorless crystalline plates were observed to have formed on the walls of the vessel; these could be identified as $Ga[HGaCl_3]$ on the basis of their Raman spectrum.[18] After 8 weeks, the crystalline plates had disappeared, giving place to a white crystalline solid **1** and a white powder. The white powder was shown by its Raman spectrum[22] to be the well-known compound $Ga[GaCl_4]$. The Raman spectrum of the crystalline solid **1** resembled quite closely that of $Ga[HGaCl_3]$[18] with prominent scattering at 1978 and 336 cm^{-1} suggestive of ν(Ga−H) and ν(Ga−Cl) vibrations, respectively. However, additional scattering at 377 and, more conspicuously, at 234 cm^{-1} gave the first hint[23] that the $[HGaCl_3]^-$ anion was accompanied by the gallium−gallium-bonded dianion $[Ga_2Cl_6]^{2-}$. No further change in the contents of the ampule occurred after an additional 4 weeks at 0 °C, at least to judge by the Raman spectra of the solids.

Hence the product **1** was found to be long-lived at 0 °C. It decomposed slowly at room temperature with the evolution of dihydrogen gas and formation of gallium metal and a white solid appearing to be $Ga[GaCl_4]$. A single crystal at 150 K was shown by X-ray diffraction to be the new mixed-valence compound $Ga_4[HGaCl_3]_2[Ga_2Cl_6]$. The structure is notable for including no less than five distinct gallium centers: (i) two different four-coordinated Ga centers in the $[HGaCl_3]^-$ and $[Ga_2Cl_6]^{2-}$ units; (ii) an eight-coordinated Ga^I cation; (iii) a six-coordinated Ga^I cation; (iv) a four-coordinated Ga^I cation. Figure 1a−c shows the essential features of these three environments, while Figure 2 is a packing diagram. Crystallographic details are given in Table 1, and selected bond lengths and interbond angles of the $[HGaCl_3]^-$ and $[Ga_2Cl_6]^{2-}$ units in Table 2.

The $[HGaCl_3]^-$ anions approximate quite closely to C_{3v} symmetry with a mean Ga−Cl bond length of 2.219 Å and Cl−Ga−Cl angle of 103.9°, values not significantly different from those reported previously (2.210 Å and 104.0°) for the same anion in $Ga[HGaCl_3]$ at 100 K.[18] For comparison, the mean Ga−Cl bond length in $[GaCl_4]^-$ in $Ga[GaCl_4]$ is 2.180(2) Å.[24] The Cl atoms of the $[HGaCl_3]^-$ anion each form either a single or a double bridge with one of the nearest Ga^I centers ($Ga^I\cdots Cl$ = 3.02−3.49 Å). Hence, the anions fulfill a multifunctional bridging role for the surrounding Ga^I cations analogous to that of the same anions and $[GaCl_4]^-$ in the compounds $Ga[HGaCl_3]$[18] and $Ga[GaCl_4]$,[24] respectively.

The $[Ga_2Cl_6]^{2-}$ ion contains a Ga−Ga bond measuring 2.4070(9) Å with roughly tetrahedral coordination of each of the Ga atoms. The pyramidal $GaCl_3$ units are characterized by Ga−Cl distances and Cl−Ga−Cl angles averaging to

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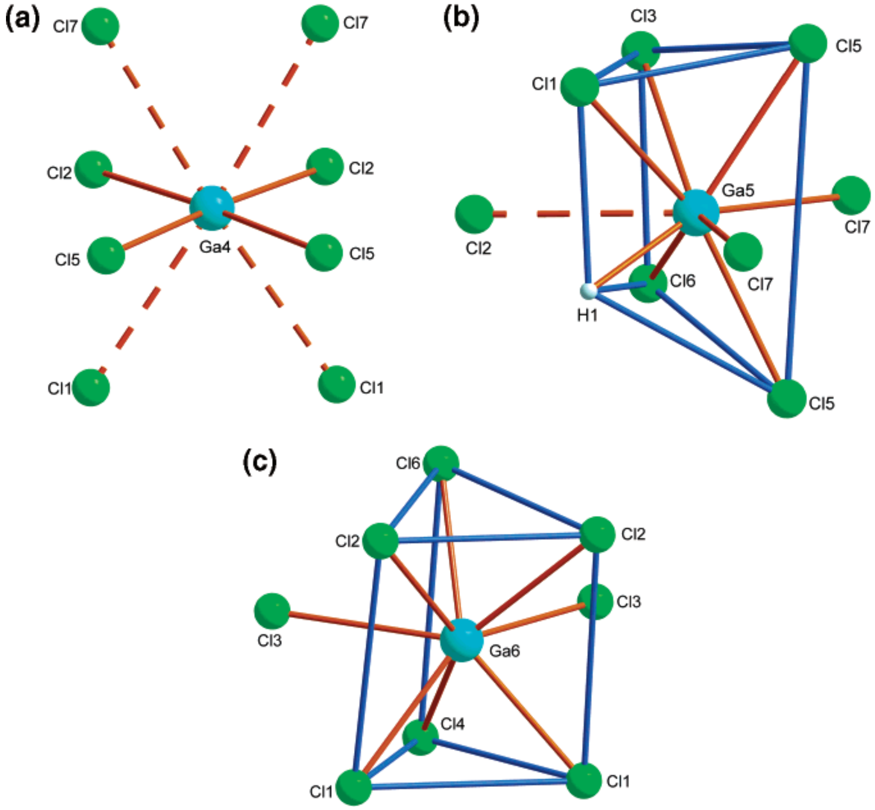

Figure 1. (a) Coordination about the Ga^{I} site Ga4 which resides on a site with *m* symmetry. Bonds to Cl2 and Cl5 are shorter [Ga4···Cl2 3.0270(12) and Ga4···Cl5 3.1101(13) Å] than to Cl1 and Cl7 [Ga4···Cl1 3.4879(14) and Ga4···Cl7 3.4727(14) Å]. (b) Coordination about the Ga^{I} site Ga5. The six contacts to H and Cl form a distorted trigonal prism with Ga5···H1 2.41 Å and Ga···Cl in the range 3.07−3.30 Å. The three "capping" contacts span 3.26−3.47 Å, the longest being shown as a broken line. Distances (Å): Ga5···Cl1, 3.0715(11); Ga5···Cl5 3.1519(12); Ga5···Cl5, 3.1567(12); Ga5···Cl6, 3.1935(9); Ga5···Cl3, 3.3028(12); Ga5···Cl7, 3.2591(12); Ga5···Cl7, 3.3801(13); Ga5···Cl2, 3.4660(12). (c) Coordination about the Ga^{I} site Ga6. Ga6, Cl4, and Cl6 all occupy sites with *m* symmetry. The six shortest contacts form a trigonal prism with Ga···Cl distances spanning 3.04−3.13 Å; two longer contacts (3.25 Å) then occur to capping Cl3 atoms. Distances (Å): Ga6···Cl6, 3.0462(14); Ga6···Cl1, 3.0668(11); Ga6···Cl2, 3.0970(12); Ga6···Cl4, 3.1319(15); Ga6···Cl3, 3.2504(11) Å.

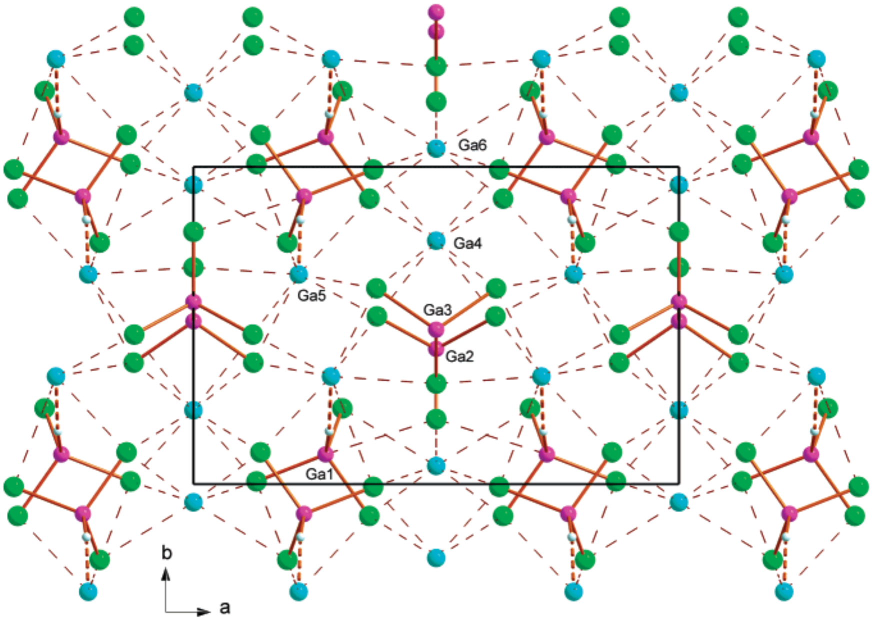

Figure 2. Packing in **1** as viewed along the *c*-axis. Ga^{I} (Ga4−Ga6) and Ga^{II} and Ga^{III} (Ga1−Ga3) sites are shown in turquoise and magenta, respectively.

2.231 Å and 102°, respectively. Hence the Ga−Cl bonds are bent away from the Ga−Ga bond (Ga−Ga−Cl$_{av}$ = 116°), in keeping with the expectations of VSEPR theory.[25] The dimensions are consistent with those reported in earlier crystallographic studies of compounds containing the $[Ga_2Cl_6]^{2-}$ ion (average distances in Å, angles in deg): $Li_2Ga_2Cl_6$, Ga−Ga 2.391, Ga−Cl 2.238, Ga−Ga−Cl 113.7;[26]

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Table 1. Crystallographic Data for Compounds **1**, **2**, and **3a**,**b**

param	**1**	**2**	**3a**	**3b**
empirical formula	$H_2Cl_{12}Ga_8$	$C_3H_{11}ClGaP$	$C_8H_{24}ClGaN_2$	$C_8H_{24}ClGaN_2$
fw	985.18	183.26	253.46	253.46
cryst dimens (mm)	0.47 × 0.39 × 0.39	0.04 × 0.12 × 0.09	0.50 × 0.19 × 0.18	0.82 × 0.48 × 0.20
cryst system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pmn2_1$	$P2_1/m$	$P2_1/c$	$P2_1/n$
unit cell dimens				
a (Å)	14.193(3)	6.215(3)	8.3160(8)	5.6404(2)
b (Å)	9.2745(19)	9.704(3)	10.7950(11)	11.4417(4)
c (Å)	8.0839(16)	7.286(3)	15.2538(16)	21.3438(9)
β (deg)		115.153(6)	96.351(2)	96.744(2)
V (Å^3)	1064.1(4)	397.7(3)	1360.9(2)	1367.91(9)
Z	2	2	4	4
d(calcd) (Mg m^{-3})	3.075	1.530	1.237	1.231
abs coeff (mm^{-1})	11.454	3.887	2.182	2.171
θ_{max} (deg)	29.22	28.27	26.39	25.00
reflcns measd	13 881	2507	7818	12 018
unique reflcns (R_{int})	2795 (0.0321)	1012 (0.0208)	2786 (0.022)	2408 (0.0427)
no. of params	101	46	133	105
conventional R [$F > 4\sigma(F)$]	0.0218	0.0464	0.0260	0.0660
weighted R (F^2 and all data)	0.0448	0.1023	0.0637	0.1815
goodness-of-fit on F^2 (S)	1.004	1.178	0.9661	1.131
largest difference peak/hole (e Å^{-3})	+0.925/−0.511	+0.95/−0.56	+0.62/−0.27	+1.221/−0.914

Table 2. Selected Distances (Å) and Interbond Angles (deg) for the Anions in $Ga_4[HGaCl_3]_2[Ga_2Cl_6]$, **1**, at 150 K[a]

$[HGaCl_3]^-$		$[Ga_2Cl_6]^{2-}$	
Ga(1)−Cl(1)	2.2254(9)	Ga(2)−Ga(3)	2.4070(9)
Ga(1)−Cl(2)	2.2269(9)	Ga(2)−Cl(4)	2.1902(13)
Ga(1)−Cl(3)	2.2052(10)	Ga(2)−Cl(5)	2.2549(9)
		Ga(2)−Cl(5)$^{\#1}$	2.2549(9)
		Ga(3)−Cl(6)	2.2278(13)
		Ga(3)−Cl(7)	2.2282(10)
		Ga(3)−Cl(7)$^{\#1}$	2.2282(10)
Cl(1)−Ga(1)−Cl(3)	105.69(4)	Cl(4)−Ga(2)−Cl(5)	103.11(4)
Cl(2)−Ga(1)−Cl(3)	104.22(4)	Cl(4)−Ga(2)−Cl(5)$^{\#1}$	103.11(4)
Cl(1)−Ga(1)−Cl(2)	101.87(3)	Cl(5)−Ga(2)−Cl(5)$^{\#1}$	100.42(5)
		Cl(4)−Ga(2)−Ga(3)	124.00(4)
		Cl(5)−Ga(2)−Ga(3)	111.67(3)
		Cl(5)#−Ga(2)−Ga(3)	111.67(3)
		Cl(6)−Ga(3)−Cl(7)$^{\#1}$	99.89(4)
		Cl(6)−Ga(3)−Cl(7)	99.89(4)
		Cl(7)−Ga(3)−Cl(7)$^{\#1}$	103.46(6)
		Cl(6)−Ga(3)−Ga(2)	121.47(4)
		Cl(7)$^{\#1}$−Ga(3)−Ga(2)	114.70(3)
		Cl(7)−Ga(3)−Ga(2)	114.70(3)

[a] See Figure 1 for atom labeling. Symmetry transformation used to generate equivalent atoms: (#1) $-x + y, y, z$.

$[Ph_3PH]_2[Ga_2Cl_6]$, Ga−Ga 2.407, Ga−Cl 2.209, Ga−Ga−Cl 116.7;[27] $[Me_4N]_2[Ga_2Cl_6]$, Ga−Ga 2.390, Ga−Cl 2.196, Ga−Ga−Cl 113.9.[28] In **1**, as in $Li_2Ga_2Cl_6$,[26] the ion adopts an eclipsed conformation approximating to D_{3h} symmetry that contrasts with the staggered ethane-like conformation found in $[Ph_3PH]_2[Ga_2Cl_6]$[27] and $[Me_4N]_2[Ga_2Cl_6]$.[28] While being less favorable for the isolated ion, the eclipsed geometry probably reflects the influence of secondary interactions, for example by maximizing the number of $Ga-Cl\cdots M^I$ contacts the $[Ga_2Cl_6]^{2-}$ ions establish with neighboring M^I cations (M = Ga or Li).

In comparison with the Ga^{III} centers, all three different Ga^I centers feature environments that are more diffuse and involve coordination numbers that may be judged to range from 4 to 8 for $Ga^I\cdots Cl$ contacts between 3.027 and 3.303 Å (as against 3.55 Å for the sum of the relevant van der Waals radii[29]). We consider each of the three centers in turn.

(i) Most unusual is the four-coordinated Ga^I center which adopts a nearly square-planar geometry with relatively short $Ga\cdots Cl$ contacts of 3.027 (×2) and 3.110 (×2) Å and a trans Cl−Ga−Cl angle of 176.3°. This is the first example of a Ga^+ ion to be found in such an environment, as compared with the more commonly observed eight-coordinated one.[18,24] Closer inspection reveals that it also possesses four other significantly longer $Ga\cdots Cl$ contacts of 3.473 (×2) and 3.488 (×2) Å, respectively (see Figure 1a). Accordingly, the center may be viewed as being coordinated by eight chlorines situated at the corners of a distorted square-based prism and thus revealing the kind of unsymmetrical hemidirected environment often favored by metal ions formally possessing an ns^2 valence shell.[30,31]

(ii) As indicated in Figure 1b, the atoms of the six-coordinated shell of the second Ga^I center make up a very distorted trigonal prism with five $Ga\cdots Cl$ contacts ranging from 3.072 to 3.303 Å and one $Ga\cdots H$ contact of 2.41 Å. With respect to the $[HGaCl_3]^-$ ions, the Ga^+ ion establishes a $Ga\cdots H$ distance much shorter (by 0.36 Å) than that found in $Ga[HGaCl_3]$;[18] the $Ga\cdots Cl$ distance (3.072 Å) is also at the short end of the range (3.069−3.552 Å) displayed by $Ga[HGaCl_3]$. In addition, however, there are three other $Ga\cdots Cl$ contacts in excess of 3.2 Å (3.259, 3.380, and 3.466 Å) that go to complete an irregular tricapped trigonal prism. With the inclusion of these longer interactions, the coordination shell of the Ga^+ ion can be seen to resemble that in $Ga[HGaCl_3]$.[18] In both cases, the barytes structure $Ba[SO_4]$[18,32,33] provides a point of reference. The eight shortest

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Ba⋯O contacts in that structure are replaced by seven shortest Ga⋯Cl contacts and one Ga⋯H contact. A ninth (longest) contact is then formed through what would be a rectangular face of the trigonal prism.

(iii) The eight-coordinated Ga^+ ion in **1** has eight Ga⋯Cl contacts at distances ranging from 3.046 to 3.250 Å, which can be separated into two sets of Ga⋯Cl interactions with average distances of 3.075 Å (×5) and 3.211 Å (×3). The six shortest contacts form what again approximates to a trigonal prism with Ga⋯Cl distances spanning 3.05−3.13 Å; the two longer contacts (3.25 Å) then complete a bicapped trigonal prism (see Figure 1c). The resulting polyhedron can also be regarded as approximating a bisdisphenoid such as that defining the coordination shell of Ca in scheelite, $Ca[WO_4]$.[32] Significantly, too, it prefigures the eight-coordinated environment of Ga^I in $Ga[GaCl_4]$,[24] i.e., one of the ultimate solid products of thermal decomposition of monochlorogallane.

Earlier studies[18] have indicated that ligand scrambling precedes the elimination of H_2 in the decomposition of liquid monochlorogallane. One such product, $H(Cl)Ga(\mu\text{-}Cl)_2GaH_2$, is then thought to lose H_2 with the formation of $Ga[HGaCl_3]$, while a second, $H_2Ga(\mu\text{-}Cl)(\mu\text{-}H)GaH_2$, decomposes to H_2, Ga metal, and $Ga[GaCl_4]$. On the evidence of the present studies, solid $Ga[HGaCl_3]$ decomposes slowly at 0 °C to **1** without any change in the proportions Ga:Cl = 2:3. Half of the $[HGaCl_3]^-$ ions eliminate H_2, presumably by pairwise interaction of adjacent ions and so give rise in **1** to the $[Ga_2Cl_6]^{2-}$ anion. **1** could thus be regarded as a double salt composed of 2 mol of $Ga[HGaCl_3]$ and 1 mol of $Ga_2[Ga_2Cl_6]$; unsurprisingly, therefore, it retains some of the structural features of $Ga[HGaCl_3]$.[18] $Ga_2[Ga_2Cl_6]$ would correspond to a binary gallium chloride with the composition Ga_2Cl_3. No such compound has been described, the solid with this composition being apparently unstable at normal temperatures to disproportionation into Ga metal and $Ga[GaCl_4]$.[30] By contrast, Ga_2Br_3 is known, being stable at temperatures up to 154 °C. Its crystal structure[34] confirms that it is indeed to be formulated as $Ga_2[Ga_2Br_6]$ with eclipsed Ga_2Br_6 units. There are two different environments for the Ga^I centers, one eight-coordinated, roughly cubic, and the other nine-coordinated, roughly tricapped trigonal prismatic (cf. **1**). The structure of the bromide is also noteworthy for some relatively close Ga^I⋯Ga^I contacts and for the vacancy it leaves in the Ga^I partial structure, implying the formulation $Ga_4\square[Ga_4Br_{12}]$ and leading to significant Ga^+ ion conductivity. Both these features may have a bearing on the instability of the corresponding chloride, $Ga_2[Ga_2Cl_6]$, but it is evident that this is effectively a key intermediate in the decomposition of $Ga[HGaCl_3]$, ultimately to H_2, Ga, and $Ga[GaCl_4]$.

2.2. Complexes of Monochlorogallane with Nitrogen and Phosphorus Bases.

Earlier experiments have established[18] that monochlorogallane adds NH_3 or NMe_3 to form a 1:2 or 1:1 adduct presumed on the evidence of its vibrational spectrum to feature either a cationic gallane unit in $[H_2Ga(NH_3)_2]^+Cl^-$ or a neutral molecule in $Me_3N{\cdot}GaH_2Cl$. However, the comparative difficulty of preparing, purifying, and manipulating monochlorogallane[18,19] has led to the devising of an alternative route to such complexes. For example, the groups of Gladfelter[9] and Raston[11] have prepared molecular complexes of the type base·GaH_2Cl by hydride/chloride redistribution between species such as base·$GaHCl_2$ and base·GaH_3 (base = quinuclidine or PCy_3). We have also used hydride/chloride exchange reactions to prepare a 1:1 complex of GaH_2Cl with Me_3P (**2**) and 1:2 complexes with $^tBuNH_2$ (**3a**) and $^sBuNH_2$ (**3b**). The method, involving in effect the reaction of the base hydrochloride with $LiGaH_4$ in ether solution, is essentially analogous to that normally favored to access the corresponding GaH_3 complexes[36,37] but with appropriate changes in the relative proportions of gallium and chloride, as in eq 2 for example.

$$2[\text{baseH}]^+Cl^- + LiGaH_4 \rightarrow [(\text{base})_2GaH_2]^+Cl^- + 2H_2 + LiCl \quad (2)$$

(a) Trimethylphosphine−Monochlorogallane, $Me_3P{\cdot}GaH_2Cl$, 2. This was synthesized, like $Me_3P{\cdot}GaH_3$,[37] from freshly prepared $LiGaH_4$ and 1 mol equiv of Me_3P but with an excess of HCl, in dry Et_2O solution at room temperature. It was isolated as a white solid at room temperature, purified by sublimation in vacuo at 50 °C, and characterized by its IR and Raman spectra and by the ^1H NMR spectrum of a toluene-d_8 solution. The Raman spectrum of the solid included, in addition to the features characteristic of internal vibrations of the Me_3P unit,[38] scattering at 1889.5, 759/724, 538, and 349 cm^{-1}. Most prominent of these is the band at 1889.5 cm^{-1} clearly identifiable with the ν(Ga−H) modes of a GaH_2 unit, occurring at higher wavenumber than the corresponding modes of $Me_3P{\cdot}GaH_3$ (average 1816 cm^{-1} [38]) but at lower wavenumber than those of matrix-isolated H_2GaCl (average 1962 cm^{-1} [39]). The other extra bands can be attributed to $\delta(GaH_2)$, $\rho(GaH_2)$, ν(Ga−P), and ν(Ga−Cl) motions, although coupling of some of these motions is likely, as in $Me_3P{\cdot}GaH_3$,[38] to preclude simple descriptions of the vibrations at wavenumbers <700 cm^{-1}. The spectroscopic properties are thus consistent with the formulation of **2** as a simple molecular complex, $Me_3P{\cdot}GaH_2Cl$.

Such a structure has been confirmed by X-ray analysis of a single crystal at 150 K. Crystallographic details are given in Table 1, and selected molecular dimensions in the legend to Figure 3. The compound resembles closely the gallane complex $Me_3P{\cdot}GaH_3$[40] featuring monomeric $Me_3P{\cdot}GaH_2Cl$ molecules with a distorted tetrahedral geometry about the metal center and no hint of significant intermolecular

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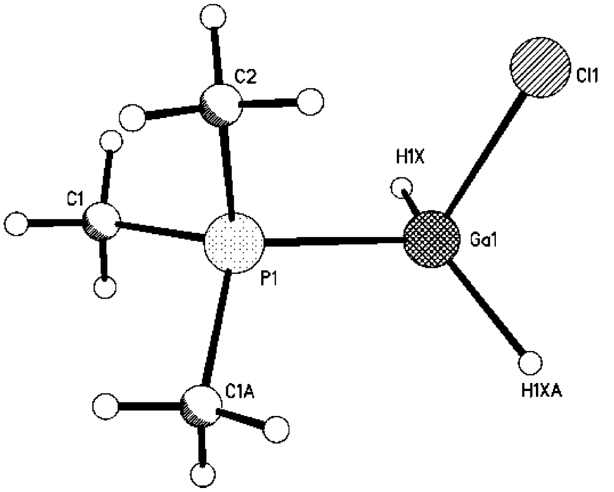

Figure 3. Structure of crystalline $Me_3P{\cdot}GaH_2Cl$, **2**. Atoms C1, P1, Ga1, and Cl1 lie on a crystallographic mirror plane. Bond distances (Å): Ga1−Cl1, 2.237(2); Ga1−P1, 2.3797(18); P1−C2, 1.791(6); P1−C1, 1.795(4). Angles (deg): Cl1−Ga1−P1, 100.48(6); C2−P1−C1, 106.3(2); C1A−P1−C1, 105.2(3); C2−P1−Ga1, 112.2(2); C1−P1−Ga1, 113.17(15). "A" refers to the symmetry operator (x, $-y + 3/2$, z).

interactions. At 2.3797(18) Å, the Ga−P distance is not significantly different from that in either $Me_3P{\cdot}GaH_3$ [2.3857(6) Å][40] or $Cy_3P{\cdot}GaH_2Cl$ [2.403(4) Å][11] but longer than that in $Me_3P{\cdot}GaCl_3$ [2.352(2) Å].[41] The Ga−Cl distance [2.237(2) Å] is somewhat longer than those found or predicted in $Me_3P{\cdot}GaCl_3$,[41] $Cy_3P{\cdot}GaH_2Cl$,[11] and free H_2GaCl [39] [2.171(2), 2.107(8), and 2.169 Å, respectively]. There is no clear pattern to the Ga−P and Ga−Cl bond lengths, and it is likely that, with bonds as polar as these, the general influence of the permittivity of the crystal environment as a whole or the particular influence of specific intermolecular interactions is at least as important as that of the acid strength of the GaH_nCl_{3-n} unit (expected to follow the order $GaH_3 < GaH_2Cl < GaCl_3$). Another noteworthy feature of crystalline **2** is the eclipsed conformation adopted by the $Me_3P{\cdot}GaH_2Cl$ molecules. In this respect, it resembles $Me_3P{\cdot}GaH_3$[40] and $Me_3P{\cdot}GaCl_3$[41] but differs from $Cy_3P{\cdot}GaH_2Cl$,[11] $Cy_3P{\cdot}GaH_3$,[43] and quin·$GaHCl_2$,[9] the molecules of which have a staggered conformation. That the eclipsed structure should be favored by any of these compounds points to crystal packing or intermolecular forces as a factor that may or may not overcome the natural preference of the free molecule for a staggered conformation, depending on the bulk of the substituents at the donor atom.

(b) 2:1 *tert*-Butylamine and *sec*-Butylamine Complexes of Monochlorogallane, $[H_2Ga(NH_2R)_2]^+Cl^-$, R = ^{t}Bu (3a) and ^{s}Bu (3b). Our recent studies of the adducts formed by gallane with the primary amines $MeNH_2$, $^tBuNH_2$, and $^sBuNH_2$[44] have led to the preparation and isolation of the 1:2 adducts of GaH_2Cl with $^tBuNH_2$ (**3a**) and $^sBuNH_2$ (**3b**).

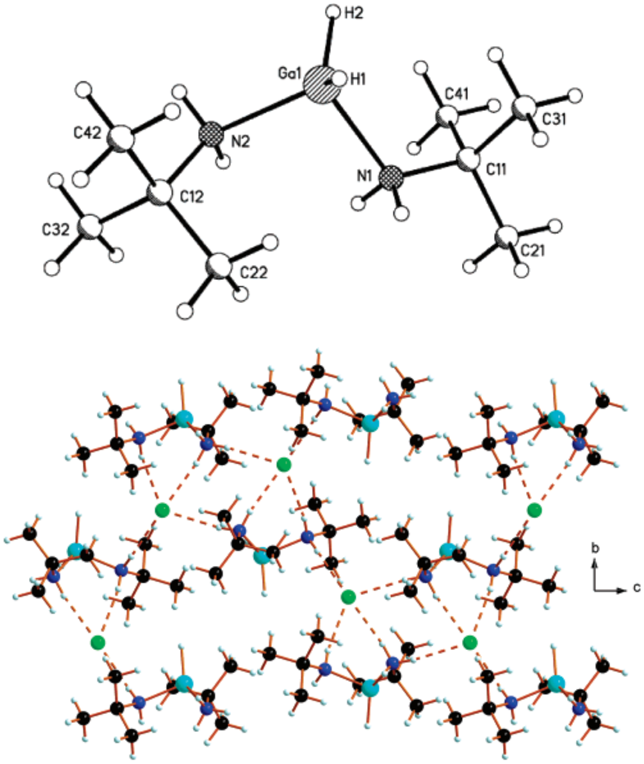

Figure 4. Structure of crystalline $[H_2Ga(NH_2{}^tBu)_2]Cl$, **3a**, showing the cation and a packing plot that highlights the NH···Cl hydrogen bonds with H···Cl = 2.5 Å.

Such compounds are of interest as potential sources of cyclic amido- or cagelike imidogallanes.[4,30,45] Prepared in accordance with eq 2, both are white, sublimable solids (cf. **2**) lastingly stable in vacuo at room temperature. Unlike **2**, they do not dissolve readily in organic solvents with which they do not react. The Raman spectra of the solids show numerous features attributable to internal vibrations of the coordinated amine molecule but, in addition, significant scattering at 1927/1910 and 762/733 cm^{-1} (**3a**) and 1923 and 740 cm^{-1} (**3b**). The intense bands at 1920−1930 cm^{-1} patently correspond to ν(Ga−H) vibrations, the high wavenumber contrasting with those of the corresponding vibrations of $Me_3P{\cdot}GaH_2Cl$ (1889.5 cm^{-1}), quin·GaH_2Cl (1892 cm^{-1} [9]), and $MeH_2N{\cdot}GaH_3$ (1815 cm^{-1} [44]). Indeed, the wavenumber is comparable with that found for the ν(Ga−H) modes (1915 cm^{-1}) in the 1:2 complex of monochlorogallane with NH_3 believed to contain cationic $[H_2Ga(NH_3)_2]^+$ units.[18]

The first definitive structural evidence of a base-supported $GaH_2{}^+$ cation has now been provided by X-ray analysis of a single crystal of **3a** at 150 K. This confirms the spectroscopic evidence that the solid comprises an array of $[H_2Ga(NH_2{}^tBu)_2]^+$ cations (Figure 4) and Cl^- anions. Selected dimensions of the cation are given in Table 3. The shortest interionic contacts are those between Cl^- and the N−H protons (ranging from 2.365 to 2.461 Å as against 2.95 Å for the sum of the relevant van der Waals radii[29]); the shortest Ga···Cl distance is >4 Å, well in excess of the normal range for covalent $Ga^{III}{\cdots}Cl$ interactions (cf. **2**). The cation is characterized by Ga−H and Ga−N distances averaging

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Table 3. Selected Distances (Å) and Interbond Angles (deg) in the $[H_2Ga(NH_2{}^tBu)_2]^+$ Cation of **3a**

	Distances[a]		
Ga(1)−N(1)	2.0163(15)	C(11)−C(31)	1.520(3)
Ga(1)−N(2)	2.0180(15)	C(11)−C(41)	1.521(3)
Ga(1)−H(1)	1.575(9)	N(2)−C(12)	1.511(2)
Ga(1)−H(2)	1.583(9)	N(2)−H(12)	0.897(9)
N(1)−C(11)	1.508(2)	N(2)−H(22)	0.896(9)
N(1)−H(11)	0.899(9)	C(12)−C(22)	1.522(3)
N(1)−H(21)	0.894(9)	C(12)−C(32)	1.526(3)
C(11)−C(21)	1.522(3)	C(12)−C(42)	1.523(3)
	Angles[a]		
N(1)−Ga(1)−N(2)	97.55(6)	Ga(1)−N(2)−C(12)	122.20(12)
N(1)−Ga(1)−H(1)	106.3(8)	Ga(1)−N(2)−H(12)	103.7(13)
N(2)−Ga(1)−H(1)	111.4(8)	Ga(1)−N(2)−H(22)	105.8(14)
N(1)−Ga(1)−H(2)	107.7(8)	C(12)−N(2)−H(12)	108.2(13)
N(2)−Ga(1)−H(2)	106.1(8)	C(12)−N(2)−H(22)	108.1(14)
H(1)−Ga(1)−H(2)	124.5(12)	C(21)−C(11)−C(31)	111.07(16)
Ga(1)−N(1)−C(11)	120.08(11)	C(21)−C(11)−C(41)	110.34(16)
Ga(1)−N(1)−H(11)	104.8(14)	C(31)−C(11)−C(41)	110.96(16)
C(11)−N(1)−H(11)	108.9(15)	H(12)−N(2)−H(22)	108.1(20)
Ga(1)−N(1)−H(21)	105.4(14)	N(2)−C(12)−C(22)	108.03(15)
C(11)−N(1)−H(21)	110.3(14)	N(2)−C(12)−C(32)	108.04(16)
H(11)−N(1)−H(21)	106.5(18)	N(2)−C(12)−C(42)	107.73(16)
N(1)−C(11)−C(21)	107.64(15)	C(22)−C(12)−C(32)	110.36(17)
N(1)−C(11)−C(31)	107.94(15)	C(22)−C(12)−C(42)	111.74(17)
N(1)−C(11)−C(41)	108.78(14)	C(32)−C(12)−C(42)	110.80(17)

[a] See Figure 4 for atom labeling.

1.579(9) and 2.017(2) Å and by H−Ga−H and N−Ga−N angles of 124.5(12) and 97.55(6)°, respectively. The Ga−N bonds are thus at the short end of the range found for coordinate links involving a tetracoordinated gallium hydride acceptor and a nitrogen donor (1.988−2.134 Å [4,44]). The two *tert*-butyl groups are bent away from the metal, giving Ga−N−C angles of 120.1(1) and 122.2(1)°, and are arranged mutually trans to each other. Despite the reduction in steric repulsion thus achieved and unremarkable internal dimensions for the coordinated $^tBuNH_2$ molecules, relatively close Ga•••H contacts of 2.83 and 2.89 Å are established between the metal and a hydrogen of one of the CH_3 groups carried by each amine (cf. 3.22 Å for the sum of the relevant van der Waals radii[29]). As shown in Figure 4, a network of hydrogen bonding engages the Cl^- anions with the NH_2 groups of the coordinated amine molecules.

Perhaps the closest analogy is provided by the cation $[Me_2Ga(NH_2{}^tBu)_2]^+$ isolated as the bromide following the reaction of Me_2GaBr with $^tBuNH_2$.[46] Although this features a slightly longer average Ga−N distance of 2.040(7) Å, the geometry is generally much like that of $[H_2Ga(NH_2{}^tBu)_2]^+$, with a wide C−Ga−C angle [121.5(5)°] and a narrow N−Ga−N one [95.6(3)°]. Cationic alane derivatives of the type $[H_2AlL]^+[AlH_4]^-$ have been prepared by treatment of $Me_3N{\cdot}AlH_3$ with a tridentate or macrocyclic tetradentate nitrogen base L.[47] The crystal structures determined for the compounds with L = $(Me_2NC_2H_4)_2NMe$ and Me_4Cyclam reveal cations with the structures **I** and **II** displaying Al−H distances and H−Al−H angles of 1.62/1.82 Å and 132° (**I**) and 1.60/1.64 Å and 171° (**II**), respectively. The penta- and hexacoordinated Al centers contrast with the tetracoordinated Ga center of $[H_2Ga(NH_2{}^tBu)_2]^+$, illustrating yet again the way in which aluminum significantly more than gallium favors coordination numbers greater than 4.[30]

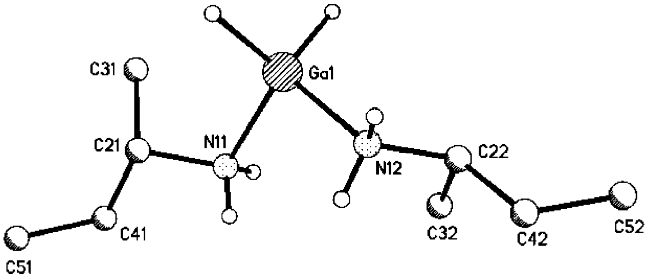
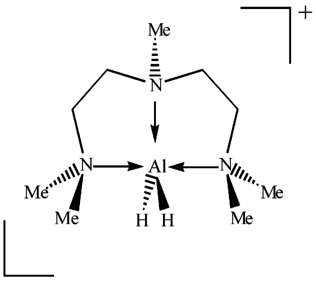


Figure 5. Structure of the framework of the cation in $[H_2Ga(NH_2{}^sBu)_2]$-Cl, **3b**.



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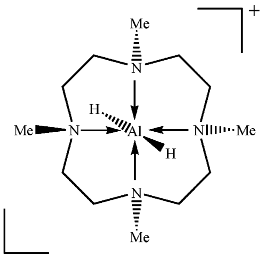

II

X-ray analysis of a single crystal of the *sec*-butylamine derivative **3b** at 150 K was frustrated by complete disordering of the amine fragments, making it impossible to establish more than a rudimentary structure. Nevertheless, the results are in keeping with the formulation $[H_2Ga(NH_2{}^sBu)_2]^+Cl^-$. The cation appears to have a skeletal geometry similar to that of the cation in **3a** (see Figure 5), with Ga−N distances of 1.998(5) and 2.027(5) Å and an N−Ga−N angle of 99.5(2)°. Unsurprisingly in the circumstances, none of the hydrogen atoms could be located.

3. Experimental Section

3.1. General Methods. The vacuum-line methods used for the preparation, purification, and manipulation of monochlorogallane have been described previously.[1−3,19] Elemental analyses were mostly ruled out by problems of scale and/or reactivity but were performed, where possible, by the analytical service of the Inorganic Chemistry Laboratory at Oxford. IR spectra were recorded in the range 4000−400 cm^{-1} with a Nicolet Magna 560 FTIR spectrometer, typically at a resolution of 1 cm^{-1}. Raman spectra were excited at $\lambda = 632.8$ nm with a He−Ne laser and recorded with a Dilor "Labram" 14/23IM instrument, typically for 10 accumulations each with a duration of 10 s; the resolution was normally 2 cm^{-1}. ^1H NMR measurements were made at 500 MHz using a Varian UNITY-plus spectrometer, and mass spectra (of **3a**) were recorded with a Micromass GCTof instrument with field ionization, using a temperature-programmed solid probe inlet.

All the source materials (LiH, $GaCl_3$, Me_3SiCl, $LiAlH_4$, Me_3P, $^tBuNH_2$, and $^sBuNH_2$) and toluene-d_8 were from Aldrich. LiH and $GaCl_3$ were used without purification, Me_3SiCl and Me_3P were purified before use by fractionation in vacuo, and $LiAlH_4$ was purified before use (to prepare Me_3SiH) by recrystallization from Et_2O. Toluene-d_8 was purified after drying over sodium by fractionation in vacuo. $^tBuNH_2$ and $^sBuNH_2$ were each converted

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to the corresponding hydrochloride which was recrystallized from dry $EtOH/Et_2O$.

3.2. Decomposition of Monochlorogallane: Characterization of $Ga_4[HGaCl_3]_2[Ga_2Cl_6]$, 1. To study the thermal decomposition, a small sample of monochlorogallane (ca. 100 mg) was isolated in a sealed, preconditioned all-glass ampule equipped with a break-seal. The progress of the change at 0 °C was monitored by periodic reference to the Raman spectrum of the liquid and/or solid contents of the ampule. Crystals of **1** formed after 8 weeks were selected and transferred under dry nitrogen to a Schlenk tube for storage and transport prior to X-ray analysis of an individual crystal. The scale was insufficient to permit elemental analysis of **1**, and NMR measurements could not be made since the crystals were not appreciably soluble in any organic solvent with which they did not react. Raman spectrum (wavenumbers in cm^{-1}): 1978 s ($[HGaCl_3]^-$), 607 w ($[HGaCl_3]^-$), 589 w ($[HGaCl_3]^-$), 377 w ($[Ga_2Cl_6]^{2-}$), 336 m ($[HGaCl_3]^-$), ca. 315 sh ($[Ga_2Cl_6]^{2-}$), 234 s ($[Ga_2Cl_6]^{2-}$).[18,23]

3.3. $Me_3P{\cdot}GaH_2Cl$, 2. This was prepared on the millimole scale in yields of ca. 60% by a method similar to that used for the synthesis of $Me_3P{\cdot}GaH_3$[37] but with an excess of HCl. After filtering of the reaction mixture, the Et_2O solvent was evaporated from the solution under vacuum. Heating the white solid residue, also under vacuum, to 50 °C resulted in sublimation of white crystals of **2**. Raman spectrum (wavenumbers in cm^{-1}): 2985 s, 2915 vs, 1889.5 s [ν(Ga−H)], 1424 w, 1121 w, 966 w, 759 m/724 w [$\delta(GaH_2)$], 672 m, 642 mw, 538 mw, 349 w. ^1H NMR ($C_6D_5CD_3$): δ 5.54 (s 2, GaH_2), 0.81 (d 9, CH_3).

3.4. $[H_2Ga(NH_2{}^tBu)_2]Cl$, 3a. This was prepared on the millimole scale in yields of ca. 20% by the reaction of $LiGaH_4$ with $[^tBuNH_3]Cl$ in Et_2O solution at room temperature following a procedure analogous to that described previously for the synthesis of $Me_3N{\cdot}GaH_3$[36] but adding the $LiGaH_4$ to the $[^tBuNH_3]Cl$ which was therefore in excess. The product was purified by fractional condensation at pressures $<10^{-4}$ Torr. A sample of **3a** was stored at 273 K for 3 weeks whereupon small colorless crystals formed on the walls of the vessel. Anal. Found: Cl, 13.7; Ga, 27.6%. Calcd for $C_8H_{24}ClGaN_2$: Cl, 14.0; Ga, 27.5%. Raman spectrum (wavenumbers in cm^{-1}): 3214 w, 3142 w, 2982 s, 2916 s, 2873 mw, 2796 w, 2734 w, 1927 vs/1910 m [ν(Ga−H)], 1479/1460 w, 1323/1310 w, 1220 w, 1164 w, 1032 w, 937 w, 912 mw, 762/733 m [$\delta(GaH_2)$], 686 w, 608 mw, 546 m, 504 mw, 431 w, 391 vw, 367 vw, 270 mw. Field ionization MS (*m*/*e*): $[M]^+$ 253/255, $[M - {}^tBuNH_2]^+$ 180/182, $[^tBuNH_2]^+$ 73.

3.5. $[H_2Ga(NH_2{}^sBu)_2]Cl$, 3b. Prepared from $LiGaH_4$ and $[^sBuNH_3]Cl$ in yields of less than 5% by a method similar to that used for **3a**, the product was purified by fractional condensation. When a sample of **3b** was stored at 273 K for 6 months, small platelike crystals formed on the walls of the vessel. Raman spectrum (wavenumbers in cm^{-1}): 3077 mw, 2980 ms, 2930 s, 2913 ms, 2881 m, 1923 s [ν(Ga−H)], 1466 mw, 1126 w, 1044 w, 1005 w, 921 w, 835 mw, 740 m, 605 w, 485 m, br.

3.6. X-ray Crystallography. Table 1 gives crystal data and other information on the structure determination and refinement for single crystals of **1**, **2**, and **3a**,**b**. Each set of measurements was made on a crystal mounted under perfluoropolyether oil on a glass fiber. X-ray diffraction data [λ(Mo Kα) = 0.710 73 Å] were collected on a Bruker Smart Apex diffractometer, the temperature of the crystal being controlled at 150 K by an Oxford Cryosystems CRYOSTREAM device.[48] Absorption corrections were performed using the program SADABS.[49] The structures of **1** and **3a**,**b** were solved by Patterson methods (DIRDIF[50]), and that of **2** was solved by direct methods (SHELXS);[51] full-matrix least-squares refinement (against F^2) was accomplished with the programs SHELXL[52] for **1**, **2**, and **3b** or CRYSTALS[53] for **3a**. The H atom attached to Ga in **1** was modeled with the Ga−H distance fixed at 1.6 Å, being placed in a calculated position and allowed to ride on its parent atom. H atoms attached to Ga in **2** and to Ga and N in **3a** were located in difference maps and refined freely; those remaining were placed in calculated positions. Non-hydrogen atoms were assigned anisotropic displacement parameters.

The structure of **3b** is extensively disordered. Both ^{s}Bu ligands are disordered over two orientations (60:40 for ligand 1 and 50:50 for ligand 2, where ligands 1 and 2 are based on N11 and N12, respectively). In the major fraction of ligand 1 the terminal C atom of the ethyl moiety is further disordered over three positions. In one fraction of ligand 2 the ethyl group is distributed over two sites. It is likely that disorder is, in reality, more extensive than described here, as some displacement parameters of the disordered methyl groups adopted very high values and a single overall U_{iso} had to be adopted for these groups. All chemically equivalent bond distances and angles were restrained to be similar. Only full-weight atoms were refined with anisotropic displacement parameters. The identity of the chloride anion was inferred from H-bonding to the NH groups. N···Cl interactions imply that the N is doubly protonated. At ca. 100°, the N−Ga−N angle implies that the Ga, too, is attached to two H atoms; these were placed in symmetrical positions assuming r(Ga−H) = 1.6 Å.

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Supporting Information Available: ORTEP plots and crystallographic data in CIF format for all the compounds **1**, **2**, and **3a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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