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Ring Systems Containing Anionic and Cationic Gallium Centers: Structural and Bonding Considerations

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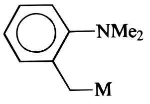
The metathetical reaction of 2-(dimethylamino)benzyllithium (Bz^NLi) with $GaCl_3$ afforded the salt $[Bz^N{}_2Ga][GaCl_4]$ (**4**), the X-ray crystal structure of which revealed a four-coordinate cationic gallium center featuring two Ga−C σ-bonds and two N→Ga dative bonds. (Crystal data for **4**: monoclinic, space group $P2_1/n$, $a = 11.519(2)$ Å, $b = 18.254(4)$ Å, $c = 12.506(3)$ Å, $\beta = 117.40(3)°$, $V = 2334.6(9)$ Å^3, $Z = 4$, $R = 0.545$). Two Ga···Cl interionic contacts, while somewhat long, are sufficiently strong to render the geometry of $\mathbf{4}^+$ roughly midway between tetrahedral and octahedral. Treatment of 1,4-di-*tert*-butyl-1,4-diazabutadiene (DAB) with 2 equiv of $GaCl_3$ afforded $[(DAB)GaCl_2][GaCl_4]$ (**7**), which, by means of X-ray analysis, was shown to possess a cation ($\mathbf{7}^+$) with localized C═N bonds and N→Ga dative interactions with a $[GaCl_2]^+$ moiety. (Crystal data for **7**: orthorhombic, space group *Pbca*, $a = 11.882(2)$ Å, $b = 17.289(3)$ Å, $c = 20.424(4)$ Å, $V = 4195.5(11)$ Å^3, $Z = 8$, $R = 0.460$). The structure of $\mathbf{7}^+$ is relevant to discussions of the bonding in both neutral DAB complexes of the group 13 elements and the skeletally isoelectronic anion $[Me_4C_4GaCl_2]^-$ ($\mathbf{9}^-$). The structure of the $[NEt_4]^+$ salt of the latter (**9**) has been determined by X-ray diffraction. (Crystal data for **9**: monoclinic, space group $P2_1/n$, $a = 9.967(1)$ Å, $b = 13.073(2)$ Å, $c = 15.345(2)$ Å, $\beta = 96.76(1)°$, $V = 1985.5(4)$ Å^3, $Z = 4$, $R = 0.721$).

Introduction

Structurally authenticated organometallic cations of gallium(III) remain rare. Although the existence of the base-stabilized $[GaMe_2]^+$ cation was reported over 60 years ago,[1] it was only in 1992 that the structure of the bis(*tert*-butylamine) complex of this cation was established by X-ray crystallography.[2,3] An alternative strategy for stabilizing organogallium cations of this type is to employ intra- rather that intermolecular Lewis base complexation. Such a strategy has proved to be viable for the synthesis of $[M(C(SiMe_3)_2C_5H_4N)_2][MCl_4]$ (M = Al(III), Ga(III)), the aluminum compound of which has been structurally characterized.[4] In the present study we have discovered that the use of ligand **1** (Bz^N) permitted the isolation of the salt $[Bz^N{}_2Ga][GaCl_4]$ which has been characterized by single-crystal X-ray diffraction.



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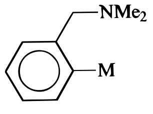

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The four-valence-electron cation $[GaCl_2]^+$ is highly electrophilic,[5] and in order to obtain isolable compounds featuring this species it is necessary to employ ample Lewis base coordination. The following salts have been structurally characterized and found to possess six-coordinate, octahedral cations: $[GaCl_2(bipy)_2][GaCl_4]$,[6] $[GaCl_2(py)_4][GaCl_4]$,[7] and $[GaCl_2(monoglyme)_2][GaCl_4]$.[8] In this contribution, we explore the use of the 1,4-di-*tert*-butyl-1,4-diazabutadiene (DAB) ligand for stabilization of the $[GaCl_2]^+$ entity, recognizing the considerable current interest in DAB rings that incorporate group 13[9] and 14[10] elements because of the question of circumannular delocalization.[11]

Results and Discussion

In contrast to the reaction of RLi (R = 2-(dimethylaminoethyl)phenyl (**2**)) with $GaCl_3$ which affords the covalent

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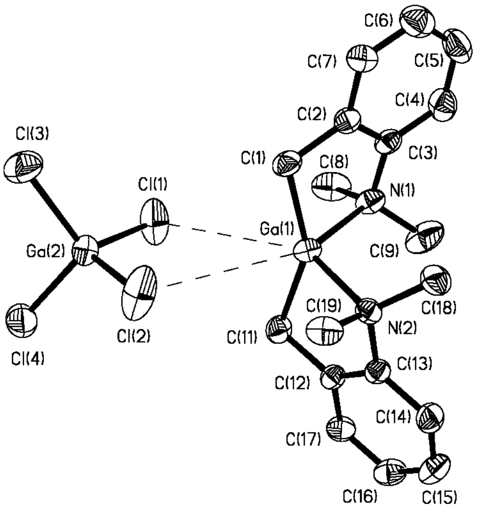
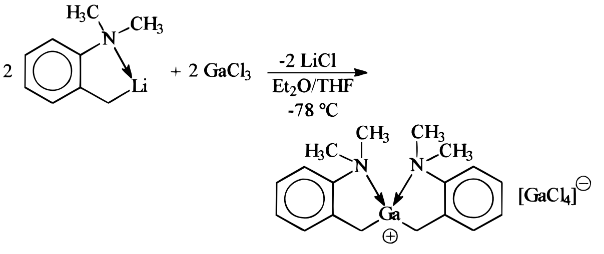


Figure 1. View of **4** showing the atom numbering scheme.

dichloride, $RGaCl_2$ (**3**),[12] the corresponding reaction of Bz^NLi with $GaCl_3$ results in the ionic alternative, $[Bz^N_2Ga][GaCl_4]$ (**4**) (eq 1). It was not immediately obvious that the colorless crystalline product was not the covalent dichloride, Bz^NGaCl_2. The proton NMR spectrum of **4** exhibited the anticipated resonances in the appropriate relative intensities for the Bz^N ligand (Experimental Section). Likewise, all of the expected ^{13}C NMR resonances were detected and identified in an attached proton test (APT) NMR experiment. The chemical ionization mass spectrum offered the first indication that an ionic product had formed. Thus, while no peak was discernible at *m*/*z* 273 corresponding to Bz^NGaCl_2, a peak due to a "dimer" of this composition was detected at *m*/*z* 546 accompanied by satellites of the appropriate intensities. Moreover, fragmentation peaks were recorded at *m*/*z* 511, 407, and 372 which are attributable to the loss of Cl, $GaCl_2$, and $GaCl_3$, respectively. Particularly significant is the observation that the 100% intensity peak is due to $[Bz^N_2Ga]^+$(*m*/*z* 337). Collectively, the MS data pointed toward an ionic formulation for **4**. However, to place this conjecture on a firmer basis it was necessary to undertake an X-ray crystallographic study.



(1)

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Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The X-ray analysis revealed that the solid state comprises an array of $[Bz^N_2Ga]^+$ and $[GaCl_4]^-$ ions. The structure of an ion pair is illustrated in Figure 1 and a selection of bond distances and angles appears in Table 1. The primary coordination sphere of the cation $\mathbf{4}^+$ features two N→Ga donor−acceptor bonds that emanate from the amine arms of the Bz^N ligand and two gallium−carbon σ-bonds. There are, however, two somewhat long contacts between two of the chloride ligands of the $[GaCl_4]^-$ anion and the cationic gallium center. These contact distances [Ga(1)···Cl(1) 3.693(2) Å and Ga(1)···Cl(2) 3.738(3) Å] greatly exceed typical covalent Ga−Cl bond distances (~2.18 Å in **3**[12]) but are slightly less than the sum of van der Waals distances for Ga and Cl (3.9 Å). Despite the length of the Ga···Cl interactions, their influence is apparent on the geometry of the gallium cation in the sense that a geometry is adopted which is approximately midway between tetrahedral and octahedral. Moreover, the interionic interactions are of sufficient strength to permit the detection of the M^+ species in a CI mass spectral experiment (*vide supra*).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Bz^N_2Ga][GaCl_4]$ (**4**), $[(DAB)GaCl_2][GaCl_4]$ (**7**), and $[Et_4N][Me_4C_4GaCl_2]$ (**9**)

Bond Distances for Compound **4**			
Ga(1)−C(1)	1.940(6)	Ga(1)−C(11)	1.957(6)
Ga(1)−N(1)	2.093(5)	Ga(1)−N(2)	2.092(5)
Ga(1)−Cl(1)	3.693(2)	Ga(1)−Cl(2)	3.738(3)
Bond Angles for Compound **4**			
C(1)−Ga(1)−C(11)	150.2(3)	C(1)−Ga(1)−N(1)	87.1(2)
N(1)−Ga(1)−N(2)	105.9(2)	C(11)−Ga(1)−N(2)	87.8(2)
Bond Distances for Compound **7**			
Ga(1)−N(1)	1.979(5)	Ga(1)−N(2)	1.982(6)
Ga(1)−Cl(1)	2.105(2)	Ga(1)−Cl(2)	2.104(2)
N(1)−C(1)	1.255(7)	N(2)−C(2)	1.251(8)
C(1)−C(2)	1.478(8)		
Bond Angles for Compound **7**			
N(1)−Ga(1)−N(2)	84.4(2)	l(1)−Ga(1)−Cl(2)	118.20(10)
Ga(1)−N(1)−C(1)	109.5(4)	Ga(1)−N(2)−C(2)	109.9(5)
N(1)−C(1)−C(2)	118.4(6)	N(2)−C(2)−C(1)	117.8(7)
Bond Distances for Compound **9**			
Ga(1)−C(1)	1.969(11)	Ga(1)−C(2)	1.948(12)
Ga(1)−Cl(1)	2.249(4)	Ga(1)−Cl(2)	2.231(4)
C(1)−C(2)	1.33(2)	C(3)−C(4)	1.33(2)
C(2)−C(3)	1.54(2)		
Bond Angles for Compound **9**			
C(1)−Ga(1)−C(4)	91.1(5)	Cl(1)−Ga(1)−Cl(2)	104.1(1)
Ga(1)−C(1)−C(2)	105.6(9)	Ga(1)−C(4)−C(3)	106.6(9)
C(1)−C(2)−C(3)	118.8(10)	C(2)−C(3)−C(4)	117.8(11)

The unsolvated cation $[GaMe_2]^+$ has not been characterized structurally. However, both by analogy with the structures of the heavier congeneric cations $[Me_2In]Br$[13] and $[Me_2Tl]Cl$[14] and on the basis of the VSEPR model,[15] a C−Ga−C bond angle of 180° would be anticipated. In the case of $\mathbf{4}^+$ this angle is 150.2(3)°. For comparison, the C−Ga−C bond angle is 121.2(5)° in the bis(amine) adduct $[Me_2Ga(t\text{-}BuNH_2)_2]^+$ ($\mathbf{5}^+$).[2] The larger C−Ga−C bond angle in $\mathbf{4}^+$ stems both from the "bite" of the chelating Bz^N ligand and also from the pair of Ga···Cl interionic contacts. Clearly, in the event of a very strong interaction between the anion/cation pair, the geometry of the cation would approach octahedral and the C−Ga−C moiety would be approximately linear. The only precedent of which we are aware for a cationic Ga−C bond distance is 1.98(1) Å in $\mathbf{5}^+$.[2] This average distance is very similar to that in $\mathbf{4}^+$ (1.948(6) Å) and, interestingly, it is commensurate with the Ga−C bond distance in the neutral chelated derivative **3** (1.951(2) Å).[12] The Ga−N bond distance in $\mathbf{4}^+$ (2.092(4) Å) exceeds those in **3** (2.071(2) Å) and $\mathbf{5}^+$ (2.039(8) Å) but is shorter than the distances reported for acyclic trialkylamine adducts: $Me_3Ga{\cdot}N(t\text{-}Bu)H_2$ (2.12(1) Å),[16] $2(Me_3SiCH_2)_3Ga{\cdot}NMe_2CH_2CH_2NMe_2$ (2.241(9) Å),[17] and $Me_3Ga{\cdot}N_4C_6H_{12}$ (2.138(9) Å).[18] As in the case of

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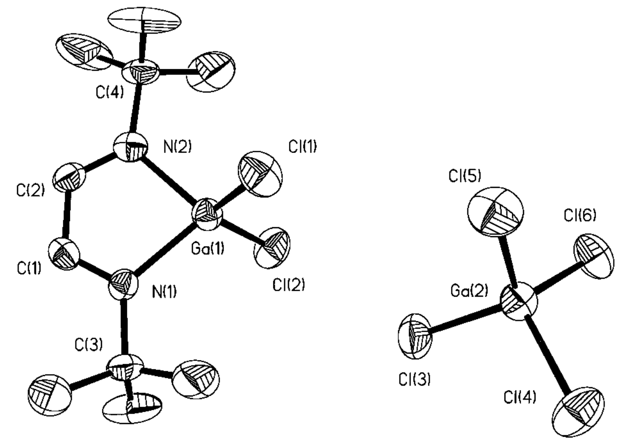
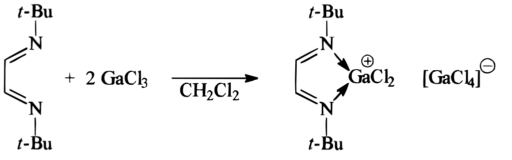


Figure 2. View of **7** showing the atom numbering scheme.

other ligands with coordinated amine arms,[19] the N→Ga−C−C−C rings are nonplanar and the "bite angles" at gallium (87.8(2) and 87.1(2)°) are very similar to that in *e.g.* **3** (87.44(7)°).[12] The metrical parameters for the $[GaCl_4]^-$ anion are unexceptional.

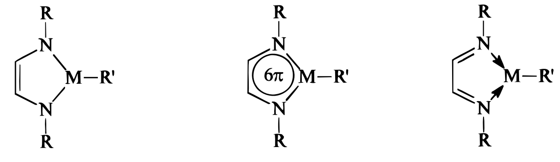
The reaction of the DAB ligand **6** with 2 equiv of $GaCl_3$ affords $[(DAB)GaCl_2][GaCl_4]$ (**7**) in 70% yield (eq 2). Proton



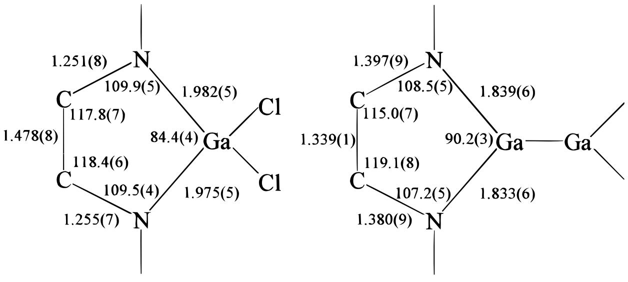
6 **7** (2)

and ^{13}C NMR data for **7** were indicative of a structure with two N=C bonds and two equivalent *t*-Bu groups. The ionic character of the product was suggested by the observation of a sharp cutoff corresponding to $[(DAB)GaCl_2]^+$ in the CI mass spectrum (*m*/*z* 307). The spectroscopic deductions were confirmed by a single-crystal X-ray diffraction study. Compound **7** crystallizes in the space group *Pbca* with 8 molecules per unit cell. The solid state structure consists of discrete anions and cations and, in contrast to the structure of **4**, there is no evidence for the existence of interionic contacts (Figure 2). As mentioned in the introduction, the metrical parameters for DAB ring systems involving group 13[9] and 14[10,11] elements are attracting significant recent attention on account of the possibility of aromatic behavior. In the context of neutral group 13 ring systems, the discussion can be couched in terms of canonical forms such as **A**, **B**, and **C**. Structure **A** involves a localized carbon−carbon double bond and localized nitrogen lone pairs, while in **B** circumannular delocalization has ensued. Structure **C** implies donor behavior on the part of a neutral DAB ligand, and by inference, the group 13 element is in the +1 oxidation state.

The aluminum and gallium structures that have been determined so far provide no support for Form **B** but tend to exhibit a more localized structure that does not involve significant conjugation between the nitrogen lone pairs and the group 13 element (Form **A**).[9] Indeed, some complexes of this type undergo dimerization *via* N→metal dative bonding. However, for further discussion and refinement of the electronic structures of these intriguing ring compounds it would be desirable to have a *bona fide* example of Structure **C**. Compound **7** is such a case, albeit as a cation. The bond distances and angles for this cation (Table 1) are compared below with those for the digallane (DAB)GaGa(DAB) (**8**),[9a] the latter having been chosen because it is base free and therefore the only species yet identified where Form **B** is possible.



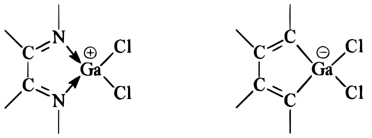
A **B** **C**



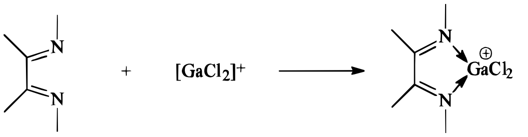
$\mathbf{7}^+$ **8**

The most conspicuous differences in the metrical parameters for the two rings are as follows: (i) the C−C bond distance in $\mathbf{7}^+$ is considerably longer than that in **8** and commensurate with a bond order of unity, (ii) the C−N bond distances in $\mathbf{7}^+$ are short and of appropriate length for carbon-nitrogen double bonds, (iii) the Ga−N bond distances in $\mathbf{7}^+$ are considerably longer than those in **8** and are of the same order as typical N→Ga donor−acceptor bond distances (*vide supra*), and (iv) the N−Ga−N bond angle is more acute in $\mathbf{7}^+$ than in **8**. Collectively, it is clear that the electronic structure of the gallium cation $\mathbf{7}^+$ is most aptly described by canonical form **C**.

Finally, attention is drawn to the isoelectronic relationship between the following two ions:



In terms of a qualitative fragment analysis these ring systems can be considered to have their parentage in the interaction of a $[GaCl_2]^+$ moiety with a 1,4-di-*tert*-butyl-1,4-diazabutadiene and 1,3-butadiene dianion as shown below in eqs 3 and 4, respectively. The tetramethyl derivative of the gallium anion has been isolated as the tetraethylammonium salt (**9**).[20] However, to our knowledge, the X-ray crystal structure has not been



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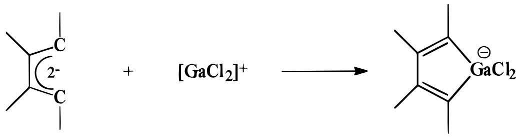

(4)

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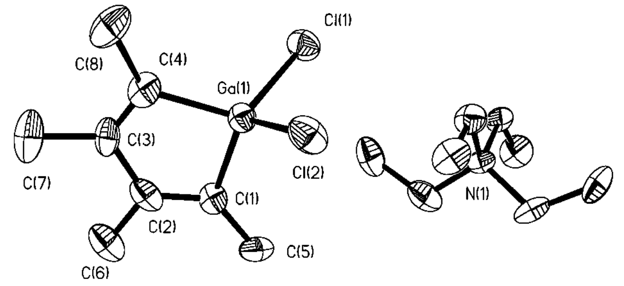
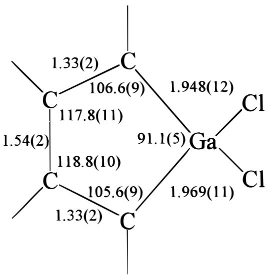
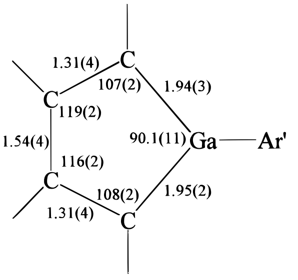


Figure 3. View of **9** showing the atom numbering scheme.



$\mathbf{9}^-$



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reported. Our interest in carrying out such an experiment was stimulated not only by the foregoing isoelectronic relationship but also by the possibility that the metrical parameters for the gallium anion might be relevant to a discussion of the bonding in gallacyclopentadienes (galloles).[21]

Compound **9** crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell. There are no unusually short interionic contacts, and the structure of an anion/cation pair is presented in Figure 3. The structure of the anion $\mathbf{9}^-$ is akin to that of the cation $\mathbf{7}^+$ in the sense that two double bonds within the ring are localized (Table 1). Thus, the C(1)−C(2) and C(3)−C(4) distances, which average 1.33(2) Å, are considerably shorter than the C(2)−C(3) distance of 1.54(2) Å. Moreover, both rings are planar and the patterns of bond angles within each ring are very similar, the major difference being the more acute angle at gallium in the cation $\mathbf{7}^+$. The geometries of the $GaCl_2$ moieties are, however, quite different in the anion and cation. The uncoordinated cation $[GaCl_2]^+$ is isolobal with $[CH_2]^{2+}$ and is anticipated to possess a linear geometry while $[GaCl_2]^-$, being a carbene analogue, is expected to possess a V-shaped structure. Incorporation of these fragments into five-membered rings is anticipated to cause a diminution of the Cl−Ga−Cl bond angle in both cases. Nevertheless, the anion would be expected to retain a smaller Cl−Ga−Cl bond angle than the cation. This is indeed the case and the difference in these bond angles in $\mathbf{7}^+$ and $\mathbf{9}^-$ exceeds 14°. Also consonant with the above arguments is the observation that the Ga−Cl bond distance in the anion $\mathbf{9}^-$ (2.240(4) Å) is larger than that in the cation $\mathbf{7}^+$ (2.104(2) Å).

Finally, it is pertinent to compare the structure of $\mathbf{9}^-$ with that of the neutral gallacyclopentadiene, (2,4,6-*t*-$Bu_3C_6H_2$)Ga(C_4Me_4) (**10**).[4] One of the bonding issues concerns the possibility of a π-type interaction between the carbon−carbon double bonds and a vacant 4p orbital on gallium. Such an interaction is precluded in $\mathbf{9}^-$ which can be regarded as a Lewis acid/base complex of Cl^- with the as-yet-unknown chloro-substituted gallacyclopentadiene, $ClGa(C_4Me_4)$. Although the X-ray crystal structure of **10** was not of stellar quality, it is clear that there is essentially no difference in the metrical parameters for the two ring systems.

Conclusions

Two new gallium cations have been synthesized and isolated as tetrachlorogallate salts. Both cations can be regarded as intramolecularly base-stabilized derivatives of $[R_2Ga]^+$. Although $\mathbf{4}^+$ is formally tetracoordinate, two somewhat weak Ga- - -Cl interactions from the counterion render the geometry approximately midway between tetrahedral and octahedral. The metrical parameters for $\mathbf{7}^+$ are pertinent to the current debate regarding diazabutadiene (DAB) complexes of the group 13 and related elements. It is concluded that the bonding in $\mathbf{7}^+$ is best described in terms of donor−acceptor interactions between a neutral DAB ligand and a $[GaCl_2]^+$ moiety. In the skeletally isoelectronic anion $\mathbf{9}^-$, the X-ray structure of which has also been determined, there is little evidence for a π-type interaction between the carbon−carbon double bonds and a vacant 4p orbital on gallium.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under a dry, oxygen-free argon atmosphere utilizing standard Schlenk manifold techniques or a Vacuum Atmospheres drybox. All solvents were dried and distilled under nitrogen immediately prior to use. 1,4-Di-*tert*-butyl-1,4-diazabutadiene[23] and Bz^NLi[24] were prepared following the literature procedures; other reagents were obtained from commercial suppliers and used without further purification. Colorless crystals of $[Et_4N][C_4Me_4GaCl_2]$ (**9**) were prepared following the literature procedure[20b] and recrystallized from tetrahydrofuran (mp 120−125 °C).

NMR spectra were recorded on a GE QE-300 spectrometer (^1H, 300.16 MHz; ^{13}C, 75.48 MHz), and chemical shifts are referenced to the solvent and are reported relative to $Si(CH_3)_4$ ($\delta = 0.00$). Low resolution mass spectra were obtained with a Finnigan MAT TSQ-70 triple stage quadrupole mass spectrometer operating in the chemical ionization mode with CH_4 as the ionizing gas. High resolution mass spectra were obtained using a VG Analytical ZAB2-E mass spectrometer operating in the chemical ionization mode with isobutane as the ionizing gas. Melting points were obtained in capillaries sealed under argon (1 atm) and are uncorrected. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA.

Preparation of 4. Gallium trichloride (3.15 g, 17.9 mmol) was dissolved in 50 mL of diethyl ether and cooled to −78 °C. To this solution was added a cold (−78 °C) solution of Bz^NLi dissolved in diethyl ether/THF (50 mL/15 mL) over a period of 1 h. The reaction mixture was allowed to stir and warm to room temperature overnight. The solvents were removed *in vacuo* and the solid residue was extracted with toluene (4 × 40 mL) and filtered through diatomaceous earth. The volume of the filtrate was reduced, and when this was allowed to stand at room temperature for several days, colorless cubic crystals of **4** were formed in 26% yield (1.3 g), mp 134−140 °C. ^1H NMR (C_6D_6): δ 2.33 (br s, 4 H, CH_2), 2.54 (br s, 12 H, NMe_2), 6.6−7.3 (m, 8 H, aromatic). ^{13}C\{APT\} NMR (C_6D_6): δ 18.6 (CH_2), 48.7 ($N(CH_3)_2$), 118.9 (aromatic *C*H), 125.8 (aromatic *C*H), 130.7 (aromatic *C*H), 132.4 (aromatic *C*H), 135.1 (quat, *C*CH_2), 149.0 (quat, *C*NMe_2). MS (CI+): *m/z* 546* (M, 5.8), 511* (M − Cl, 75.8), 407* ($Bz^N{}_2GaCl_2$, 6.0), 372* ($Bz^N{}_2GaCl$, 57.7), 337* ($Bz^N{}_2Ga$, 100.), 238* (Bz^NGaCl, 9.7) (an asterisk indicates the presence of an appropriate Ga_xCl_y isotope pattern). HRMS (CI+): calculated for $C_{18}H_{24}N_2Ga_2Cl_4$ (M^+), 545.920522; found 545.919049. Anal. Calcd for $C_{18}H_{24}N_2Ga_2Cl_4$: C, 39.93; H, 4.40; N, 5.10. Found: C, 39.50; H, 4.45; N, 4.98.

Preparation of 7. 1,4-Di-*tert*-butyl-1,4-diazabutadiene (4.30 g, 25.6 mmol) in 50 mL of CH_2Cl_2 was added over a period of *ca.* 15 min to

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a stirred solution of $GaCl_3$ (9.00 g, 51.1 mmol) in 150 mL of CH_2Cl_2. The clear yellow solution was stirred at room temperature for 1 h, following which the solvent and volatiles were removed *in vacuo*. The resulting solid was recrystallized from CH_2Cl_2 giving large pale yellow crystals of **7** (mp 155−156 °C) in 70% yield (9.35 g). ^1H NMR (CD_2Cl_2), δ 1.73 (s, 18 H, *t*-Bu), 9.12 (s, 2 H, CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.0 (CH_3), 67.3 (N*C*Me$_3$), 161.9 (*C*═N). MS (CI+): *m/z* 459* (M − C_4H_9, 9.7), 307* ((DAB)$GaCl_2$, 59.0), 251* ((DAB)$GaCl_2$ − C_4H_8, 12.5), 169 (DAB + H, 100) (an asterisk indicates the presence of an appropriate Ga_xCl_y isotope pattern). Anal. Calcd for $C_{10}H_{20}N_2Ga_2Cl_6$: C, 23.08; H, 3.87; N, 5.38. Found: C, 22.93; H, 3.90; N, 5.28.

X-ray Crystallography. Crystals of **4** and **7** were mounted inside thin-walled glass capillaries and sealed under argon (1 atm). Intensity data were collected at 25 °C on an Enraf Nonius CAD4 diffractometer utilizing graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) and operating in the $2\theta-\theta$ scan mode ($2\theta < 50.0°$). The structures were solved using direct methods and refined using full-matrix least-squares methods on F^2 using Siemens SHELXTL PLUS 5.0 (PC) software.[25a] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms except those of the methyl groups were placed in idealized positions and refined using the riding model with general isotropic temperature factors. The methyl hydrogens were placed by using a difference electron density synthesis to set the initial torsion angle and then refined as a riding−rotating model with general isotropic temperature factors.

Because of decay, it was necessary to collect intensity data for **9** using two different crystals. Both crystals, one of dimensions 0.19 × 0.57 × 0.83 mm and the other of dimensions 0.16 × 0.51 × 0.57, were mounted in thin wall capillaries. The unit cell was obtained by centering 25 randomly found peaks and refined using 25 identical high angle reflections ($32 < 2\theta < 48°$). The first crystal was used for data collection for $2\theta = 4.0-45.0°$ and the second crystal was used to collect data for $2\theta = 40.0-50.0°$. Both data sets were combined and batch scale factors applied using common reflections and the linear least-squares method of Rae and Blake.[26] The structure was solved using direct methods and refined using full-matrix least-squares methods on *F* using Siemens SHELXTL PC (4.2) software.[25b] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms were placed in idealized positions and refined using the riding model with general isotropic temperature factors. Details of the crystal data and a summary of intensity data collection parameters for all structures are given in Table 2.

Table 2. Selected Crystal Data for $[Bz^N{}_2Ga][GaCl_4]$ (**4**), $[(DAB)GaCl_2][GaCl_4]$ (**7**), and $[Et_4N][Me_4C_4GaCl_2]$ (**9**)

	4	7	9
emp formula	$C_{18}H_{24}N_2Ga_2Cl_4$	$C_{10}H_{20}N_2Ga_2Cl_6$	$C_{16}H_{32}NGaCl_2$
fw	549.63	520.42	379.0
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	Pbca	$P2_1/n$
color	colorless	pale yellow	colorless
a, Å	11.519(2)	11.882(2)	9.967(1)
b, Å	18.254(4)	17.289(3)	13.073(2)
c, Å	12.506(3)	20.424(4)	15.345(2)
α, deg	90	90	90
β, deg	117.40(3)	90	96.76(1)
γ, deg	90	90	90
V, Å^3	2334.6(9)	4195.5(11)	1985.5(4)
Z	4	8	4
R [$I > 2\sigma(I)$]	0.0545	0.0460	0.0721
R_w (all data)	0.1099	0.1165	0.1012
GOF	1.055	1.017	1.28
based on	F^2	F^2	F

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Supporting Information Available: A complete listing of bond distances, bond angles, atomic coordinates, and thermal parameters for **4**, **7**, and **9** and text containing additional experimental details for **9** (20 pages). Ordering and access information is given on any current masthead page.

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