## On the Chemistry of Gallium, V[◇]

# Cyclic Compounds of Gallium and Indium with the 2,2-Dimethyl-1,3-bis[(trimethylsilyl)amino]propane Ligand☆

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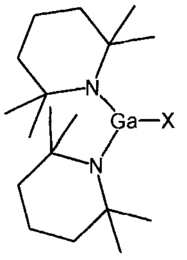
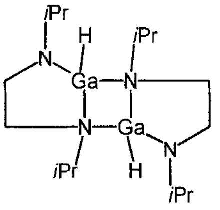
Reaction of 2,2-Dimethyl-*N*-lithio-1,3-bis[(trimethylsilyl)amino]propane (**4a**) with $RGaBr_2$ (R = Br, Mes) allows the isolation of the cyclic monomeric amine(amino)gallanes **5** and **6**. The cyclic bis(amino)gallanes **7** and **9** as well as the indium homologue **10** were obtained by reaction of gallium halides $RGaCl_2$ (R = Cl, Mes) or $InCl_3$ with dilithiated **4**. In the case of R = Mes the product is a monomer. In addition, the tetrakis(amino)gallate **8** was isolated. Single-crystal X-ray diffraction studies confirmed the constitutions. Compound **5** has one short Ga–N single bond (184 pm) and a longer Ga–N dative bond (204 pm). Compound **7** exhibits a central asymmetrical four-membered $Ga_2N_2$ ring [*d*(Ga–N) = 199.4, 205.6 pm] with *syn*-oriented substituents. The terminal Ga–N bond length is 184.3 pm. Two nitrogen atoms bridge the lithium and gallium atom in the gallate **8** [*d*(Li–N) = 206 pm]. Two Li–H contacts complete the coordination sphere at the lithium atom.

In the past a series of dimeric mono(amino)gallium compounds have been structurally characterized[2], e.g. $[Me_2GaN(H)tBu]_2$[3]. Unassociated derivatives have only been reported in the last two years, e.g. $tBu_2GaN(SiPh_3)R$ (R = *t*Bu, adamantyl)[4] and $Et_2GaN(tBu)BMes_2$[5]. Bis(amino)gallanes have been examined less intensely, but the dimeric bis(amino)gallium chloride $[(Me_2N)_2GaCl]_2$[6] has been known for some time. Recently, we prepared and characterized a series of monomeric bis(2,2,6,6-tetramethylpiperidino)gallanes **1**[1,7]. Other related derivatives are the monomeric bis(amino)gallanes $[(Me_3Si)_2N]_2GaCl$, Mes* $Ga[N(H)Ph]_2$ (Mes* = 2,4,6-$tBu_3C_6H_2$)[8] and the dimeric cyclic bis(amino)gallium hydride **2**[9], prepared by hydrogallation of a diazabutadiene. We were interested in using a substituted 1,3-bis(amino)propane to synthesize six-membered bis(amino)gallanes and study their oligomerization.



**1**
X = Hal, OPh, Ph, $Si(SiMe_3)_3$



**2**

### Reactions

1,3-Diamino-2,2-dimethylpropane (**3**) was easily converted to the *N,N'*-disilylated amine **4** by reaction with $Me_3SiCl$ according to eq. (1). Compound **4** itself may be lithiated once or twice with *n*-butyllithium in hexane (**4a**, **b**). When the monolithiated amine **4a** was allowed to react with gallium tribromide according to eq. (2) the aminogallium dibromide **5** was formed as a crystalline solid. In the same manner mesitylgallium dibromide forms **6** when combined with **4a**. Both **5** and **6** are monomeric in benzene solution, but by means of NMR data one cannot distinguish unambiguously between a chain structure and a six-membered ring, which would contain two different kinds of gallium-nitrogen bonds. An attempt to prepare the cyclic bis(amino)gallium halide from **5** and phenyllithium ended in a messy mixture of substitution and dehydrohalogenation products. Consequently, we allowed the dilithio amine **4b** to react with gallium trichloride in diethyl ether according to eq. (3) in order to synthesize the desired bis(amino)gallium halide with a six-membered ring structure. This reaction, however, does not proceed in a unique fashion, producing **7** accompanied by **8**. The product distribution can be directed by varying the reaction conditions. Addition of a $GaCl_3$ solution in $Et_2O$ to a suspension of **4b** in hexane produced an approximate 1:1 mixture of **7** and **8**. These compounds could be separated by fractional crystallization. Compound **7** proved to be a dimeric bis-

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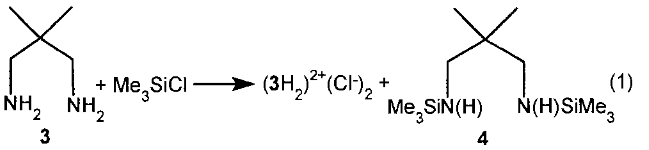
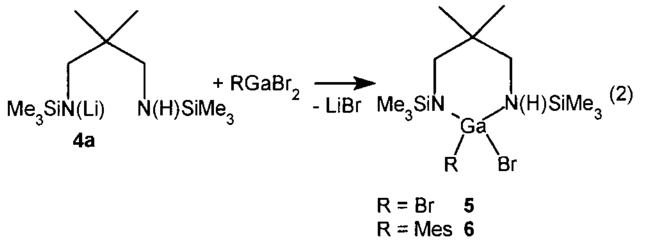
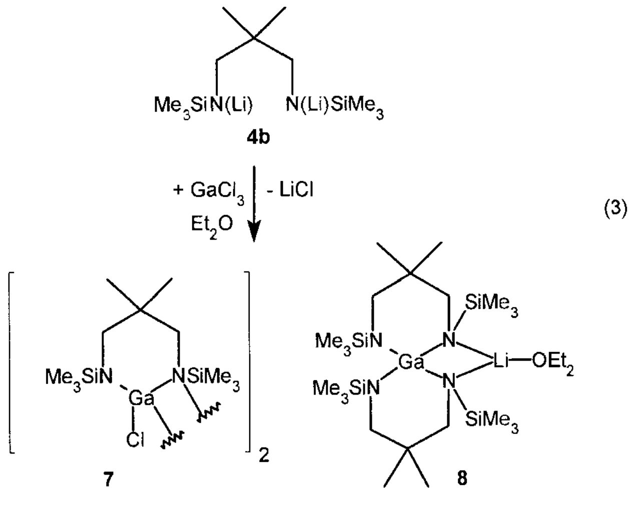
(amino)gallium chloride, and **8** was analyzed as a lithium tetra(amino)gallate–ether adduct. Very slow addition of an ether solution of **4b** to a cooled $GaCl_3$ solution in $Et_2O$ minimized the portion of **8**. On the other hand, **8** was prepared in moderate yields by applying a 2:1 stoichiometry in the above reaction.



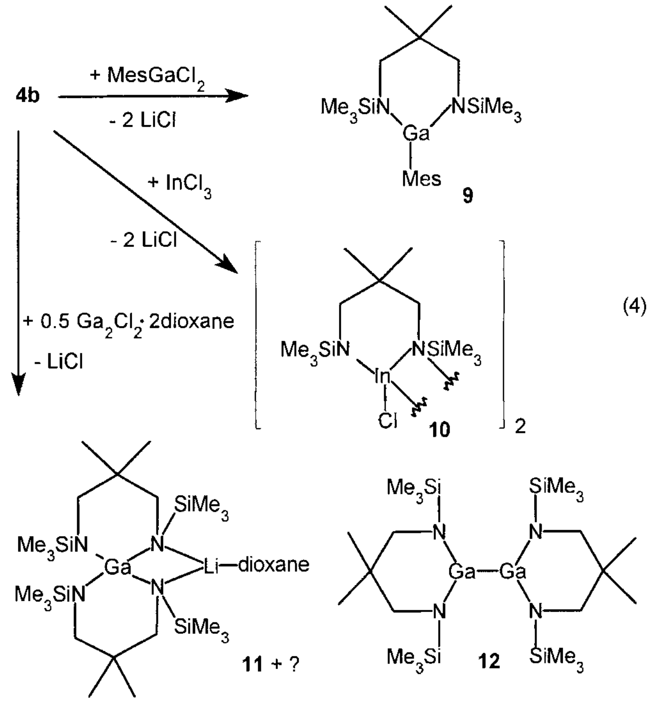


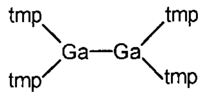


If mesitylgallium dichloride was used instead of $GaCl_3$ the corresponding mesityl-substituted bis(amino)gallane **9** was formed without side products as a monomer [eq. (4)]. When the element homologue indium trichloride was treated with **4b** a cyclic bis(amino)indium chloride **10** could be isolated as a dimer, too. Compound **11**, which is very similar to **8**, was formed by reaction of **4b** with $Ga_2Cl_4 \cdot 2$ dioxane instead of the tetrakis(amino)digallane **12**. No gallium metal was observed during the reaction, but the gallium(I) compound postulated in this disproportionation reaction could not be detected. This constrasts with the reaction of tmpLi with $Ga_2Cl_4 \cdot 2$ dioxane, in which digallane **13**[10] was formed.

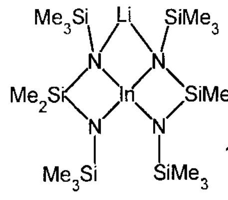
## Spectroscopic Data

In the $^1$H-NMR spectrum of **5** four sets of equally intense multiplets are observed, which are assigned to the four methylene protons. Two of them are doublets and two of them have a triplet structure resulting from an additional coupling with the NH proton. The methyl and trimethylsilyl substituents give rise to two singlets each. Similarly, the $^{13}$C-NMR spectrum shows two signals for the methylene carbon atoms, two for methyl carbon atoms and two for the trimethylsilyl groups, but only one singlet for the quaternary carbon atom. This pattern is indicative of the proposed six-membered ring structure of **5** and makes an acyclic structure less probable, which should give rise to fewer signals. Similar spectra are observed for the mesityl-substituted **6** as far as the amine part is concerned, and therefore an analogous structure is proposed.





**13**



**14**

The $^1$H- and $^{13}$C-NMR spectra of the gallium and indium bis(amino) chlorides **7** and **10** do not differ very much in their patterns. In both cases two signals for the methyl and trimethylsilyl groups are observed, accompanied by four multiplets for the methylene protons. In the $^1$H-NMR spectra of **7** and **10** not only the geminal H,H couplings resulting in four doublets are observed, but, in addition, a $^4J_{HH}$ coupling of 2 Hz results in splitting two of the doublets. The observation of a $^4J$ coupling in alkane systems like this is an indication of a rigid frame. Spectra like those exclude monomeric molecules for **7** and **10**, but are in good consonance with nitrogen-bridged dimers, featuring a central $M_2N_2$ ring with tetracoordinated gallium atoms and two terminal triply coordinated nitrogen atoms. In contrast, monomer **9** reveals a very simple $^1$H-NMR spectrum consisting of a single set of singlets, indicating at least a twofold symmetry for the molecule.

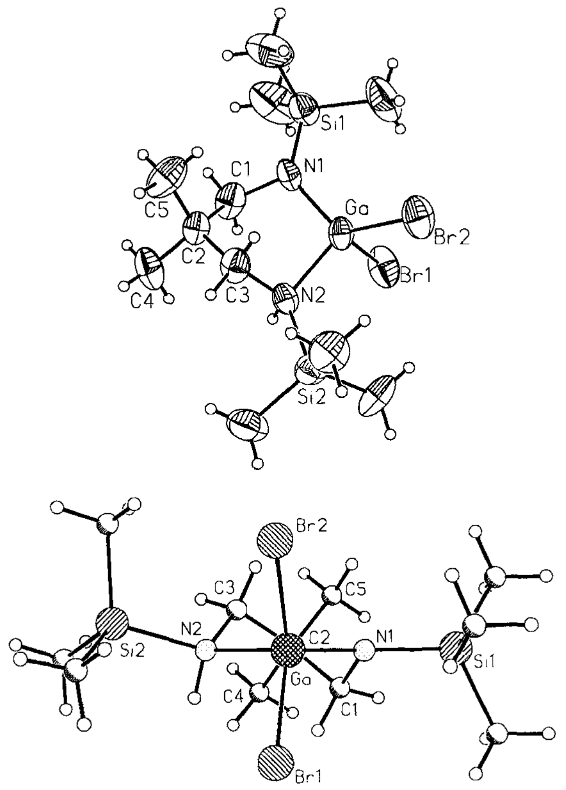
At 296 K the spirocyclic tetrakis(amino)gallate **8** shows only single sets of signals in the $^1$H- and $^{13}$C-NMR spectra. The signal for the methylene groups in the proton NMR spectrum is a very broad unstructured one. On cooling a solution of **8** in [D$_8$]toluene this signal becomes sharper, giving rise to two AB spin systems below $T = 263$ K [$\delta = 3.14, 2.96$ ($^1J_{HH} = 12.7$ Hz) and 2.74, 2.60 ($^1J_{HH} = 12.2$ Hz)]. Two singlets each are observed for the methyl and trimethylsilyl groups in the ratio 1:1.

In the $^{13}$C-NMR spectrum the corresponding signals also appear as doublets. These findings are consistent with the solid-state structure for **8** described in the next section and indicate a dynamic behavior of the lithium atom comparable to that found for the spirocyclic tetrakis(silazanido)indate **14**[11]. The activation barrier for this process was estimated to be 57 kJ/mol by using the Eyring equation[12]. The $^1$H- and $^{13}$C-NMR spectra for **11** are very similar to those of **8**.

## Crystal Structure Determinations

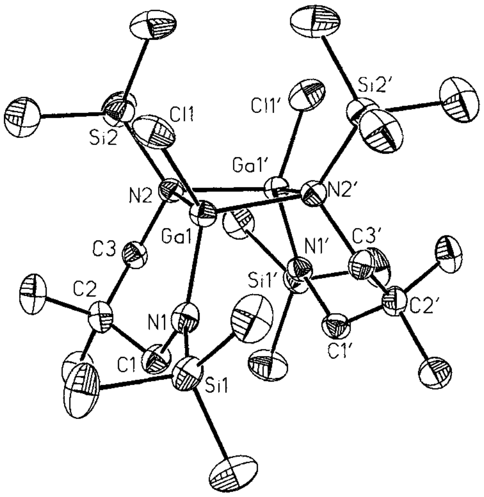
A single-crystal structure determination by X-ray diffraction[13] of **5** confirmed a six-membered ring structure (Figure 1, above). **5** crystallizes in the monoclinic system, space group $P2_1/n$. The six-membered $C_3GaN_2$ ring skeleton has a *twist* conformation, incorporating a distorted tetrahedral gallium atom, an almost planar triply coordinated nitrogen atom (sum of angles 354.1°) as well as a distorted tetrahedral nitrogen atom. Consequently, the Ga–N bond lengths are different. The dative Ga–N bond is 204(1) pm long, which is in the expected range for bond lengths between tetracoordinated nitrogen and gallium centers. For example, the averaged bridging Ga–N bond lengths in $[Ga(NMe_2)_3]_2$ are 201 pm[14] and the Ga–N bond length in $Me_3GaNH_2t$Bu is 212(1) pm[3]. The other Ga–N bond length is shorter [184(1) pm], due to the lower coordination number at the nitrogen atom (see below). The different coordination spheres at the nitrogen atoms do not only result in different GaN bonds but are reflected in one short and one long SiN bond, too [$d$(Si1–N1) = 169(1), $d$(Si2–N2) = 182(1) pm]. This shows the influence of the availability of the lone pair at the nitrogen centres on the Si–N bond. The carbon-nitrogen bond lengths do not change with the coordination number at the nitrogen atoms. A view down the line Ga–C2 (Figure 1, below) shows the all-*staggered* arrangement minimizing steric contacts. Three of the bond angles at the gallium center deviate from the tetrahedral angle. Thus, the N1–Ga–N2 bond angle [99.9(5)°] is sharp, the Br–Ga–N1 angles (116°) are wide. The average Ga–Br bond length of 232.2 pm is slightly longer than the terminal Ga–Br bonds in $Ga_2Br_6$[15]. On the other hand, bis(2,4,6-triisopropylphenyl)gallium bromide featuring a triply coordinated gallium atom has a comparable Ga–Br atom distance[16].

Figure 1. Top: View of a molecule of **5** in ORTEP presentation; thermal ellipsoids represent 50% probability. – Bottom: View in a Newman projection down the Ga–C2 axis; selected bond lengths [pm] and angles [°] (esds in parentheses): Ga–N1 183.5(12), Ga–N2 204.0(10), Ga–Br1 233.7(2), Ga–Br2 230.6(2), N1–Si1 169.4(13), N2–Si2 182.4(12); N1–Ga–N2 99.9(5), Br1–Ga–Br2 107.7(1), Br1–Ga–N1 115.0(3), Br1–Ga–N2 107.8(3), Br2–Ga–N1 117.1(3), Br2–Ga–N2 108.7(3), Ga–N1–C1 109.0(9), Ga–N1–Si1 127.0(6), C1–N1–Si1 118.1(9)



The bis(amino)gallium chloride **7** crystallizes as a dimer in the monoclinic space group $C2/c$ (Figure 2). The molecule resides on a twofold crystallographic axis, orthogonal to the central $Ga_2N_2$ four-membered ring. At the first glance the most striking feature is the *syn* arrangement of the chlorine atoms and trimethylsilyl groups and, consequently, of the two six-membered ring parts. This stereochemistry can be rationalized, because in the case of an *anti* conformation the trimethylsilyl groups at the bridging and nonbridging nitrogen atoms of the two parts of the molecule would suffer considerable overlap as is shown by molecular modeling studies[17]. The conformation of the six-membered rings are best described as an *envelope* with atoms Ga1, N1, N2, C1, and C3 in plane and C2 as flap. The $Ga_2N_2$ unit is not exactly planar, the Ga1N2Ga1′ and Ga1N2′Ga1′ planes enclose an angle of 12.5°. The inner ring angle at Ga1 is 92.1°, those at the nitrogen atoms are more acute with 87.1°. The two independent Ga–N bond lengths in the four-membered ring differ from one another, that in the six-membered ring system is shorter by 6 pm. But both are in the normal range usually found for dimeric aminogallanes. Examples are the already mentioned amides $[Ga(NMe_2)_3]_2$ and $[(Me_2N)_2GaCl]_2$ [$d$(Ga–N) = 196 to 200 pm][6]. The terminal Ga–N bonds which feature a trigonal-planar nitrogen atom (sum of angles 359.4°) are shorter by 18 pm compared to the bridging ones. This bond length is comparable to that in $[(Me_3Si)_2N]_3Ga$[18] and [tmp(Cl)Ga-μ-OEt]$_2$[6] and is markedly shorter than in most monomeric mono(amino)gallanes[1,4,5]. Another dimeric bis(amino)gallane, Raston's[9] hydrido compound **2**, exhibits comparable differences between bridging and terminal Ga−N bonds. Similar to **5**, the different Ga−N bond lengths show up in the Si−N bond lengths, too. The Ga−Cl bond length [217.01(9) pm] is typical for gallium chloro compounds in general.

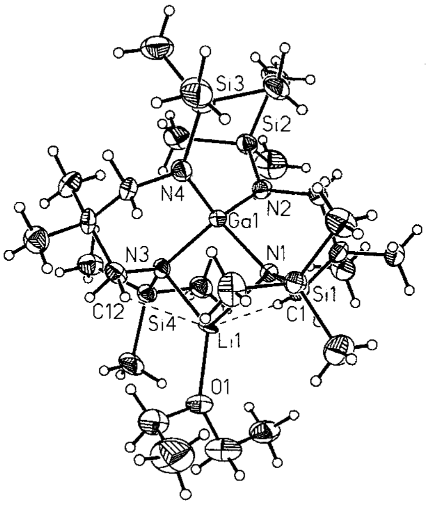
Figure 2. View of a molecule of **7** in ORTEP presentation; thermal ellipsoids represent 50% probability; hydrogen atoms are omitted for clarity; selected bond lengths [pm] and angles [°] (esds in parentheses): Ga1−Cl1 217.01(9), Ga1−N1 184.3(2), Ga1−N2′ 205.6(2), Ga1−N2 199.3(2), N1−Si1 172.4(2), N2−Si2 181.5(2); N2−Ga1−N2′ 92.14(9), Ga1−N2−Ga1′ 87.15(6), Cl1−Ga1−N2′ 114.47(6), Cl1−Ga1−N2 112.43(6), N1−Ga1−N2′ 111.66(9), N1−Ga1−N2 109.26(8), Ga1−N1−Si1 127.8(1), Ga1−N1−C1 116.2(2), Si1−N1−C1 115.4(2)



The spirocyclic **8** (Figure 3) crystallizes in the orthorhombic system, space group $Pca2_1$[19]. The two six-membered rings in the molecule are orthogonal to one another, the lithium atom is in an almost symmetric bridging position between N3 and N4 [*d*(Li−N) = 205.3(12), 207.8(14) pm]. The Li−N distance is comparable to that of tmeda-complexed organolithium compounds or in the spirocyclic tetrakis(silazanido)indate **14**. The bis(alkylamino)gallate [$(c\mathrm{Hex})_2\mathrm{Ga}(\mathrm{N}t\mathrm{Bu})_2\mathrm{Li}(\mathrm{thf})_2$][20] has shorther Li−N bonds [204.2(2) and 197(2) pm] but comparable Ga−N bonds (199 pm). A consequence of the lithium coordination in **8** are two sets of different nitrogen atoms: two are trigonal-planar and two distorted tetrahedrally coordinated centers having Ga−N bond lengths of 198 pm for lithium-coordinated nitrogen atoms and 189 pm (av.) for the others. In contrast to structures **5** and **7**, the change of the coordination number of the nitrogen atom has no influence on the Si−N bond lengths, all of them are approximately 173 pm. This is understood as a consequence of the weaker Li−N bond compared to the Ga−N dative bond. The coordination geometry at the gallium center is a distorted tetrahedral one with N−Ga−N angles of 99.2(3) and 104.7(2)° within the six-membered rings and large angles of nearly 120° between the rings. The N−Ga−N angle within the $\mathrm{GaN_2Li}$ ring is 97.6(2)°.

Regarding the coordination of the lithium atom, a diethyl ether molecule binds via its oxygen atom to the lithium ion, giving rise to distorted trigonal-planar arrangement of two nitrogen atoms and one oxygen atom around the lithium center. Two short lithium-hydrogen contacts to the methylene groups C1 and C12 [*d*(Li−H) = 227(7) and 242(7) pm] complete the coordination sphere, resulting in a nonideal trigonal bipyramid. The geometry for molecule **8** is not in agreement with the NMR spectra at ambient temperature but in accordance with the low-temperature measurement and a fluxional structure in solution as described previously.

Figure 3. View of a molecule of **8** in ORTEP presentation; thermal ellipsoids represent 50% probability; selected bond lengths [pm] and angles [°] (esds in parentheses): Ga1−N1 198.9(5), Ga1−N2 190.3(6), Ga1−N3 197.1(6), Ga1−N4 188.1(6), Li1−N1 205.3(12), Li1−N3 207.8(14), Li1−O1 194.0(11), Li1−C1 255(2), Li1−C12 263(2), N−Si 1.730 (av.); N1−Ga1−N2 99.2(3), N1−Ga1−N3 97.6(2), N1−Ga1−N4 115.8(3), N2−Ga1−N3 118.3(3), N2−Ga1−N4 119.5(3), N3−Ga1−N4 104.7(2), O1−Li1−N1 129.1(7), O1−Li1−N3 137.4(7), N1−Li1−N3 92.4(5), Si3−N4−Ga1 129.0(3), Si3−N4−C14 112.4(5), Ga1−N4−C14 118.6(5)



## Conclusions

Compound **4** allows the isolation of cyclic bis(amino) compounds of gallium and indium, the chlorides **7** and **10** being nitrogen-bridged dimers. Obviously, the steric demand of this amino substituent is insufficient to stabilize monomeric halide compounds as the tetramethylpiperidino group does. On the other hand, it was possible to isolate a tetracoordinated gallate incorporating a pentacoordinated lithium atom. Sterically demanding substituents at the gallium atom like mesityl allow the isolation of a monomeric bis(amino)organogallium compound.

We thank Mr. *S. Huber* for recording many NMR spectra. We are also indebted to the *Deutsche Forschungsgemeinschaft* for financial support.

## Experimental

All experiments were performed under purified nitrogen or in vacuo by using Schlenk techniques. − NMR: Bruker ACP 200,

Table 1. Crystallographic data for the structural analyses of **5**, **7**, and **8**

| | **5** | **7** | **8** |
|---|---|---|---|
| *Crystal data and data colection* | | | |
| Formula | $C_{11}H_{29}Br_2GaN_2Si_2$ | $C_{22}H_{56}Cl_2Ga_2Si_4N_4$ | $C_{26}H_{66}GaLiN_4OSi_4$ |
| *M* | 475.1 | 699.4 | 639.8 |
| *a* [pm] | 1266.5 (5) | 2190.9 (6) | 1936.7 (7) |
| *b* [pm] | 1180.9 (4) | 985.0 (1) | 1130.2 (4) |
| *c* [pm] | 1410.2 (5) | 1963.5 (5) | 1745.4 (8) |
| β [°] | 99.65 (3) | 123.38 (2) | - |
| *V* [nm$^3$] | 2.079 (1) | 3.538 (3) | 3.820 (3) |
| *Z* | 4 | 4 | 4 |
| $d_{calcd.}$ [g/cm$^{-3}$] | 1.518 | 1.313 | 1.112 |
| Space group | $P2_1/n$<br>monoclinic | $C2/c$<br>monoclinic | $Pca2_1$<br>orthorhombic |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| Cystal size [mm$^3$] | 0.28 x 0.44 x 0.46 | 0.25 x 0.45 x 0.60 | 0.4 x .25 x .17 |
| *T* [K] | 298 | 298 | 203 |
| Scan type | ω | ω | ω |
| 2Θ range | 5 - 50 | 4 - 46 | 3.6 - 45.0 |
| No. of refl. collect. | 3846<br>in $hk\pm l$ | 2722<br>in $\pm hkl$ | 8543<br>in $\pm hk\pm l$ |
| No. of unique refl. | 3672 | 2633 | 4976 |
| $F > n\,\sigma(F)$ [obs.] | 3 [1846] | 3 [2191] | 4 [3606] |
| μ [mm$^{-1}$] | 5.272 | 1.821 | 0.868 |
| Absorp. correct. | face-indexed num. | semiempirical | n.a. |
| min/max transm. | 0.115/0.270 | 0.818/0.999 | |
| *Solution and Refinement* | | | |
| Solution | Direct methods | Direct methods | Direct methods |
| Refinement method | full matrix | full matrix | full matrix on $F^2$ |
| Hydrogen Atoms | riding model, fixed isotr. *U* | riding model, fixed isotr. *U* | riding model, fixed isotr. *U* |
| Data/parameter | 11.1 | 17.1 | 13.7 |
| Final *R* indices | $R = 0.091$<br>$R_w = 0.085$ | $R = 0.026$<br>$R_w = 0.043$ | $R = 0.054$<br>$wR2 = 0.099$ |
| $w^{-1}$ = | $\sigma^2 F + 0.0007\,F^2$ | $\sigma^2(F)$ | $\sigma^2 F_o^2 + (0.052P)^2$<br>$P = (F_o^2 + 2F_c^2)/3$ |
| Programs used | SHELXTL Plus (PC) | SHELXS-86<br>MolEn | Siemens XS<br>SHELXL93 |

Jeol GSX 400; $^{13}C$, $^1H$ (TMS). – Single-crystal X-ray diffraction: suitable crystals were mounted under Ar in predried Lindemann capillaries which were sealed. Data collections were performed with Siemens R3 (**5**), P4 (**8**), and Enraf Nonius CAD4 (**7**) machines (Table 1). Gallium halides were prepared from the elements[21], $(Me_3Si)N(H)CH_2C(Me)_2CH_2N(H)SiMe_3$[22] was prepared by using standard procedures, and $InCl_3$ was used as purchased.

*2,2-Dibromo-5,5-dimethyl-1,3-bis(trimethylsilyl)-1-aza-3-azonia-2-gallatacyclohexane* (**5**): A solution of **4** (1.27 g, 5.14 mmol) was lithiated with 1 equiv. of *n*-butyllithium in hexane. The amide solution was transferred to a dropping funnel and added slowly to a suspension of $GaBr_3$ (1.59 g, 5.14 mmol) in 20 ml of pentane at room temp. An exothermic reaction occurred leading to a sticky precipitate. After stirring the mixture for 16 h it was filtered and the filtrate concentrated to half its volume. On cooling the solution to −78°C 1.74 g of **5** (71%) precipitated as colorless crystals; m.p. 212–217°C. – $C_{11}H_{29}Br_2GaN_2Si_2$ (475.1): calcd. C 27.81, H 6.15, N 5.90; found C 24.22, H 5.84, N 5.95. – $^1H$ NMR ($CDCl_3$): δ = 2.94 [t, 1H, N(H)C*H*$_2$], 2.83 [t, 1H, N(H)C*H*$_2$], 2.71 (d, 1H, $NCH_2$), 2.51 (d, 1H, $NCH_2$), 1.90 (br., 1H, NH), 1.00 (s, 3H, $CH_3$), 0.88 (s, 3H, $CH_3$), 0.48 (s, 9H, Si*Me*$_3$NH), 0.09 (s, 9H, $SiMe_3$). – $^{13}C$ NMR ($CDCl_3$): δ = 56.1, 55.0 ($CH_2$), 35.2 (*C*$Me_2$), 26.5, 22.0 ($CH_3$), 1.1, −0.6 ($SiMe_3$).

*2-Bromo-2-mesityl-5,5-dimethyl-1,3-bis(trimethylsilyl)-1-aza-3-azonia-2-gallatacyclohexane* (**6**): An amide solution prepared from **4** (0.55 g, 2.22 mmol) was added slowly at ambient temp. to a suspension of $MesGaBr_2$ (0.78 g, 2.22 mmol) in 20 ml of hexane. After the mixture had been stirred overnight filtration gave a colorless solution. This was concentrated in vacuo. The oily residue was crystallized from 5 ml of pentane, yield 0.92 g of **6** (81%), m.p. 135–139°C. – $C_{20}H_{40}BrGaN_2Si_2$ (514.4): calcd. C 46.70, H 7.84, N 5.45; found C 45.39, H 7.58, N 6.08. – $^1H$ NMR ($CDCl_3$): δ = 6.74 (s, 2H, *m*-CH), 2.64 (s, 6H, *o*-$CH_3$), 2.58–2.41 (m, 4H, $CH_2$), 2.21 (s, 3H, *p*-$CH_3$), 2.01 (m, 1 NH), 1.08, 0.86 (s, 6H, $CH_3$), 0.10, −0.19 (s, 18H, $SiMe_3$). – $^{13}C$ NMR ($CDCl_3$): δ = 145.2 (*i*-C), 143.4 (*p*-C), 137.9 (*o*-C), 128.3 (*m*-C), 55.9 ($CH_2$), 35.3 (*C*$Me_2$), 27.4, 26.0 ($CH_3$), 22.0 (*o*-$CH_3$), 21.0 (*p*-$CH_3$), 0.8, −0.9 ($SiMe_3$). – $^1H$-NMR ($C_6D_6$): δ = 6.75 (s, 2H, CH), 2.81 (s, 6H, *o*-$CH_3$), 3.71, 3.49, 2.70 (m, 4H, $CH_2$), 2.11 (s, 3H, *p*-$CH_3$), 1.92 (m, 1 NH), 0.98, 0.65 (s, 6H, $CH_3$), 0.11, −0.11 (s, 18H, $SiMe_3$). – $^{13}C$-NMR ($C_6D_6$): δ = 145.1 (*i*-C), 143.7 (*p*-C), 138.1 (*o*-C), 128.9 (*m*-C), 56.3, 56.1 ($CH_2$), 35.3 (*C*$Me_2$), 27.2, 26.3 ($CH_3$), 22.1 (*o*-$CH_3$), 21.1 (*p*-$CH_3$), 1.2, −1.2 ($SiMe_3$).

*syn-2,8-Dichloro-5,5,11,11-tetramethyl-1,3,7,9-tetrakis(trimethylsilyl)-3,9-diaza-1,7-diazonia-2,8-digallatatricyclo[6.4.0.0$^{2,7}$]-dodecane* (**7**) *and Lithium 3,3,9,9-Tetramethyl-1,5,7,11-tetra-*

*kis(trimethylsilyl)-1,5,7,11-tetraaza-6-gallataspiro[5.5]undecane–Diethyl Ether* (**8**): A solution of **4** (2.89 g, 11.6 mmol) was lithiated with 15.5 ml of a 1.56 M *n*-butyllithium solution in hexane. The resulting suspension of **4b** was added at −50°C during 30 min to a stirred solution of $GaCl_3$ (2.11 g, 11.9 mmol) in 20 ml of $Et_2O$. The mixture was slowly warmed to ambient temp. and heated at reflux for 15 h. All volatile products were then removed in vacuo, and the residue was extracted with 20 ml of $Et_2O$. After filtration of the extract and cooling of the filtrate to −30°C 1.14 g of **7** (28%) precipitated as colorless prisms, m.p. 99–101°C. From the reduced mother liquor compound **8** crystallized, yield: 1.94 g (52%), m.p. 105–107°C.

**7**: $C_{22}H_{56}Cl_2Ga_2N_4Si_4$ (699.4): calcd. C 37.78, H 8.07, N 8.01; found C 37.91, H 7.79, N 7.94. – $^1H$ NMR ($C_6D_6$): δ = 3.86 (d, $^2J_{HH}$ = 14.2 Hz, 2H, $NCH_2$), 3.24 (d, $^2J_{HH}$ = 13.0 Hz, 2H, $NCH_2$), 2.71 (dd, $^2J_{HH}$ = 14.2, $^4J_{HH}$ = 2 Hz, 2H, $NCH_2$), 2.69 (dd, $^2J_{HH}$ = 13.0, $^4J_{HH}$ = 2 Hz, 2H, $NCH_2$), 1.07, 0.63 (s, 12H, $CH_3$), 0.49, 0.25 (s, 36H, $SiMe_3$). – $^{13}C$ NMR ($C_6D_6$): δ = 58.8, 58.3 ($NCH_2$), 35.5 ($CMe_2$), 28.2, 25.5 ($CH_3$), 3.9, 1.4 ($SiMe_3$).

**8**: $C_{26}H_{66}GaLiN_4OSi_4$ (639.8): calcd. C 48.81, H 10.40, N 8.76; found C 47.94, H 9.28, N 8.34. – $^1H$ NMR (300 K, $C_6D_6$): δ = 3.11 (q, 4H, $OCH_2CH_3$), 2.90 (br., 8H, $NCH_2$), 1.01 (s, 12H, $CH_3$), 0.86 (t, 6H, $OCH_2CH_3$), 0.42 (s, 36H, $SiMe_3$). – $^{13}C$ NMR (300 K, $C_6D_6$): δ = 65.6 ($OCH_2CH_3$), 57.2 ($NCH_2$), 36.9 ($CMe_2$), 27.1 ($CH_3$), 14.3 ($OCH_2CH_3$), 3.4 ($SiMe_3$). – $^1H$ NMR (243 K, $C_6D_5CD_3$): δ = 3.14, 2.96 ($d_{AB}$, 2H, $^2J_{HH}$ = 12.7 Hz, $NCH_2$), 2.74, 2.60 ($d_{AB}$, 2H, $^2J_{HH}$ = 12.2 Hz, $NCH_2$), 3.02 (br., $OCH_2CH_3$), 1.13, 0.91 (s, 12H, $CH_3$), 0.80 (br., $OCH_2CH_3$), 0.51, 0.36 (s, 36H, $SiMe_3$). – $^{13}C$ NMR (243 K, $C_6D_5CD_3$): δ = 65.1 ($OCH_2CH_3$), 57.2, 56.1 ($NCH_2$), 36.9 ($CMe_2$), 27.4, 25.6 ($CH_3$), 13.8 ($OCH_2CH_3$), 3.8, 2.5 ($SiMe_3$).

*2-Mesityl-5,5-dimethyl-1,3-bis(trimethylsilyl)-1-aza-3-azonia-2-gallatacyclohexane* (**9**): A solution of $MesGaCl_2$ (1.25 g, 4.8 mmol) in 10 ml $Et_2O$ was slowly added to a suspension of **4b** in 10 ml of hexane prepared from **4** (1.19 g, 4.8 mmol) and 6.4 ml (9.9 mol) of a 1.56 M *n*-butyllithium solution in hexane. After the mixture had been stirred for 12 h it was filtrated. From the filtrate colorless crystals precipitated on cooling to −78°C; yield: 0.64 g of **9** (31%), m.p. 127–130°C. – $C_{20}H_{39}GaN_2Si_2$ (433.4): calcd. C 55.42, H 9.07, N 6.46; found C 54.75, H 8.76, N 6.14. – $^1H$ NMR ($C_6D_6$): δ = 6.70 (s, 2H, *m*-CH), 3.06 (s, 4H, $NCH_2$), 2.36 (s, 6H, *o*-$CH_3$), 2.08 (s, 3H, *p*-$CH_3$), 0.98 (s, 6H, $CH_3$), 0.03 (s, 18H, $SiMe_3$). – $^{13}C$ NMR ($C_6D_6$): δ = 144.0 (*i*-C), 141.6 (*o*-C), 138.8 (*p*-C), 127.3 (*m*-C), 58.6 ($NCH_2$), 34.3 ($CMe_2$), 26.1 [$C(CH_3)_2$], 24.7 (*o*-$CH_3$), 21.3 (*p*-$CH_3$), 0.7 ($SiMe_3$).

*2,8-Dichloro-5,5,11,11-tetramethyl-1,3,7,9-tetrakis(trimethylsilyl)-3,9-diaza-1,7-diazonia-2,8-diindatatricyclo[6.4.0.0$^{2,7}$]dodecane* (**10**): A suspension of $InCl_3$ (1.15 g, 5.20 mmol) in 10 ml of $Et_2O$ was added slowly with stirring to a suspension of **4b** (1.36 g, 5.23 mmol) in 20 ml of hexane. The mixture was heated at reflux for 12 h. After filtration the yellow solution was concentrated to half of its volume and cooled to −30°C. 0.92 g of **10** (45%) precipitated as colorless tiny needles, m.p. 160–162°C. – $C_{22}H_{56}Cl_2In_2N_4Si_4$ (789.6): calcd. C 33.47, H 7.15, N 7.10; found C 34.28, H 7.13, N 7.44. – $^1H$ NMR ($C_6D_6$): δ = 3.95 (d, $^2J_{HH}$ = 13.8 Hz, 2H, $NCH_2$), 3.44 (d, $^2J_{HH}$ = 12.8 Hz, 2H, $NCH_2$), 2.83 (dd, $^2J_{HH}$ = 12.8, $^4J_{HH}$ = 1.8 Hz, 2H, $NCH_2$), 2.76 (dd, $^2J_{HH}$ = 13.8, $^4J_{HH}$ = 2.0 Hz, 2H, $NCH_2$), 1.04, 0.63 (s, 12H, $CH_3$), 0.41, 0.21 (s, 36H, $SiMe_3$). – $^{13}C$ NMR ($C_6D_6$): δ = 60.8, 60.6 ($NCH_2$), 37.0 ($CMe_2$), 28.8, 23.4 ($CH_3$), 3.0, 1.3 ($SiMe_3$).

*Lithium 3,3,9,9-Tetramethyl-1,5,7,11-tetrakis(trimethylsilyl)-1,5,7,11-tetraaza-6-gallataspiro[5.5]undecane–Dioxane* (**11**): 1.72 g of **4** (6.93 mmol) was lithiated with 2 equiv. of *n*-butyllithium. A suspension of $Ga_2Cl_4 \cdot 2$ dioxane (1.59 g, 3.47 mmol) in 20 ml of hexane was added slowly at −78°C. After stirring overnight filtration gave a dark brown solution, from which **11** precipitated on cooling to −78°C; yield: 1.24 g of **11** (55%) in colorless prisms, m.p. 143–144°C. – $C_{26}H_{64}GaLiN_4O_2Si_4$ (653.8): calcd. C 47.76, H 9.87, N 8.57; found C 45.15, H 10.08, N 9.18. – $^1H$ NMR data (300 K, $C_6D_6$): δ = 3.12 (s, 8H, $OCH_2$), 2.84 (br., 8H, $NCH_2$), 1.01 (s, 12H, $CH_3$), 0.41 (s, 36H, $SiMe_3$). – $^{13}C$ NMR (300 K, $C_6D_6$): δ = 66.9 ($OCH_2$), 57.3 ($NCH_2$), 36.9 ($CMe_2$), 26.6 ($CH_3$), 3.3 ($SiMe_3$).

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[1] G. Linti, R. Frey, K. Polborn, M. Schmidt, *Chem. Ber.* **1994**, *127*, 1387–1393.

[2] M. F. Lappert, A. R. Sanger, R. C. Srivastana, P. P. Power, *Metal and Metalloid Amides*, John Wiley, New York, **1980**, chapter 4.

[3] [3a] D. A. Atwood, R. A. Jones, A. H. Cowley, S. G. Bott, J. L. Atwood, *J. Organomet. Chem.* **1992**, *434*, 143–150. – [3b] J. T. Park, Y. Kim, J. Kim, K. Kim, Y. Kim, *Organometallics* **1992**, *11*, 3320–3323.

[4] K. M. Waggoner, K. Ruhlandt-Senge, R. J. Wehmschulte, X. He, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2557–2561.

[5] G. Linti, *J. Organomet. Chem.* **1994**, *465*, 79–83.

[6] D. A. Atwood, A. H. Cowley, R. A. Jones, M. A. Mardones, J. L. Atwood, S. G. Bott, *J. Coord. Chem.* **1992**, *26*, 285–291.

[7] R. Frey, G. Linti, K. Polborn, *Chem. Ber.* **1994**, *127*, 101–103.

[8] P. J. Brothers, R. J. Wehmschulte, M. M. Olmstead, K. Ruhlandt-Senge, S. R. Parkin, P. P. Power, *Organometallics* **1994**, *13*, 2792–2799.

[9] J. L. Atwood, S. G. Bott, C. Jones, C. L. Raston, *Inorg. Chem.* **1991**, *30*, 4868–4870.

[10] G. Linti, R. Frey, M. Schmidt, *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 958–962.

[11] M. Veith, M. Zimmer, S. Müller-Becker, *Angew. Chem.* **1993**, *105*, 1771–1772; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1731–1732.

[12] H. Günther, *NMR-Spektroskopie*, 2nd ed., G. Thieme Verlag, Stuttgart, New York, **1983**.

[13] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58802, the names of the authors, and the journal citation.

[14] K. M. Waggoner, M. M. Olmstead, P. P. Power, *Polyhedron* **1990**, *9*, 257–263.

[15] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, London, New York, **1984**, p. 444.

[16] M. A. Petrie, P. P. Power, H. V. R. Dias, K. Ruhlandt-Senge, K. M. Waggoner, R. J. Wehmschulte, *Organometallics* **1993**, *12*, 1086–1093.

[17] *Hyperchem*, V3.0, Autodesk Inc., **1993**.

[18] H. Nöth, P. Konrad, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30*, 681–687. – Structure in: P. G. Eller, D. C. Bradley, M. B. Hursthouse, D. W. Meck, *Coord. Chem. Rev.* **1977**, *24*, 1–95, and in ref.[8].

[19] An attempted solution in the centrosymmetric space group *Pbcm* was unsuccessful.

[20] D. A. Atwood, A. H. Cowley, R. A. Jones, *Organometallics* **1993**, *12*, 236–238.

[21] Brauer, *Handbuch der präparativen Anorganischen Chemie*, F. Enke, Verlag, Stuttgart, **1975**.

[22] H. Mack, Doctoral thesis, University of Munich, in preparation.

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