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Oligonuclear Gallium Nitrogen Cage Compounds: Molecular Intermediates on the Way from Gallium Hydrazides to Gallium Nitride

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Gallium hydrazides are potentially applicable as facile starting compounds for the generation of GaN by thermolysis. The decomposition pathways are, however, complicated and depend strongly on the substituents attached to the gallium atoms and the hydrazido groups. This paper describes some systematic investigations into the thermolysis of the gallium hydrazine adduct $Bu^t_3Ga{\leftarrow}NH_2\text{-}NHMe$ (**1a**) and the dimeric gallium hydrazides $[R_2Ga(N_2H_2R')]_2$ (**2b**, R = Bu^t, R′ = Bu^t; **2c**, R = Pr^i, R′ = Ph; **2d**, R = Me, R′ = Bu^t) which have four- or five-membered heterocycles in their molecular cores. Heating of the adduct **1a** to 170 °C gave the heterocyclic compound $Bu^t_2Ga(\mu\text{-}NH_2)[\mu\text{-}N(Me)\text{-}N({=}CH_2)]GaBu^t_2$ (**3**) by cleavage of N−N bonds and rearrangement. **3** was further converted at 400 °C into the tetrameric gallium cyanide $(Bu^t_2GaCN)_4$ (**4**). The thermolysis of the hydrazide $(Bu^t_2Ga)_2(NH\text{-}NHBu^t)_2$ (**2b**) at temperatures between 270 and 420 °C resulted in cleavage of all N−N bonds and the formation of an octanuclear gallium imide, $(Bu^tGaNH)_8$ (**6**). The trimeric dialkylgallium amide $(Bu^t_2GaNH_2)_3$ (**5**) was isolated as an intermediate. Thermolysis of the hydrazides $(Pr^i_2Ga)_2(NH\text{-}NHPh)(NH_2\text{-}NPh)$ (**2c**) and $(Me_2Ga)_2(NH\text{-}NHBu^t)_2$ (**2d**) proceeded in contrast with retention of the N−N bonds and afforded a variety of novel gallium hydrazido cage compounds with four gallium atoms and up to four hydrazido groups in a single molecule: $(Pr^iGa)_4(NH\text{-}NPh)_3NH$ (**7**), $(MeGa)_4(NH\text{-}NBu^t)_4$ (**8**), $(MeGa)_4(NH\text{-}NBu^t)_3NBu^t$ (**9**), and $(MeGa)_4(NHNBu^t)_3NH$ (**10**). Partial hydrolysis gave reproducibly the unique octanuclear mixed hydrazido oxo compound $(MeGa)_8(NHNBu^t)_4O_4$ (**11**).

1. Introduction

Metal hydrazides form a fascinating class of compounds which have found wide attention in different fields of research. Transition metal hydrazides, for instance, are believed to play an important role as intermediates in the biological and laboratory-based reduction of dinitrogen to ammonia[1] and are of interest in the context of N−C bond formation reactions starting from hydrazines and unsaturated substrates.[2] Aluminum, gallium, and indium hydrazides have been tested as molecular precursors for the synthesis of element nitrides via metallo organic chemical vapor deposition (MOCVD) and related procedures.[3] Further, the two directly connected nitrogen donor atoms of a hydrazide group generate a fascinating structural diversity in hydrazine chemistry, and many different hydrazine transition metal complexes have been isolated and characterized.[4] The synthesis and structural features of the corresponding Group 13 element hydrazides have recently been reviewed,[5] and similar features have been reported for the isoelectronic peroxo[6] or hydroxylamido ligands.[7] The most convenient method for the generation of aluminum, gallium, or indium hydrazides is the treatment of

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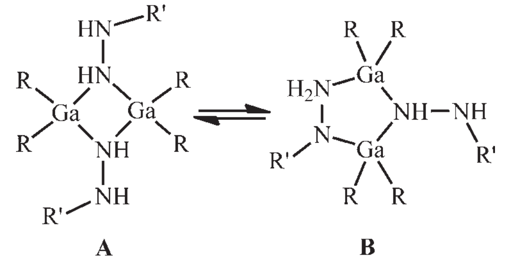
trialkylelement compounds with hydrazine derivatives $N_2H_{4-x}R'_x$ which contain at least one hydrogen atom attached to nitrogen. These reactions proceed via adducts $R_3E \leftarrow N_2H_{4-x}R'_x$ which in some cases were isolated and characterized.[8-10] The adducts eliminate the corresponding alkanes spontaneously or upon gentle heating to yield the corresponding hydrazides in which generally the monoanionic hydrazido ligands bridge two metal atoms to give four-, five-, or six-membered heterocycles with no, one, or two endocyclic N−N bonds.[5,10-12] Further heating should in principle result in the formation of three-dimensional cage compounds, examples of which have so far only been isolated in a few instances from the corresponding aluminum and gallium hydrazides. They possess a tetra(hydrazinediido)-tetragallium skeleton as the preferred structural motif.[5,10,11,13,14] In a recent investigation we have observed the formation of an unexpected and unique cage compound in which a completely deprotonated tetraanionic hydrazine fragment (hydrazinetetraide) is stabilized by coordination to six gallium atoms.[15] A concise understanding of the thermolytic pathways starting with hydrazides that have monoanionic hydrazido ligands to give GaN as the final product is crucial for a potential application of these precursor molecules in MOCVD processes and for the selection of suitable starting materials in particular with respect to the optimization of the substituents of the hydrazine derivatives. This paper describes a systematic investigation into the thermolysis reactions of selected gallium hydrazides.

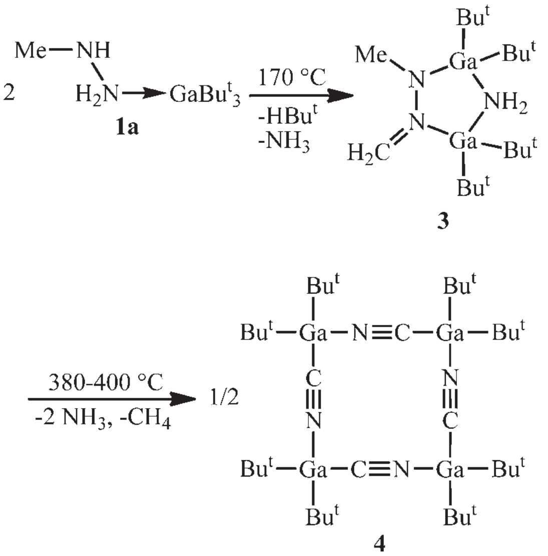
2. Results and Discussion

2.1. Thermolysis of the Hydrazine Adduct $Bu^t_3Ga \leftarrow NH_2$-NHMe 1a. We have previously described the synthesis of the hydrazine adduct $Bu^t_3Ga \leftarrow NH_2$-NHMe (**1a**)[8a] and the corresponding dimeric hydrazide $[Bu^t_2Ga(NH\text{-}NHMe)]_2$ (**2a**).[11] The latter was found to consist in the solid state of a four-membered Ga_2N_2 heterocycle, while solution NMR spectra were consistent with an equilibrium between the four-membered heterocycle **A** and the five-membered heterocycle **B** (Scheme 1).[11] Heating the hydrazine adduct **1a** in the absence of a solvent to 170 °C for 16 h resulted in the formal loss of isobutane and ammonia and the unexpected formation of the five-membered gallium hydrazonide **3** (Scheme 2) in 74% yield. Further heating of pure compound **3** to about 400 °C afforded the tetrameric gallium cyanide $[Bu^t_2Ga(CN)]_4$ **4** (Scheme 2) in 55% yield by the formal loss of ammonia and methane. The reaction pathway leading to this unexpected product under such drastic reaction conditions is not fully understood. The aluminum congeners of both compounds **3** and **4** have been described previously. They were obtained by thermolysis of solid aluminum hydrazide $[Bu^t_2Al(NHNHMe)]_2$[11] at 160 °C or from the reaction of Bu^t_2AlBr or Bu^t_2AlH with Me_3SiCN.[16]

Scheme 1



Scheme 2



Owing to the comparable covalent and ionic radii of gallium and aluminum, the analytical data of the two congeners are very similar. **3** is isostructural to its aluminum analogue and features an essentially planar Ga_2N_3 heterocycle at the core of the molecule (Figure 1). The largest deviation from the plane is found for the two nitrogen atoms N1 and N2 that are 11 pm above or below the plane. The GaC_2 fragments are perpendicular (angle Ga_2N_3/GaC_2 88°) to the central plane. The hydrogen atoms of the methylene ($N{=}CH_2$) and the methyl group (NMe) were located in the electron density map hereby allowing for the unambiguous identification of the two

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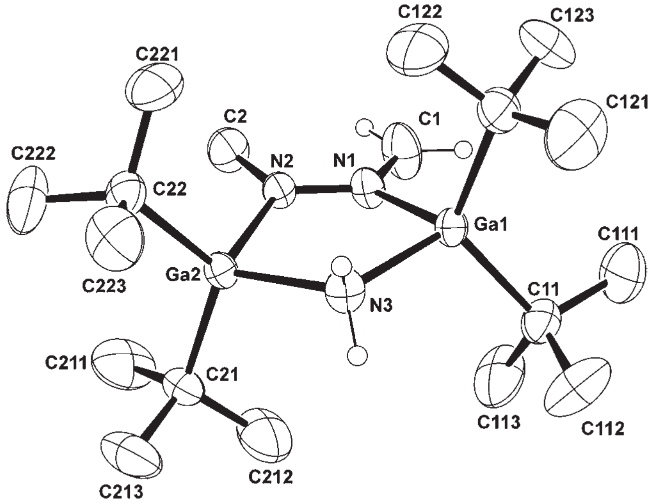

Figure 1. Molecular structure and numbering scheme of **3**; displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (NH, CH_2 only) have been drawn with arbitrary radius. Important bond lengths [pm]: Ga1−N1 201.0(3), Ga1−N3 200.1(3), Ga2−N2 200.2(3), Ga2−N3 200.1(3), N1−N2 132.6(4), N1−C1 135.2(5), N2−C2 138.3(5), Ga−C 200.1(4)−201.3(4).

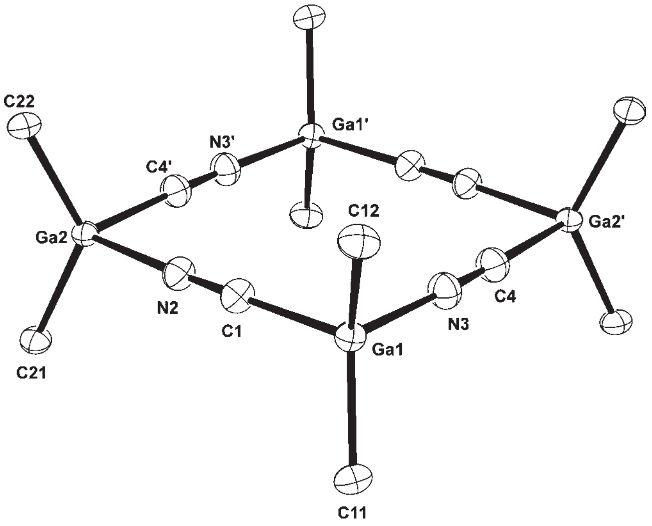

Figure 2. Molecular structure and numbering scheme of **4**; displacement ellipsoids are drawn at the 40% level. Methyl groups have been omitted for clarity. Important bond lengths [pm] and angles [deg]: Ga1−C1/N3 204.4(2), Ga2−N2/C4′ 204.4(2); C1−N2 114.9(4), C4−N3 114.6(4); Ga−C(Bu^t) 198.3(2)−198.9(2), C1−Ga1−N3 94.7(1), N2−Ga2−C4′ 93.6(1), Ga1−C1−N2 178.5(2), Ga2−N2−C1 176.8(2), Ga1−N3−C4 178.1(2), Ga2′−C4−N3 178.0(3). Symmetry transformations: $-x$, $-y + 2$, $-z + 2$.

groups. The bond distances $N{=}CH_2$, $N{-}CH_3$, and N−N are with 135.2(5), 138.3(5), and 132.6(4) pm indicative of a delocalized bonding situation in the backbone of the molecule. These values are very similar to those of the aluminum analogue,[11] but differ from those observed in related gallium hydrazonides with a more localized bonding situation.[17] The Ga−N distances are with values between 200.1(3) and 201.0(3) pm within experimental error identical and only slightly longer than those in the aluminum derivative, hereby supporting the above-mentioned notion of a delocalized bonding situation in the backbone. The ^1H and ^{13}C NMR spectra are consistent with the solid state structure being preserved in solution. There are two signals for the two non-equivalent Bu^t groups on Ga1 and Ga2, respectively. The geminal hydrogen atoms of the $N{=}CH_2$ group show a typical pattern of an AB spin system (J = 8.7 Hz) with calculated chemical shifts of δ = 5.38 and 5.41.[18] The signal of the NH_2 group bridging the two Ga atoms is with δ = 0.14 located in the high field region of the spectrum.

This is the second time (cf. thermolysis of $[Bu^t_2Al(NHNHMe)]_2$[11]) that we have observed such a strange and up to now not fully understood rearrangement process in a thermolysis reaction of hydrazides. The formation of **3** is likely to be the result of the cleavage of both N−N bonds of the intermediate hydrazide and the subsequent new formation of one N−N bond with both nitrogen atoms bound to carbon atoms. A nitrene fragment N-R may occur as an intermediate and may insert into a Ga−N bond to give the hydrazonide group of **3**. The likely formation of such a nitrene in the course of the decomposition of hydrazides is supported by the isolation and characterization of a weak diazene adduct with a heterocubane Al_4N_4 cage compound, $(Pr^i\text{-}N{=}N\text{-}Pr^i)\cdot(HAlNPr^i)_4$, as its rational secondary product.[19] The nitrogen atoms of the diazene molecule are located above a face of the heterocubane and are each coordinated to a single aluminum atom with relatively long Al−N distances. The diazene can be readily removed by heating of the solid material. On the basis of the results of quantum-chemical calculations nitrene was postulated as a product of the thermal decomposition of *tert*-butylhydrazine.[20]

Compound **4** is insoluble in non polar solvents and only sparingly soluble in 1,2-difluorobenzene. This has prevented a complete characterization by NMR spectroscopy, but its constitution was confirmed by mass spectrometry (M^+) and X-ray crystallography. The backbone of the molecule shows an essentially planar 12-membered $Ga_4C_4N_4$ heterocycle (Figure 2). The carbon and nitrogen atoms are statistically disordered as was also observed in the isostructural aluminum derivative.[16] The C≡N bonds are with an average value of 114.8 pm in the expected range,[21−24] and their coordination deviates with Ga−C−N and C−N−Ga bond angles of 176.8(2) to 178.5(2)° only slightly from linearity. **4** is only the second

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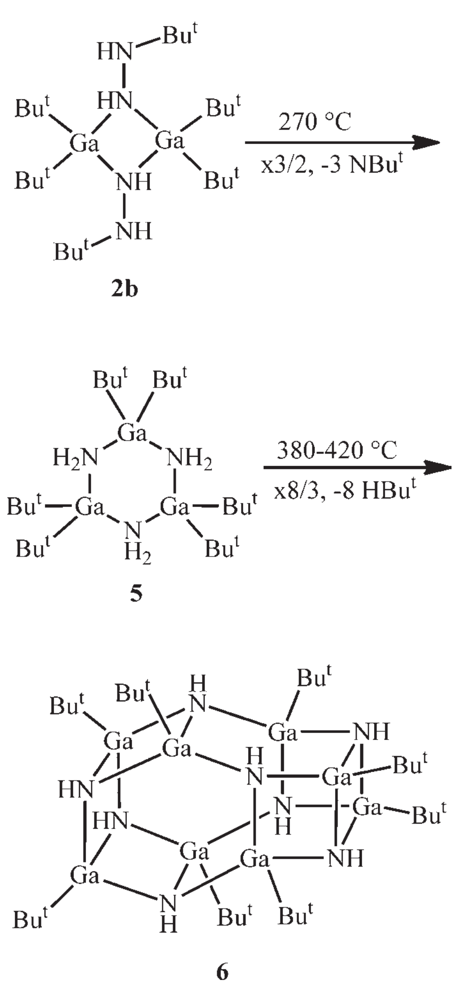
Scheme 3



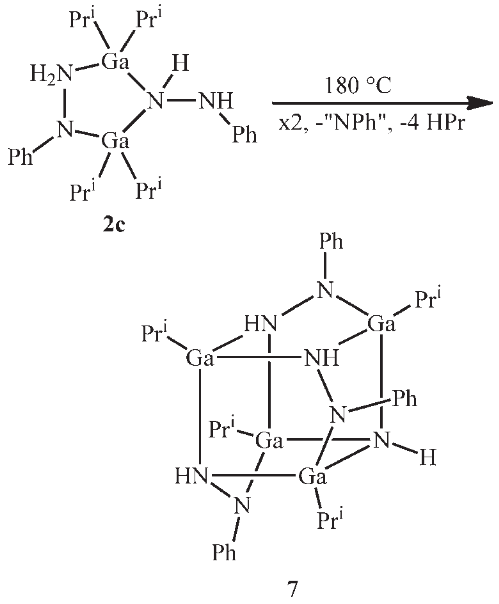
example of a crystallographically characterized neutral organometallic gallium cyanide. It may be compared to the trimeric $[(\{Me_3Si)_2CH\}_2Ga(CN)]_3$[22] that features a nine-membered $(GaCN)_3$ heterocycle and the ionic gallanates $Cs[(Me_3Ga)_2(CN)]$[23] and $NEt_4[Ga(Mes)(CN)_3]$.[24]

2.2. Thermolysis of the Hydrazide $[Bu^t_2Ga(NH\text{-}NHBu^t)]_2$ 2b. When $[Bu^t_2Ga(NH\text{-}NHBu^t)]_2$ **2b**[25] was heated for 3 h to about 270 °C all N−N bonds were cleaved, and the trimeric gallium amide $[Bu^t_2GaNH_2]_3$ **5** was obtained in good yield (70%) after crystallization from *n*-pentane (Scheme 3). ***Caution!*** *The reaction temperature must not exceed 270 °C because explosive decomposition was observed upon rapid heating of* ***2b*** *to higher temperatures.* Further thermolysis of the pure product (after complete consumption of **2b**) at about 400 °C for 3 h yielded the gallium imido cage compound $[Bu^tGaNH]_8$ **6** in 45% yield (Scheme 3). Formal loss of a nitrene ("NBu^t") as required for the formation of $[Bu^t_2GaNH_2]_3$ has been observed previously in related thermal reactions of Group 13 El-N compounds[11,19] and has been discussed above. The synthesis of $[Bu^t_2GaNH_2]_3$ **5** via an alternative route by the thermolysis of $Bu^t_3Ga{\leftarrow}NH_3$ at 160 °C and its full characterization have already been reported.[26] The cage compound **6** possesses in the solid state a crystallographic C_2 axis that passes through the centers of the two four-membered heterocycles Ga3N1Ga3′N1′ and Ga2N2Ga2′N2′ (Figure 7; for a full discussion of the crystal structure see below). In solution the C_2 axis becomes an approximate S_4 inversion axis resulting in only two different types of gallium and nitrogen atoms, the elements being either part of two four-membered and one six-membered or one four-membered and two six-membered rings. Consequently there are only two different Bu^t and NH groups observed in the ^1H and ^{13}C NMR spectrum of **6**. The resonances of the N−H groups are located with $\delta = 1.03$ and 0.67 in the high field region of the spectrum, which is comparable to the values of the $NHGa_3$ protons of the related cage compounds $(Pr^iGa)_4(NH\text{-}NPh)_3NH$ (**7**) and $(MeGa)_4(NH\text{-}NBu^t)_3NH$ (**10**, see Table 1). The electron impact mass spectrum of **6** shows the molar mass minus a Bu^t group $[M^+ - Bu^t]$ as the 100% peak.

Table 1. Selected ^1H NMR Parameters of Compounds **6**−**11**

compound	NHNR	NH	GaR
6		1.03, 0.67	1.20, 1.14
7	2.37	0.27	1.2 m
8[13a]	2.09		−0.02
9	2.22		0.27, 0.11
10	2.37	0.27	0.07
11	2.73, 2.57, 2.20, 2.18		0.02−0.23

Scheme 4



2.3. Thermolysis of the Hydrazides $(Pr^i_2Ga)_2(NH\text{-}NHPh)(NH_2\text{-}NPh)$ 2c and $[Me_2Ga(NH\text{-}NHBu^t)]_2$ 2d. We have previously published the conversion of the sterically less hindered hydrazine adduct $Pr^i_3Ga{\leftarrow}NH_2\text{-}NHPh$ to the hydrazide $(Pr^i_2Ga)_2(NH\text{-}NHPh)(NH_2\text{-}NPh)$ **2c** in refluxing toluene.[10] Further thermolysis of **2c** at 180 °C led in good yield (69%) to the formation of the cage compound $(Pr^iGa)_4(NHNPh)_3NH$ **7** (Scheme 4) that was obtained as colorless crystals after crystallization from 1,2-difluorobenzene. The related hydrazide $[Me_2Ga(NH\text{-}NHBu^t)]_2$ **2d** was obtained similarly from $GaMe_3$ and $Bu^tHN\text{-}NH_2$ via the isolable and relatively persistent adduct $Me_3Ga{\leftarrow}NH_2\text{-}NHBu^t$ (**1b**) (Scheme 5). These compounds have

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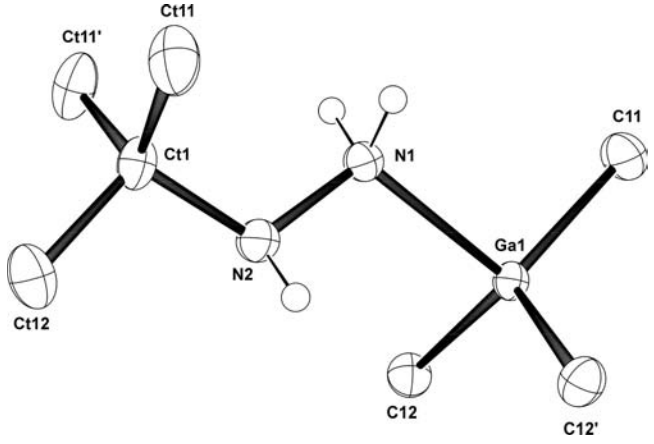


Figure 3. Molecular structure and numbering scheme of **1b**; displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Important bond lengths [pm]: Ga1−N1 211.2(2), Ga1−C11 197.7(3), Ga1−C12 198.7(3), Ga1−C12′ 198.7(2), N1−N2 144.1(3). Symmetry transformations: −*x*, *y*, *z*.

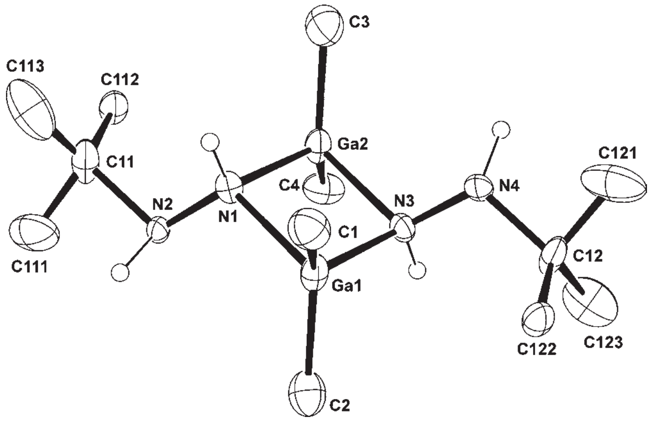
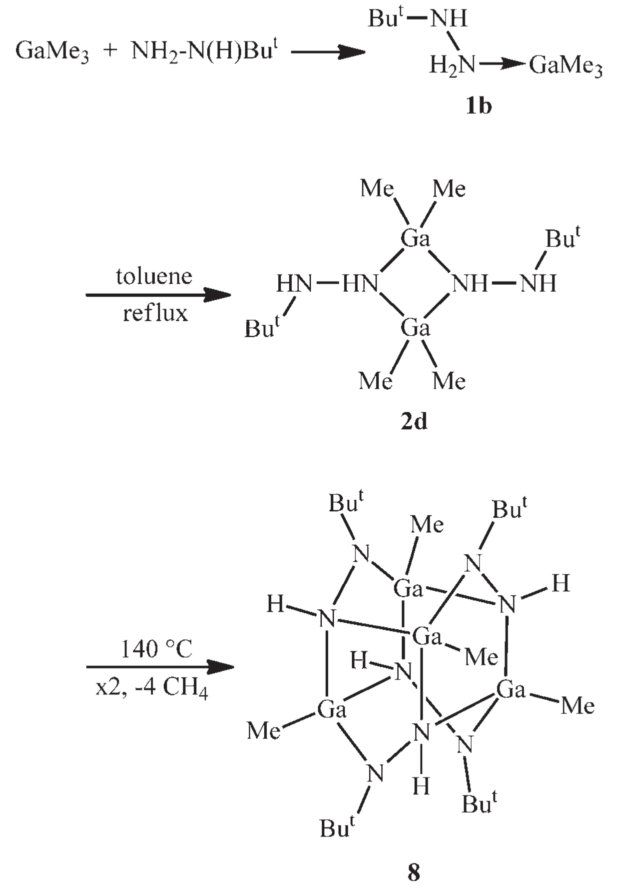


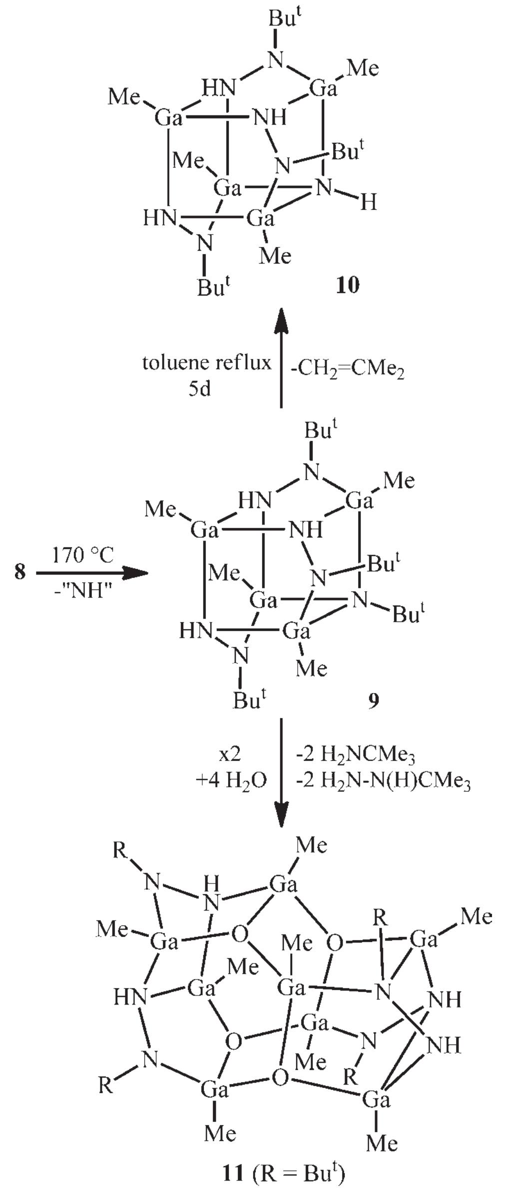
Figure 4. Molecular structure and numbering scheme of **2d**; displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Important bond lengths [pm] and angles [deg] (values for one set of the disordered atoms): Ga1−N1 205.6(7), Ga1−N3 201.6(7), Ga2−N1 201.7(7), Ga2−N3 206.3(6), N1−N2 145.2(4), N3−N4 145.1(4), Ga−N−Ga 92.3 (av.), N−Ga−N 87.7 (av.).

Scheme 5



been described previously,[13b] but their solid state structures were unknown. The hydrazine ligand of **1b** (Figure 3) is coordinated via the sterically less shielded NH_2 nitrogen atom, and the bond parameters correspond to values of related compounds.[8−10] The crystal structure of **2d** shows a four-membered Ga_2N_2 heterocycle in the molecular core with two exocyclic N−N bonds (Figure 4). This structural motif is generally observed for aluminum, gallium and indium *tert*-butylhydrazides and may be the preferred arrangement because of a minimization of steric repulsion.[12c,25] NMR data of **1b** and **2d** in solution are in complete agreement with the molecular structures and reveal the expected singlets for *tert*-butyl and Ga-Me groups and two resonances for the chemically different N−H protons. When the isolated hydrazide **2d** was heated in the absence of a solvent for 2 h to 140 °C the tetranuclear cage compound $(MeGa)_4(NH\text{-}NBu^t)_4$ **8** was obtained under retention of the N−N bonds. It was isolated in good yield (82%) after recrystallization from *n*-hexane (Scheme 5) and has been previously synthesized by heating of the hydrazide **2d** in refluxing toluene for 36 h.[13a] Further thermolysis of the hydrazindiide **8** at 170 °C yielded under formal loss of the nitrene "NH" from a single hydrazindiido ligand the cage compound $(MeGa)_4(NHNBu^t)_3NBu^t$ **9** (Scheme 6) which still possesses three intact N−N bonds. Crystallization of **9** yielded colorless crystals of relatively poor quality. A crystal structure determination allowed the unambiguous assignment of the constitution of **9** as schematically given in Scheme 6. The refinement did, however, not give reasonable results with respect to R-values and standard deviations. Therefore, we abstain from a more detailed discussion of the structural parameters. **9** was further converted in refluxing toluene to the cluster compound $(MeGa)_4(NHNBu^t)_3NH$ **10** by elimination of 1 equiv of isobutene (5 d). Traces of water gave few colorless single crystals of the unique octanuclear hydrazindiido oxo compound $(MeGa)_8(NH\text{-}NBu^t)_4O_4$ **11** by partial replacement of hydrazido ligands and loss of the *tert*-butylimido group (Scheme 6). Compound **11** was reproducibly obtained in a moderate yield of 23% by the specific reaction of **9** with stoichiometric quantities of water in toluene and heating of the mixture for 22 h. The NMR spectra of compounds **7**−**11** are characterized by typical resonances of hydrazine protons in the region of $\delta = 2.18{-}2.73$ ppm (Table 1) and, where present, $NHGa_3$ protons that are shifted high-field to $\delta = 0.27$ ppm as expected for protons connected to an electron rich nitrogen atom. The alkyl groups bound to gallium are found in a similar region of the spectrum. The spectra of the closely related cage compounds **7**, **9**, and **10** are

Scheme 6



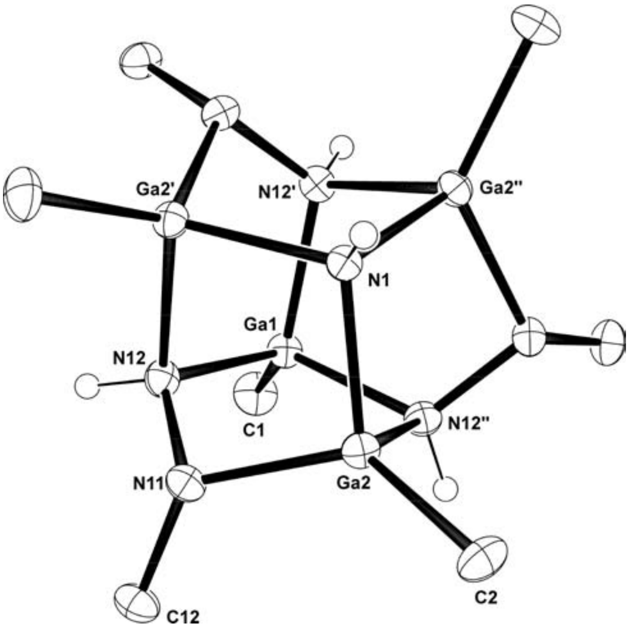


Figure 5. Molecular structure and numbering scheme of **10**; displacement ellipsoids are drawn at the 40% level. Methyl groups have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Important bond lengths [pm]: Ga1−N12 198.3(3), Ga2−N1 195.1(2), Ga2−N11 191.8(3), Ga2−N12'' 202.8(3), N11−N12 149.2(4). Symmetry transformations: $' -x+y, -x+1, z; '' -y+1, x-y+1, z$.

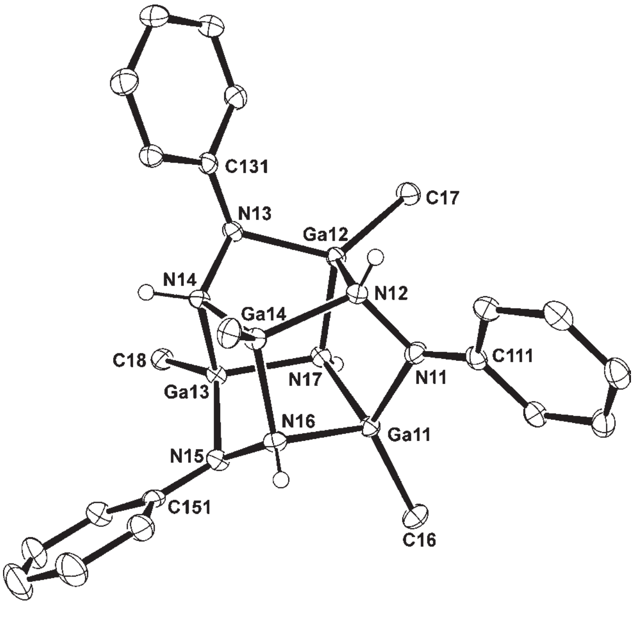


Figure 6. Molecular structure and numbering scheme of **7** (only one of two independent molecules is shown); displacement ellipsoids are drawn at the 40% level. Methyl groups have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Important bond lengths [pm] (average values): Ga−N (imido, Ga_3N) 194.6, Ga−N (NH of hydrazindiide, Ga_2N) 200.3, Ga−N (N−C_6H_5, GaN) 192.5, N−N 146.5.

surprisingly simple as the result of an approximate C_3 axis that passes through one of the GaR groups and the unique NH or NBu^t group (cf. Figures 5 and 6). All three hydrazine and the attached GaR substituents are therefore magnetically equivalent. This is in marked contrast to the irregular cluster of $(MeGa)_8(NHNBu^t)_4O_4$ **11** that shows no intrinsic molecular symmetry (cf. Figure 8), and consequently NMR spectra with eight non-equivalent methyl and four non-equivalent Bu^t groups are observed. The assignment of characteristic vibrational frequencies including the breathing frequencies of the cages together with some relevant examples from the literature are summarized in Table 2.

2.4. Molecular Structures of the Cages 6, 7, 10, and 11. Compounds **7** and **10** possess in solution a 3-fold rotation axis (see above). In the solid state structure of compound **10** this axis is preserved as a crystallographic C_3-axis through the atoms H1−N1···Ga1−C1 (Figure 5). As a result of the lower symmetry of an isopropyl as compared to a methyl group this high symmetry is only approximately fulfilled in the related molecular structure of compound **7** (Figure 6). The cages may be derived from a Ga_4N_4 cube, three edges of which are in accordance with the 3-fold rotational symmetry alternately bridged by N-Ph or N-Bu^t groups. This structural motif closely resembles the arrangement of the phosphorus atoms in the anion $[P_{11}]^{3-}$ (ufosane).[27] The cages may be alternatively viewed as six connected five-membered GaN_2GaN heterocycles in an envelope conformation in which the NR' groups of the hydrazindiido ligands (**7**, R′ = Ph; **10**, R′ = Bu^t) bind to one gallium atom, the hydrazine NH groups to two metal atoms. The isolated NH group is coordinated to three gallium atoms. The corresponding Ga−N distances (Table 3) differ considerably with values in the range of 192 [(NH)*N*R′], 201 [*N*H(NR′)] and 195 pm (*N*HGa_3), respectively. The bond lengths are therefore shortest for the three-coordinate and longest for the four-coordinate nitrogen atoms of the hydrazine groups with those of the single $NHGa_3$ group ranging in between. Ga−C and N−N bond distances are with approximately 197 and 148 pm in the expected region. Compound **10** is chiral (Ga2, N11 and N12 are asymmetric) and the absolute configuration was crystallographically determined to be S(Ga2)R(N11)R(N12) [Flack parameter −0.01(2)]. It is, however, likely that the solution is a racemic mixture of both enantiomers that crystallize separately. In the case of compound **7** there are two independent molecules of the same configuration in the asymmetric unit and as a result of the centro-symmetric space group there is a racemic mixture of both enantiomers present in the solid state. The two compounds may be compared to the related clusters $[EtGa(NHNPh)]_4$,[10] $[MeGa(NHNPh)]_4$,[13b] and $[MeGa(NHNBu^t)]_4$[13a] that differ from **7** and **10** by replacing the unique NH group with an additional hydrazide ligand. In this context reference should also be made to the related mixed hydrazide hydroxide cages of zinc, $[(RZn)_4(NHNMe_2)_3(OR')]$[28] (R = Pr^i, R′ = Et, Pr^i; R = Me, Et, R′ = H; R = Et, R′ = OMe), that adopt similar but less symmetrical molecular structures. To compensate for the different charges of Ga^{3+} and Zn^{2+} the dianionic hydrazindiide, $[RN\text{-}NH]^{2-}$, and NR^{2-} substituents in the gallium compounds are replaced by monoanionic hydrazide, $[Me_2N\text{-}NH]^-$, and OR^- groups.

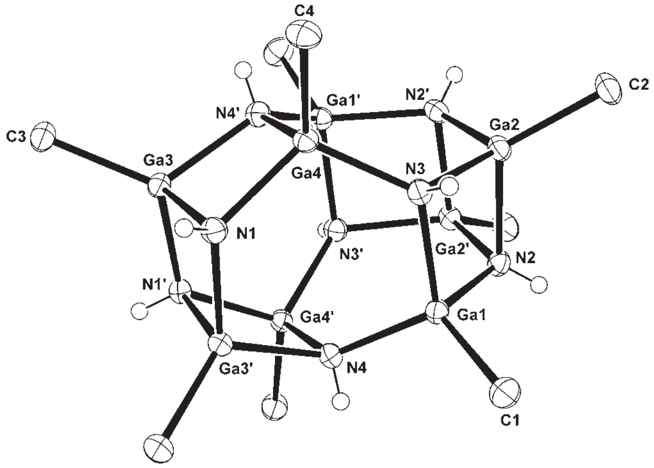


Figure 7. Molecular structure and numbering scheme of **6**; displacement ellipsoids are drawn at the 40% level. Methyl groups have been omitted for clarity. Hydrogen atoms have been drawn with arbitrary radius. Important bond lengths [pm]: Ga−N 202.5 (av., common edges of two Ga_2N_2 rings), 196.2 (av., common edges of Ga_2N_2 and Ga_3N_3 rings), 192.5(av., common edges of two Ga_3N_3 rings). Symmetry transformations: $-x, y, -z + {}^1/_2$.

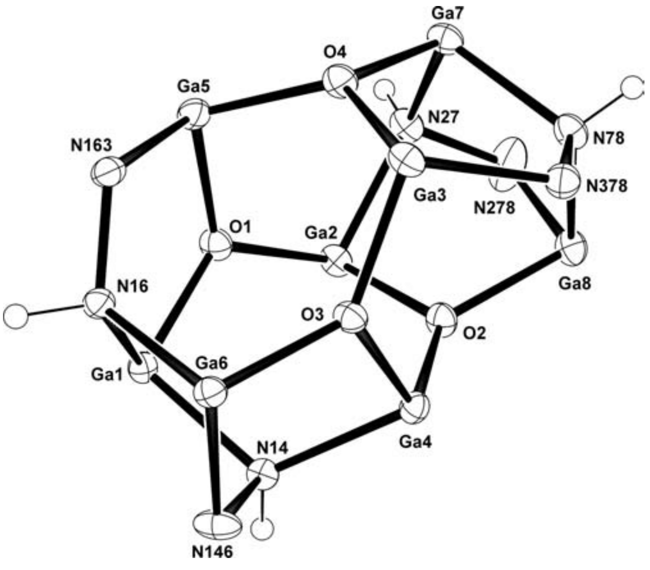


Figure 8. Molecular structure and numbering scheme of **11**; displacement ellipsoids are drawn at the 40% level. Methyl and Bu^t groups have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Important bond lengths [pm] (average values): Ga−O 188.1, Ga−N (NH of hydrazindiide, Ga_2N) 198.7, Ga−N (N-CMe_3, GaN) 192.5, N−N 149.9.

The molecular structures of the octanuclear compounds $[Bu^tGaNH]_8$ **6** and $(MeGa)_8(NHNBu^t)_4O_4$ **11** (Figures 7 and 8) are formally quite similar and exhibit decahedral cages of eight gallium and eight imido nitrogen atoms (**6**) or of eight gallium atoms, four oxygen atoms, and four hydrazindiido ligands (**11**), respectively. The cage of **6** consists of four six-membered Ga_3N_3 heterocycles, that are annulated with six four-membered Ga_2N_2 heterocycles. As a result of the presence of intact hydrazido groups and oxygen atoms the four-membered Ga_2N_2 rings are replaced completely by four five-membered Ga_2N_2O and two five-membered Ga_2N_3 heterocycles in compound **11** which in addition to two Ga_3NO_2 rings further possesses two annulated seven-membered $Ga_3N_2O_4$ heterocycles as a unique structural motif. Compound **6** has a C_2 axis that passes through the centers of two four-membered Ga_2N_2 heterocycles (Ga3N1Ga3′N1′ and Ga2N2Ga2′N2′). The GaN_2 bond angles in the six-membered rings are close to tetrahedral (approximately

Table 2. Selected IR (and Raman) Parameters of GaN Cage Compounds

compound	ν_{NH}	$\nu_{NH(NR)}$	$v_{as,GaN}$ (cage)	$v_{s,GaN}$ (cage)	$v_{s,GaC}$
$[MeGaNBu^i]_6$[32]			659, 581	567	557, 552
$[MeGaNBu^t]_4$[28]			645	619	565
$[MeGaNPr^i]_4$[28]			633	611	565
6	3350	3287	640	590	526
7	3391, 3338	3298, 3246	638	581	532
8[13a]		3286	610	566	500
9		3298	651	568	513
10	3352	3296	611	567	509
11		3298 - 3262	613	567	542

Table 3. Selected Bond Lengths of Compounds **6**, **7**, **8**, **10**, and **11**

compound	Ga−C	Ga−N (Ga_3NH)	Ga-NH(NR)	Ga-NR(NH)	N−N
6	199.3(av)	192.5(av), 196.2(av), 202.5(av)			
7	196.1(av)	194.6(av)	200.3(av)	192.5(av)	146.5(av)
8[13a]	195.6(av)		199.7(av)	187.9(av)	149.1(av)
10	195.6(av)	195.1(2)	200.6(av)	191.8(3)	149.2(4)
11	195.5(av)		198.7(av)	190.7(av)	149.9(av)

109°) while the corresponding NGa_2 angles are with close to 124° significantly larger. The corresponding angles in the four-membered rings are close to 90° with the GaN_2 angles being slightly more acute than the NGa_2 angles. The Ga−N nitrogen bond lengths depend on the size of the connected rings (Table 3). Ga−N bonds that connect two six-membered rings are short (193 pm) while those that connect two four-membered rings are much longer (203 pm). Ga−N distances between a six- and a four-membered ring lie between those values (194−199 pm). Compound **11** has no crystallographic symmetry, and solution NMR spectra show eight different Ga-Me and four different Bu^t groups. The Ga−N distances depend on the nature of the nitrogen atom as was the case for compound **7** and **10**. The shortest Ga−N distances result for the groups $(NH)(Bu^tN)Ga$ (190−193 pm) with the *N*-Bu^t nitrogen atoms coordinated to only one gallium atom, while longer Ga−N bond lengths are detected to the N−H groups containing tetracoordinated nitrogen atoms, $(NBu^t)(HN)Ga_2$ (199 pm). Distances in the expected range of about 188 pm were observed for the Ga−O bonds. The Ga−C bond lengths are unexceptional and lie within the range of values reported in the literature.

3. Conclusion

The presented oligonuclear imido and hydrazido compounds expand our knowledge on GaN cages considerably. While some heterocubanes $[RGaNR']_4$ (R = Me, R′ = Pr^i,[29] Bu^t,[29] $SiMe_3$,[30] C_6F_5;[31] R = Ph, R′ = Ph[32]) and hexagonal heteroprismanes $[RGaNR']_6$ (R = Me, R′ = Bu^i,[33] C_6F_5;[34] R = Et, R′ = Et[35]) have been described, more irregular and nitrogen-rich cages are so far extremely rare and only few compounds such as $(PhGa)_4(NHBu^i)_4(NBu^i)_2$,[36] $(PhGa)_7(NHMe)_4(NMe)_5$,[36] $(Me_2GaNHMe)_2(MeGaNMe)_6$,[37] $(PhGaNMe)_7$[32] and $HN\{[HGaNMe][H_2GaNC(NMe_2)_2]\}_3GaH$[38,39] have been reported in the literature. Even less common are hydrazido cages which have been mentioned in the text. The cage compound $(GaMe)_4(GaMe_2)_4(N_2)(NHNMe)_4$[15] which was obtained in our group only recently and contains a completely deprotonated hydrazine, $[N_2]^{4-}$, is a particularly interesting and important result of our investigations into the chemistry of gallium hydrazides.

The thermolysis reactions of gallium hydrazides proceed via a fascinating variety of different cage compounds in particular in those cases where the N−N bonds remain intact. The special situation with two adjacent donor atoms in the hydrazinido groups opens access to unique structural motifs, and cages of high nuclearity become easily available. Even larger cages similar to that one of the mixed hydrazindiido-oxo compound **11** may be generated in the near future. The course of these reactions is influenced strongly by the substituents of the gallium atoms and the hydrazine ligands. A concise knowledge of these balanced effects is crucial for the development of a reasonable strategy for the application of these compounds in the generation of GaN materials which represents the next step in our research activities. It must be emphasized, however, that these reactions have to be conducted very cautiously. In rare cases, depending once more on the substitution of the hydrazides, these compounds are highly explosive upon heating. The cage compound $(MeGa)_4(NH\text{-}NPh)_4$ which has already been described in the literature,[13b] but was synthesized differently, exploded above 225 °C. It showed a strong exothermic peak in a DTA experiment at this temperature. The produced gaseous material consists, as detected by mass spectrometry, essentially of methane, dinitrogen, and benzene. Another example is the thermolysis of the hydrazide **2b** which slowly decomposed at 270 °C, while above this temperature explosive decomposition was observed. Again a strong exothermic peak which was accompanied by the formation of elemental nitrogen was found in the DTA experiment. Hence, it is strongly recommended to start every new experiment in this fascinating research area with an analysis of the thermal parameters. In most cases the decomposition proceeds smoothly on a scale of up to several grams in starting material.

4. Experimental Section

General Remarks. All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. NMR spectra were

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recorded in benzene-d_6 or THF-d_8 at ambient probe temperature using the following Bruker instruments: Avance I (^{1}H 400.13, ^{13}C 100.6 MHz), Avance III (^{1}H, 400.03, ^{13}C 100.59 MHz), or AC200 (^{1}H 200.13 MHz, 50.32 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton-decoupled. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelms-Universität Münster. IR-spectra were recorded as Nujol mull between KBr plates on a Shimadzu Prestige 21 spectrometer, electron impact mass spectra on a Varian mass spectrometer. The hydrazine adduct $Me_3Ga\leftarrow NH_2\text{-}NHBu^t$ (**1a**) and the dimeric hydrazide $[Me_2Ga(NH\text{-}NHBu^t)]_2$ (**2d**) were obtained in accordance with literature procedures.[13a] Compound **2d** is unstable in solution and difficult to obtain in pure form. The melting point of a pure sample was determined to be 134 °C.

$Bu^t_2Ga(\mu\text{-}NH_2)[\mu\text{-}N(Me)\text{-}N(=CH_2)]GaBu^t_2$ (3). Neat $Bu^t_3Ga\leftarrow NH_2\text{-}NHMe$[8a] (2.30 g, 8.01 mmol) was heated to 170 °C for 16 h. The reaction was accompanied by a visible gas evolution. The obtained pale yellow viscous liquid was then treated with *n*-pentane (10 cm^3). This solution was decanted to remove small quantities of solid particles and then concentrated and cooled (+2 °C) to give colorless crystals of **3** (1.3 g, 74%). M.p.: 107 °C. Anal. Calcd. (Found) for $C_{18}H_{43}Ga_2N_3$ (%): C, 49.0 (49.0); H 9.8 (9.8); N 9.5 (9.5). ^{1}H NMR (benzene-d_6, 400 MHz, 300 K): δ 0.14 (2H, s, br, NH_2), 1.12 and 1.15 (each 18H, s, CMe_3), 2.52 (3H, s, NMe), 5.38 (1H, d (AB), $^3J_{H-H}$ = 8.66 Hz, CH cis to N), 5.41 (1H, d (AB), $^3J_{H-H}$ = 8.66 Hz, CH cis to Ga). ^{13}C NMR (benzene-d_6, 100 MHz, 300 K): δ 21.9 and 22.5 (CMe$_3$), 31.4 and 32.0 (CMe_3), 37.9 (NMe), 114.2 (CH$_2$). IR (nujol, KBr, cm^{-1}): 3364 (w), 3307 (w) υNH; 2951 (vs), 2924 (vs), 2853 (vs) nujol; 1503 (m) δNH; 1460 (s), 1377 (m) nujol; 1273 (m) δCH$_3$; 1193 (m), 1113(m), 1007 (w), 976 (m), 937 (w), 876 (m) δCH$_3$, υ_{as}CC$_3$, υCN, υNN, 813 (m), 785 (m) υ_sCC$_3$; 723 (w) paraffin; 700 (w), 569 (m), 523 (w), 488 (m), 448 (w) υGaC, υGaN, δCC$_3$. MS (EI, 20 eV, 298 K, *m*/*z*, experimental intensities agree with expected isotopic distribution; only the most intense peak of the fragment is given): 384 (100%) M$^+$ − CMe$_3$.

$(GaBu^t_2)_4(CN)_4$ (4). Compound **3** (2.70 g, 6.12 mmol) was heated in the absence of a solvent to 380 °C for 2 h. Keeping the reaction mixture a few minutes at that temperature was accompanied by a significant gas evolution. The reaction temperature was then, over the course of an hour, increased to 400 °C. During this period there was a color-change from yellow to red and finally a black precipitate started to form. At this point the reaction was discontinued, and the residue treated with 1,2-difluorobenzene (15 cm^3). The red solution was filtered, concentrated, and cooled to −28 °C to give compound **4** as colorless crystals (1.40 g, 55%). **4** is insoluble in non-coordinating solvents. Anal. Calcd (Found) for $C_{36}H_{72}Ga_4N_4$ (%): C, 51.5 (51.5); H 8.6 (8.2); N 6.7 (6.6). M.p.: 179 °C. ^{1}H NMR (THF-d_8, 400 MHz, 300 K): δ 1.10 (18H, s, CMe_3); probably the THF adduct. IR (nujol, KBr, cm^{-1}): 2199 (m) υC≡N; 1464 (s), 1454 (s), 1375 (m) nujol; 1364 (m) δCH$_3$; 1180 (vw), 1012 (w), 941 (vw), 818 (m) υCC; 721 (vw) nujol; 530 (vw), 422 (s) υGaC, υGaN. MS (EI, 20 eV, 373 K, *m*/*z*, experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 840 (0.8%) M$^+$, 783 (25%) M$^+$ − CMe$_3$, 572 (65%) M$^+$ − GaBu$^t_3$CN, 394 (100%) (Bu$^t_2$Ga)$_2$CN$^+$.

$(Bu^t_2GaNH_2)_3$ (5).[18]. Neat $(Bu^t_2GaNH\text{-}HNBu^t)_2$[25] (**2b**) (1.80 g, 3.32 mmol) was heated to 270 °C and kept at this temperature until the solid had been transformed completely into a pale yellow liquid. The temperature was then slowly raised to 300 °C, and the reaction mixture kept at this temperature for a total reaction time of 3 h. The product was then recrystallized from *n*-pentane (10 cm^3; +20/+2 °C) to give colorless crystals of $(Bu^t_2GaNH_2)_3$ (0.93 g, 70%). Characterization: See ref 18. ***Caution!*** *The reaction should be carried out with great care as the product may violently decompose if the solid starting material is heated above 270 °C.*

$(GaBu^t)_8(NH)_8$ (6). Neat $(Bu^t_2GaNH_2)_3$ (**5**) (1.50 g, 2.50 mmol) was heated to 380 °C for 1 h. After 15 min at this temperature a gas evolution was observed. The temperature was kept constant for another hour and then very slowly raised to 420 °C. After an overall reaction period of 3 h a black residue started to appear, and the heating was discontinued. The obtained residue was dissolved in *n*-pentane (15 cm^3) and cooled to −28 °C to give colorless crystals of compound **6** (0.48 g, 45%). Anal. Calcd. (Found) for $C_{32}H_{80}Ga_8N_8$ (%): C, 33.9 (33.9); H 7.1 (7.1); N 9.9 (9.1). M.p.: 304 °C (subl.). ^{1}H NMR (benzene-d_6, 400 MHz, 300 K): δ 0.67 and 1.03 (each 1H, s, br, NH), 1.14 and 1.20 (each 9H, s, CMe_3). ^{13}C NMR (benzene-d_6, 100 MHz, 300 K): δ 20.6 and 22.2 (CMe$_3$), 30.3 and 30.5 (CMe_3). IR (nujol, KBr, cm^{-1}): 3350 (vw), 3287 (vw) υNH; 2942 (vs), 2922 (vs), 2853 (vs) nujol; 1466 (vs), 1454 (vs), 1377(s) nujol; 1362 (s) δCH$_3$; 1179 (w, br), 1009 (m, sh), 993 (m), 914 (m), 849 (m), 812 (m), 745 (m), 683 (w) υ_{as}CC$_3$, υ_sCC$_3$; 590 (w), 527 (vw), 503 (vw), 478 (w), 438 (m) υGaN, υGaC. MS (EI, 20 eV, 333 K, *m*/*z*, experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 1077 (100%) M$^+$ − CMe$_3$, 963 (6%) M$^+$ − 3CMe$_3$.

$(Pr^iGa)_4(NH\text{-}NPh)_3NH$ (7). Neat $(Pr^i_2Ga)_2(NH\text{-}NHPh)(H_2N\text{-}NPh)$[10] (**2c**) (1.70 g, 3.23 mmol) was heated to 180 °C for 4 h to give a pale red, glassy solid, which was washed with *n*-pentane (25 cm^3). The remaining solid was dissolved in 1, 2-difluorobenzene (10 cm^3). Colorless crystals of compound **7** formed spontaneously at room temperature (2 d, 0.87 g, 69%). M.p.: 175 °C. Anal. Calcd. (Found) for $C_{30}H_{47}Ga_4N_7$ (%): C, 45.9 (46.4); H 6.0 (5.7); N 12.5 (12.6). ^{1}H NMR (THF-d_8, 400 MHz, 300 K): δ 0.73 (1H, s, NH), 1.20, 1.22, 1.24, 1.33 (28H, broad s with shoulders, CMe_2, CH), 4.97 (3H, NH-NPh), 6.38 (3H, t, $^3J_{H-H}$ = 7.2 Hz, *p*-H), 6.61 (6H, d, $^3J_{H-H}$ = 8.6 Hz, *o*-H), 7.01 (6H, pseudo-t, *m*-H). ^{13}C NMR (THF-d_8, 100 MHz, 300 K): δ 21.0 and 21.2 (CHMe_2), 20.8 and 20.9 (CHMe$_2$), 111.7 (*o*/*m*-C), 115.4 (*p*-C), 129.8 (*o*/*m*-C), 155.8 (*ipso*-C). IR (nujol, KBr, cm^{-1}): 3391 (vw), 3339 (vw), 3246 (vw) υNH; 2953 (s), 2924 (vs), 2851 (s) nujol; 1599 (vs) δNH; 1495 (s), 1454 (s), 1377 (s) nujol; 1310 (vw), 1261 (m) δCH$_3$; 1206 (vw), 1180 (m), 1152 (w), 1101 (w), 1072 (w), 1026 (w), 988 (w), 951 (vw), 908 (vw), 876 (w) υNN, 750 (m) υCN, υCC; 692 (m), 638 (m), 581 (vw), 532 (vw), 459 (w) υGaN, υGaC. MS (EI, 20 eV, 413 K, *m*/*z*, experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 783 (22%) M$^+$, 679 (100%) M$^+$ − PhNNH, 588 (8%) M$^+$ − PhNNH − NPh.

$(MeGa)_4(NH\text{-}NBu^t)_4$ (8).[13a]**.** In a modification of the literature procedure $(Me_2Ga)_2(NH\text{-}NHBu^t)_2$ (**2d**) (2.00 g, 5.35 mmol) was heated in the absence of a solvent to 140 °C, at which temperature the substance liquefied. After 2 h at this temperature the mixture solidified and was then recrystallized from hexane (15 cm^3; +20/−28 °C) to give compound **8** as a colorless solid (1.50 g, 82%). Decomposition above 150 °C. Further characterization: See ref 13a.

$(MeGa)_4(NH\text{-}NBu^t)_3(NBu^t)$ (9). $(MeGa)_4(NH\text{-}NBu^t)_4$ (**8**) (1.80 g, 2.63 mmol) was heated for 3 h to 170 °C. After a few minutes at this temperature gas evolution was observed. The initially liquid substance solidified after 2.5 h reaction time. This solid was recrystallized from toluene (10 cm^3, +20/+2 °C) to yield colorless crystals of $(MeGa)_4(NH\text{-}NBu^t)_3(NBu^t)$ (**9**) (1.30 g, 74%). Anal. Calcd. (Found) for $C_{20}H_{51}Ga_4N_7$ (%): C, 35.9 (35.6); H 7.7 (7.6); N 14.7 (14.4). M.p.: 182 °C. ^{1}H NMR (benzene-d_6, 200 MHz, 300 K): δ 0.12 (3H, s, MeGaNH), 0.27 (9H, s, MeGaNBu^t), 1.05 (27H, s, HNNCMe_3), 1.41 (9H, NCMe_3) 2.22 (3H, s NH). ^{13}C NMR (benzene-d_6, 100 MHz, 300 K): δ −9.1 (NHGaMe), −2.7 (NBu^{t}GaMe), 29.4 (NHNCMe_3), 34.4 (NCMe_3), 54.7 (NCMe$_3$), 55.2 (NHNCMe$_3$). IR (nujol, KBr, cm^{-1}): 3298 (vw) υNH; 2951(vs), 2922 (vs), 2853 (vs), 1454 (vs), 1375 (s) nujol; 1290 (vw) δCH$_3$; 1209 (m), 1028 (vw), 976 (w), 945 (w), 926 (w), 903 (w), 822 (vw), 770 (vw) υNN, υCN, υCC; 723 (m) nujol; 652 (vw), 567 (vw), 513 (vw), 461 (vw) υGaN,

Table 4. Crystal Data and Structure Refinement for Compounds **1b**, **2d**, **3**, **4**, **6**, **7**, **10**, and **11**

	1b	**2d**	**3**	**4**	**6**	**7**·$(C_6H_4F_2)_{0.5}$	**10**	**11**
empirical formula	$C_7H_{21}GaN_2$	$C_{12}H_{34}Ga_2N_4$	$C_{18}H_{43}Ga_2N_3$	$C_{36}H_{72}Ga_4N_4$	$C_{32}H_{80}Ga_8N_8$	$C_{33}H_{49}FGa_4N_7$	$C_{16}H_{43}Ga_4N_7$	$C_{24}H_{64}Ga_8N_8O_4$
formula weight (M/g mol^{-1})	202.98	373.87	440.99	839.86	1134.80	841.67	612.45	1086.59
crystal system	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	trigonal	orthorhombic
space group	$Pmn2_1$[c]	$Pca2_1$[d]	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P31c$	$Pbca$
a (pm)	929.6(2)	2400.63(9)	1211.3(2)	891.43(1)	1997.1(2)	2389.19(7)	1117.68(3)	1612.51(9)
b (pm)	900.6(2)	660.37(3)	1396.5(3)	1192.41(2)	1314.3(1)	1626.58(5)	1117.68(3)	1835.4(1)
c (pm)	650.8(1)	1166.94(5)	1435.1(3)	1267.67(2)	1950.7(2)	1940.90(6)	1205.90(6)	2774.5(2)
α (deg)	90	90	90	69.385(1)	90	90	90	90
β (deg)	90	90	100.98(3)	71.980(1)	103.139(2)	107.882(1)	90	90
γ (deg)	90	90	90	85.393(1)	90	90	120	90
volume (nm^3)	0.5449(2)	1.8500(1)	2.3832(8)	1.19871(3)	4.9860(8)	7.1784(4)	1.30460(8)	8.2113(8)
Z	2	4	4	1	4	8	2	8
temperature (K)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
density (calculated; Mg/m^3)	1.237	1.342	1.229	1.163	1.512	1.558	1.559	1.758
absorption coefficient (mm^{-1})	2.471 (Mo K_α)	2.906 (Mo K_α)	2.265 (Mo K_α)	2.731 (Cu K_α)	4.282 (Mo K_α)	3.730 (Cu K_α)	4.101 (Mo K_α)	5.203 (Mo K_α)
θ range (deg)	2.26−29.99	1.70−31.02	2.05−29.01	3.91−72.33	1.87−31.87	1.94−73.05	2.10−27.88	1.47−27.85
reflections collected	5992	21539	18822	7067	30392	42744	11138	80030
independent reflections	1659 [R_{int} = 0.0315]	5836 [R_{int} = 0.0338]	6121[R_{int} = 0.0393]	4031 [R_{int} = 0.0675]	8096 [R_{int} = 0.0317]	13603 [R_{int} = 0.0325]	2081 [R_{int} = 0.0857]	9748 [R_{int} = 0.0381)
parameters	63	212	252	211	245	868	87	417
R1[a]	0.0233	0.0330	0.0588	0.0393	0.0276	0.0330	0.0300	0.0238
wR2(all data)[b]	0.0502	0.0753	0.1023	0.1086	0.0619	0.0886	0.0710	0.0603
largest diff. peak and hole (e·nm^{-3})	479, −222	567, −353	490, −581	398; −732	1485; −482	1324, −872	899; −396	646, −359

[a] Observation criterion: $I > 2\sigma(I)$. R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. [b] wR2 $= \{[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Flack parameter: 0.08(2). [d] See Experimental Section for discussion.

υGaC. MS (EI, 20 eV, 373 K, m/z, experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 667 (21%) M^+, 652 (4%) $M^+ - CH_3$, 566 (100%) M^+ − butene −3 CH_3.

$(MeGa)_4(NH\text{-}NBu^t)_3(NH)$ (10). $(MeGa)_4(NHNBu^t)_3(NBu^t)$ (**9**) (2.20 g, 3.29 mmol) was heated under reflux conditions for 5 d in toluene. The solvent was then removed in vacuo, and the obtained solid recrystallized from *n*-pentane (10 cm^3; +20/+2 °C) to give colorless crystals of **10** (1.40 g, 70%). Anal. Calcd. (Found) for $C_{16}H_{43}Ga_4N_7$ (%): C, 31.4 (31.2); H 7.1 (6.8); N 16.0 (15.5). Mp 197 °C. ^{1}H NMR (benzene-d_6, 400 MHz, 300 K): δ 0.07 (9H, s, *Me*GaNH), 0.11 (3H, s, *Me*Ga(NHNBu^t)$_3$), 0.27 (1H, s, N*H*), 1.06 (27H, s, NC*Me*$_3$), 2.37 (3H, s N*H*NBu^t). ^{13}C NMR (benzene-d_6, 100 MHz, 300 K): δ −9.2 (*Me*Ga(NH-NBu^t)$_3$), −7.9 (*Me*GaNH), 29.8 (NC*Me*$_3$), 55.1 (N*C*Me$_3$). IR (nujol, KBr, cm^{-1}): 3352 (vw), 3296 (vw) υNH; 2953 (vs), 2922 (vs), 2852 (vs) nujol; 1769 (vw) δNH; 1464 (s), 1454 (s), 1377 (s) nujol; 1285 (vw) δCH_3; 1211 (vw), 1092 (vw), 1026 (vw), 1011 (vw), 974 (w), 897 (vw), 810 (vw) υNN, υNC, υCC; 723 (vw) nujol; 611 (vw), 567 (vw), 509 (vw), 482 (vw), 464 (vw) υGaN, υGaC.

$(MeGa)_8(NH\text{-}NBu^t)_4O_4$ (11). $(MeGa)_4(NH\text{-}NBu^t)_3(NBu^t)$ (**9**) (0.58 g, 0.87 mmol) was dissolved in 100 cm^3 of toluene and stirred at room temperature. A 0.03 cm^3 portion of distilled water was added. A colorless solid of unknown composition precipitated immediately. The mixture was heated under reflux conditions for 22 h. After filtration all volatiles were removed in vacuo. The remaining solid was recrystallized from *n*-hexane (+20/+2 °C) to give colorless crystals of $(MeGa)_8(NH\text{-}NBu^t)_4O_4$ (**11**) (0.11 g, 23%). Anal. Calcd. (Found) for $C_{24}H_{64}Ga_8N_8O_4$ (%): C, 26.5 (27.0); H 5.9 (5.9); N 10.3 (10.1). Mp 238 °C. ^{1}H NMR (benzene-d_6, 400 MHz, 300 K): δ 0.00, 0.03, 0.095, 0.106, 0.113, 0.17, 0.22, and 0.27 (each 3H, s, *Me*Ga), 0.92, 0.94, 1.16, and 1.17 (each 9H, s, C*Me*$_3$), 2.18, 2.20, 2.57, and 2.73 (each 1H, s, N*H*NBu^t). ^{13}C NMR (benzene-d_6, 100 MHz, 300 K): δ −8.44, −8.36, −7.3, −7.0, −5.9, −5.5, −2.1, and −1.5 (*Me*Ga), 29.2, 29.4, 30.1, and 30.3 (C*Me*$_3$), 54.9, 55.0, 55.7, 55.8 (*C*Me$_3$). ^{15}N NMR (C_6D_6, 40.5 MHz, 300 K, from N−H correlated spectra): δ 60 (N−H of hydrazide, ^{1}H: δ = 2.73 and 2.18), 61 (N−H of hydrazide, ^{1}H: δ = 2.20) and 62 (N−H of hydrazide, ^{1}H: δ = 2.57), 101 (N-Bu^t, ^{1}H: δ = 1.16) and 102 (N-Bu^t of the remaining hydrazide ligands). IR (nujol, KBr, cm^{-1}): 3298 (w), 3285 (w), 3262 (w) υNH; 2951 (vs); 2922 (vs), 2852 (vs), 1468 (s), 1454 (s), 1439 (m), 1358 (m) nujol; 1308 (w), 1279 (vw) δCH_3; 1204 (m), 1078 (vw), 1030 (m), 1017 (w), 984 (w), 937 (vw), 891 (vw), 864 (vw), 772 (vw) υNN, υNC, υCC; 733 (w) nujol; 567 (w), 542 (vw) υGaN, υGaC. MS (EI, 20 eV, 443 K, m/z, experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 1085 (100%) M^+ − H, 1070 (12%) $M^+ - H - CH_3$, 983 (4%) $M^+ - CMe_3 - 3CH_3 - H$.

X-ray Crystallography. Crystals suitable for X-ray crystallography were obtained by recrystallization from *n*-pentane (**3**, **6**, **10**, **11**), *c*-pentane (**2d**), hexane (**1b**), or 1,2-difluorobenzene (**4**, **7**). Intensity data were collected on a Bruker APEX II diffractometer with monochromated Mo K_α or Cu K_α (**4**, **7**) radiation. The collection method involved ω-scans. Data reduction was carried out using the program SAINT+.[40] The crystal structures were solved by direct methods using SHELXTL.[41] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms (except NH of compounds **6** and **7**, which were refined isotropically) were positioned geometrically and allowed to ride on their respective parent atoms. The molecules of **1b** are located on crystallographic

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[40] (a) *SAINT+ (includes XPREP and SADABS)*, Version 6.02; Bruker AXS Inc.: Madison, WI, 1999. (b) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

[41] (a) *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Structures*; Universität Göttingen: Göttingen, Germany, 1997.

mirror planes; the atoms are partially disordered because of the special position. The structure of **2d** was refined in the noncentrosymmetric space group *Pca*2_1. Refinement in the centrosymmetric space-group *Pbcm* gave unsatisfactory results; also, the program PLATON[42] found no space group of higher symmetry. The hydrazide groups are disordered and were refined with occupancy factors of 0.56: 0.44 (N3, N4) and 0.59 to 0.41 (N1, N2). One Bu^t group of compound **3** (C12) was rotationally disordered and refined in split positions (0.76: 0.24). The hydrogen atoms of the methylene group were unequivocally located on the electron density map and then positioned geometrically. Carbon and nitrogen atoms of the CN groups of compound **4** were found to be statistically disordered and refined on the same position. **7** crystallized with two independent molecules in the asymmetric unit. One molecule of 1,2-difluorobenzene was enclosed per two formula units of **7**. One of its fluorine atoms was disordered over two positions and refined with a site occupation factor of 0.5. The molecules of **10** resided on 3-fold rotation axis. Further crystallographic data are summarized in Table 4. CCDC-786160 (**1b**), −786161 (**2d**), −786162 (**3**), −786163 (**4**), −786164 (**6**), −786165 (**7**$\cdot(C_6H_4F_2)_{0.5}$), −786166 (**10**), and −786167 (**11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Database Centre via www.ccdc.cam.ac.uk/data_request/cif.

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

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[42] (a) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201. (b) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.