DOI: 10.1002/zaac.201100252

# Reactions of the Tetraalkyldigallium Compound $R_2$Ga–Ga$R_2$ [$R$ = CH($SiMe_3$)$_2$] with Acidic Reagents, Retention vs. Cleavage of the Ga–Ga Bond and Formation of Supramolecular Aggregates via Hydrogen Bonding

**Werner Uhl,*[a] Matthias Voß,[a] and Alexander Hepp[a]**

*In Memory of Professor Kurt Dehnicke*

**Keywords:** Gallium; Hydrazides; Phosphinic acid; Subvalent compounds; Hydrogen bonding

**Abstract.** Treatment of the tetraalkyldigallium compound $R_2$Ga–Ga$R_2$ [**1**, $R$ = CH($SiMe_3$)$_2$] with two equivalents of carboxylic acid hydrazides (4-trifluormethylbenzhydrazide, 2-fuoric acid hydrazide and 2-chlor-6-hydrazineisonicotinic acid hydrazide) afforded new digallium species by the release of $CH_2(SiMe_3)_2$. The intact Ga–Ga bonds of the products (**2** to **4**) are terminally coordinated by two chelating hydrazide ligands via $NH_2$ groups and the carbonyl oxygen atoms. Interesting supramolecular aggregates are formed in the solid state, which contain dimeric formula units of the digallium species connected via a complex system of hydrogen bonds. Two ether molecules are additionally coordinated to terminal N–H functions. Phenylphosphinic acid and **1** gave the analogous substituent replacement reaction with the formation of a dimeric tetragallium compound (**5**). Its two Ga–Ga bonds are in a perpendicular arrangement with four phosphinate ligands in the bridging positions. Oxidation of the gallium atoms and insertion of an N=N double bond into the Ga–Ga bond was observed upon treatment of **1** with azodicarbonamide.

## Introduction

The tetraalkyldigallium compound $R_2$Ga–Ga$R_2$ [**1**, $R$ = CH($SiMe_3$)$_2$] is accessible on a facile route by the treatment of the digallium subhalide $Ga_2Br_4$•2dioxane with four equivalents of bis(trimethylsilyl)methyllithium.[1] It shows a fascinating and unique chemical reactivity which afforded a broad variety of different secondary products by electron transfer, insertion, adduct formation, deprotonation or metathesis.[2] One of the most exciting secondary reactions comprises the treatment of **1** with carboxylic acids[3–5] or other acidic substrates[6] having chelating residues. Unexpectedly the Ga–Ga bonds are retained in most cases, and two alkyl groups of **1** are replaced by two chelating ligands in very selective transformations. Different reaction courses were observed for the corresponding dialuminium or diindium derivatives,[7] which gave oxidation of the metal atoms and the quantitative cleavage of the metal–metal bonds under similar conditions.[8] The dicarboxylatedigallium compounds have the chelating ligands in bridging positions across the Ga–Ga bonds and in an almost ideal perpendicular arrangement. With this unusual configuration these compounds are perfectly preorganized to form macrocycles or cages upon treatment of **1** with bifunctional dicarboxylic acids. Indeed we isolated large squaric molecules with an inner diameter of up to 1.9 nm in which four Ga–Ga bonds are bridged by four spacer ligands.[9] However, the distortion of the angles at the gallium atoms (O–Ga–O ≈ 90°, C–Ga–Ga ≈ 155°) and relatively short Ga–Ga distances verify a considerable strain in the resulting molecules. Donor functionalized acids gave large cages with up to six Ga–Ga bonds, which encapsulated solvent molecules very effectively[10] or formed supramolecular aggregates by hydrogen bonding.[11] Further acidic components may be suitable to replace alkyl groups of **1** and may help to increase the variability of accessible structural motifs and functionalities of the digallium compounds. Reactions with acid hydrazides, phenylphosphinic acid and a diaza compound are reported here.

## Results and Discussion

### *Reactions of the Digallium Compound 1 with Carboxyhydrazides*

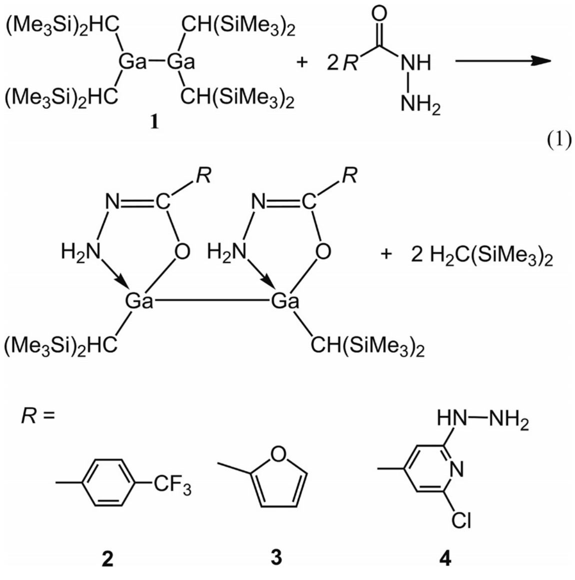
Following a standard procedure the digallium compound **1** and two equivalents of acid hydrazides (4-trifluormethylbenzhydrazide, 2-fuoric acid hydrazide and 2-chlor-6-hydrazineisonicotinic acid hydrazide) were dissolved in THF and stirred for different reaction times between 12 h and 3 d at room temperature [Equation (1)]. $H_2C(SiMe_3)_2$ was identified as a by-product by its characteristic singlet signals in the $^1$H NMR spectra. The reaction mixtures were concentrated and cooled to yield the colorless, solid products in yields of 62 (**2**), 83 (**3**) and 65 % (**4**). Single crystals were obtained from diethyl ether

---

* Prof. Dr. W. Uhl
Fax: +49-251-8336660
E-Mail: uhlw@uni-muenster.de
[a] Institut für Anorganische und Analytische Chemie
Universität Münster
Corrensstraße 30
48149 Münster, Germany

Dedicated Issue

(**2**) and THF (**3**); compound **4** was isolated only as an amorphous powder. Crystal structure determinations revealed the expected molecular structures (Figure 1 and Figure 2). Two alkyl groups of **1** were replaced by two hydrazide ligands which adopt terminal positions at the Ga–Ga bonds in the solid state and are bonded to the gallium atoms via their carboxyl oxygen atoms and an $NH_2$ group. Five-membered $GaCN_2O$ heterocycles including only one metal atom resulted by this particular coordination mode. This is in remarkable contrast to the dicarboxylate species which have the chelating ligands in a bridging position across the metal–metal bond. Quantum-chemical calculations[5] showed that in these cases this structural motif is strongly favored over the terminal arrangement by essentially two reasons: (i) The O–C–O angle is relatively inflexible. The terminal coordination of a carboxylato group requires a considerable deformation with a high energetic barrier. (ii) The hypothetical four-membered $GaCO_2$ heterocycle resulting from the terminal arrangement has a relatively short transannular distance between the positively charged gallium and carbon atoms which results in electrostatic repulsion. The bridging coordination of the $Ga_2$ moieties is limited to carboxylates, but leads to some strain in the molecules as discussed above (see Introduction). In other cases with the formation of larger heterocycles the terminal arrangement of the chelating ligands is preferred as in **2** and **3**.[6] The more relaxed bonding situation results in relatively long Ga–Ga distances (245.5 pm on average for **2** and **3**) compared to the carboxylate bridged molecules (238 pm) and a closer approach of the angles at the metal atoms to the ideal value of a tetrahedral coordination.



(1)

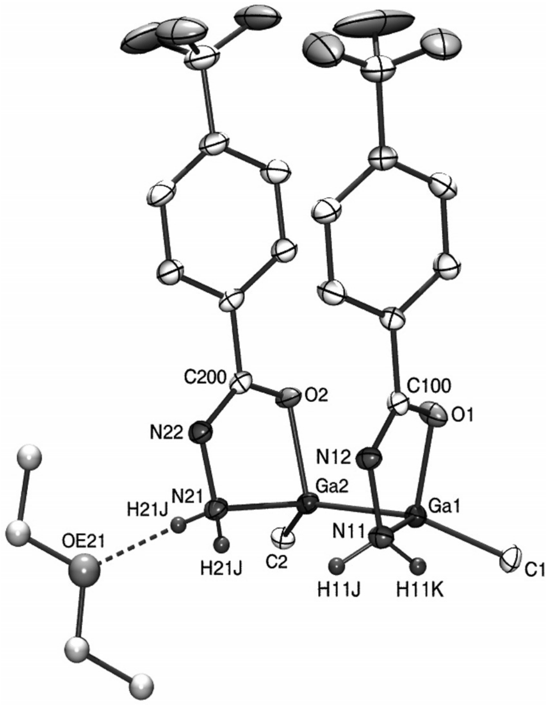


**Figure 1.** Molecular structure and numbering scheme of **2**; the thermal ellipsoids are drawn at the 40 % probability level; trimethylsilyl groups and hydrogen atoms with the exception of N–H are omitted, atoms of the ether molecule with artificial radii. Selected bond lengths /pm and angles /° (data of the second molecule in square brackets): Ga1–Ga2 245.82(6) [245.57(6)], Ga1–O1 195.6(3) [196.2(3)], Ga1–N11 210.3(3) [209.8(3)], Ga2–O2 193.2(3) [193.7(3)], Ga2–N21 206.9(3) [206.4(3)], O1–C100 129.0(4) [129.4(4)], C100–N12 129.9(5) [130.0(5)], N11–N12 147.9(4) [146.0(4)], O2–C200 130.2(4) [129.7(4)], C200–N22 130.4(5) [130.6(5)], N21–N22 147.3(4) [146.5(4)], O1–Ga1–N11 79.4(1) [79.5(1)], Ga2–Ga1–O1 105.89(8) [103.79(8)], N12–C100–O1 125.9(3) [125.3(3)], O2–Ga2–N21 80.7(1) [79.5(1)], Ga1–Ga2–O2 100.92(9) [101.18(8)], N22–C200–O2 125.9(3) [125.9(3)].

A schematic drawing of the molecular structures of the monomeric formula units of **2** and **3** is given in Equation (1). The $NH_2$ groups adopt *cis*-positions and are on the same side of the molecules. The N–N distances (146.7 pm on average) correspond to standard values of N–N single bonds in acid hydrazides.[12] C=N (130.1 pm) and C–O bond lengths (129.6 pm) are in accordance with π-delocalization in the O–C=N group.[13] The Ga–N distances are long (207.9 pm) indicating a donor interaction of a neutral nitrogen atom with the Lewis-acidic metal atom,[14] whereas the Ga–O distances (194.7 pm) are in the upper range of values observed for example in alcoholates with negatively charged oxygen atoms.[15]

Both compounds **2** and **3** are dimeric in the solid state via a complex, but almost identical pattern of hydrogen bonds, which is described here with the atomic numbering scheme of **2** (Figure 3). There are two different kinds of $NH_2$ groups. Two $NH_2$ groups of each dimeric formula unit (N11 and N31) point towards the center of the resulting cage. One hydrogen atom of each group has a close contact to the nitrogen atom of a C=N double bond (H11J···N32: 215 pm, H31K···N12: 211 pm; for a discussion of N–H···N bonding see[16]), whereas two longer distances were detected for the remaining two hydrogen atoms (H11K···N22: 255 pm, H11K···N42: 261 pm). Also one half of the hydrogen atoms of the other type of $NH_2$ groups (N21 and N41) has short distances to nitrogen atoms of C=N double bonds (N12···H41J: 220 pm, N32···H21K: 208 pm), while the others interact with the oxygen atoms of the ether molecules (H21J···OE21: 209 pm; H41K···OE11: 205 pm[16]).

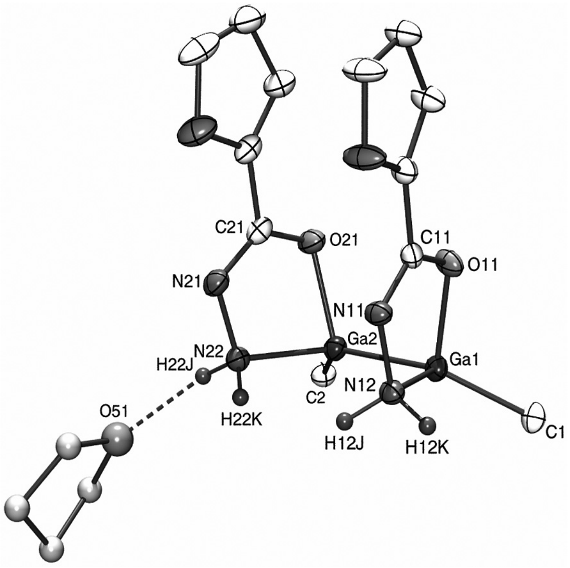


**Figure 2.** Molecular structure and numbering scheme of **3**; the thermal ellipsoids are drawn at the 40 % probability level; trimethylsilyl groups and hydrogen atoms with the exception of NH are omitted; atoms of the THF molecules with artificial radii. Selected bond lengths /pm and angles /° (data of the second molecule in square brackets): Ga1–Ga2 245.19(4) [245.61(5)], Ga1–O11 195.4(2) [195.2(2)], Ga1–N12 208.6(2) [209.7(2)], Ga2–O21 194.4(2) [193.5(2)], Ga2–N22 205.6(2) [205.8(3)], O11–C11 128.8(3) [129.0(4)], C11–N11 130.4(3) [130.0(4)], N11–N12 146.0(3) [146.9(3)], O21–C21 129.7(3) [130.9(4)], C21–N21 129.6(4) [129.5(5)], N21–N22 147.1(3) [145.6(4)], O11–Ga1–N12 80.68(8) [80.39(9)], Ga2–Ga1–O11 102.49(6) [102.54(7)], N11–C11–O11 127.3(2) [126.8(3)], O21–Ga2–N22 81.03(9) [80.7(1)], Ga1–Ga2–O21 104.35(7) [103.33(8)], N21–C21–O21 127.6(3) [127.3(3)].

Polymerization of the molecules by hydrogen bonds to give one-dimensional coordination polymers is probably prevented by these interactions.

The NMR spectra of **2**–**4** are complicated and give evidence for at least two species in solution. Two sets of resonances were detected with the expected number of resonances and intensity ratios. Caused by the chiral coordination sphere of the gallium atoms the trimethylsilyl groups of each species give two resonances in the $^{1}$H, $^{13}$C and $^{29}$Si NMR spectra. A singlet resulted for the GaC*H*Si$_2$ protons at a relatively high field ($\delta$ = –0.46 to –0.54) in accordance with coordination number four at the metal atoms.[6,9,17] The NH$_2$ hydrogen atoms of the hydrazide ligands are diastereotopic and give two doublets in the $^{1}$H NMR spectra. For **2** an AB type of splitting for one species could only be resolved upon cooling of a sample to –43 °C. The N–H resonances were completely assigned based on $^{15}$N–$^{1}$H correlated NMR spectroscopic data. A similar equilibrium between two isomers has previously been observed for solutions of dimeric carboxylato-hydroxo digallium compounds.[4] It was explained by a different coordination mode of the carboxylate groups which bridge the gallium atoms of a single Ga–Ga bond or are bonded to two gallium atoms of different Ga$_2$ pairs. In one case disorder in the solid state resulted in superposition of both forms which gives very nice evidence for this description. A similar situation may hold for compounds **2**–**4** as schematically shown in Scheme 1. The formation of *cis*/*trans* isomers having a different orientation of the amino groups (Scheme 1) is an alternative explanation. Cooling had a considerable influence on the ratio between both isomeric forms. For **2** it changed from 1:0.4 at room temperature to 1:5 at –63 °C. The products of these reactions contain sometimes an impurity in a concentration of about 5 %, which could be removed by treatment with *n*-pentane. It could not be identified because we were not able to determine a complete set of resonances in the NMR spectra. We suppose that cleavage of the Ga–Ga bond occurs in a minor side reaction to give mononuclear dialkylgallium compounds similar to previous observations.[3] Few transition metal complexes of such acid hydrazides were reported in the literature.[18] However, we could not find any structural information.

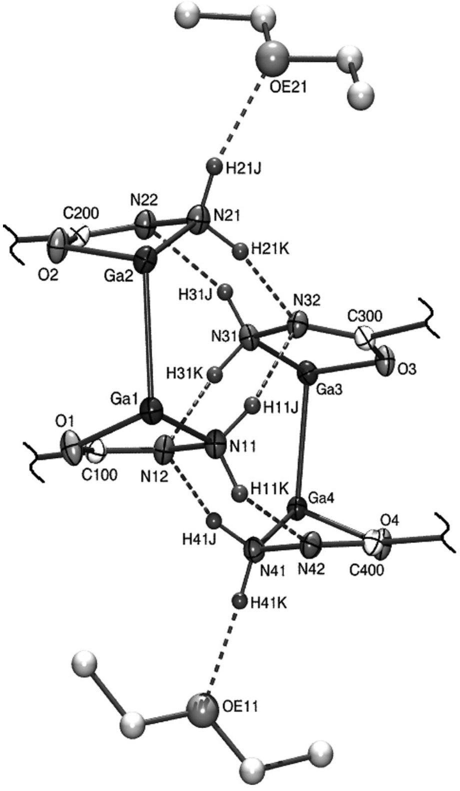
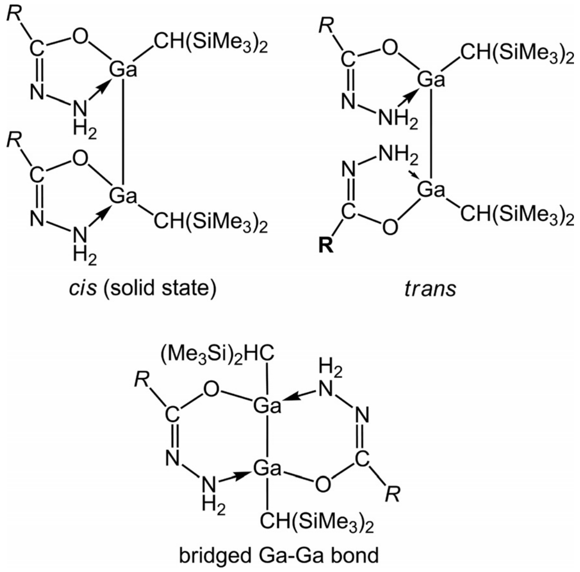


**Figure 3.** Hydrogen bonding in the dimeric formula unit of **2**; CH(SiMe$_3$)$_2$ and C$_6$H$_4$(CF$_3$) groups are omitted; hydrogen atoms and the atoms of the ether molecules are drawn with artificial radii.

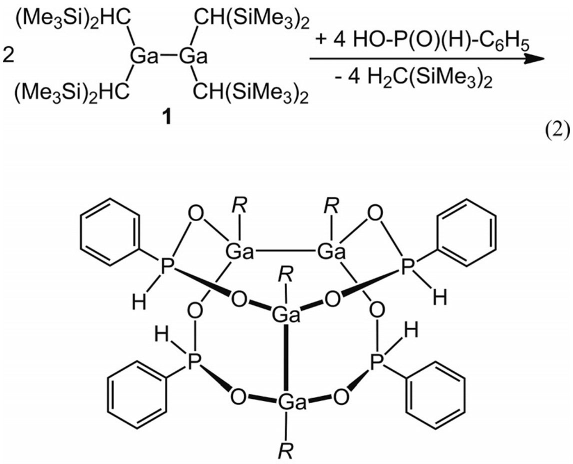
### *Reaction of 1 with Phenylphosphinic Acid*

The digallium compound **1** and two equivalents of phenylphosphinic acid were dissolved in THF. After 12 h at room temperature the starting compounds were completely consumed [Equation (2)]. Concentration and cooling of the reaction mixture to 4 °C yielded colorless crystals of product **5** in 67 % yield. **5** slowly decomposed in solution at room temperature to afford a mixture of unknown components. Therefore, the complete NMR spectroscopic characterization proved to be difficult. Two resonances were observed for trimethylsilyl



**Scheme 1.** Possible configurations of compounds **2**–**4** in solution.

groups in the $^{1}$H and $^{29}$Si NMR spectra which may indicate a chiral environment of the gallium atoms. The singlet of the inner GaC*H*Si$_2$ proton occurred at $\delta$ = –0.82 in the $^{1}$H NMR spectrum which is in the characteristic range of four-coordinate gallium atoms.[6,9,17] Elemental analysis verified the constitution of **5** by an excellent agreement of experimental and calculated data. The mass spectrum showed the molar mass of the dimeric formula unit minus a bis(trimethylsilyl)methyl group.



(2)

**5** [$R$ = CH(SiMe$_3$)$_2$]

Crystal structure determination (Figure 4) revealed an unprecedented dimeric molecular structure with a perpendicular arrangement of two Ga–Ga bonds which are bridged by four chelating phosphinate ligands. The metal–metal distance of 244.11(6) pm is in accordance with an unsupported Ga–Ga bond coordinated by electronegative substituents. The phenylphosphinate ligands occupy bridging positions and connect two gallium atoms of different Ga–Ga bonds. The molecular structure may be derived from a distorted tetrahedron of gallium atoms. Two opposite edges are metal–metal bonds, the remaining four edges are bridged by the chelating ligands. A tetracyclic compound is formed which possesses four nine-membered Ga$_3$O$_4$P$_2$ heterocycles. Ga–O (193.3(2) and 196.1(2) pm)[15] and P–O distances (151.1(2) and 151.9(2) pm) [19] are in the expected ranges. Some complexes of phenylphosphinate with transition metal atoms are reported in the literature.[19] They show terminal and bridging coordination modes of the phosphinate groups. Bond lengths and angles are similar to those of **5**.

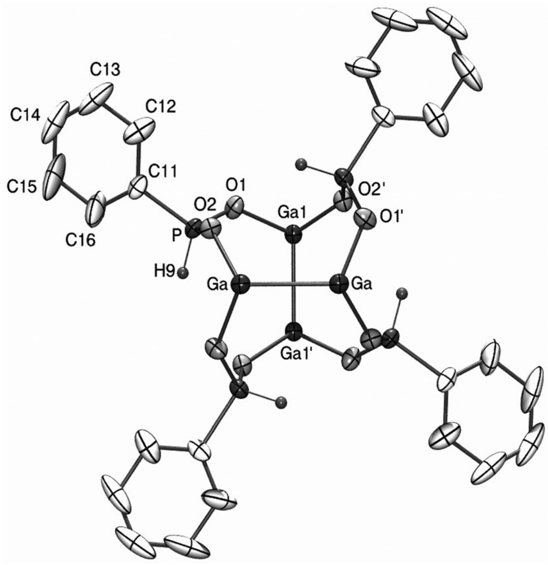
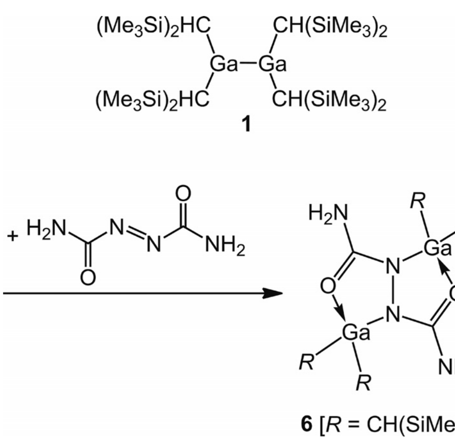


**Figure 4.** Molecular structure and numbering scheme of **5**; the thermal ellipsoids are drawn at the 40 % probability level; bis(trimethylsilyl) methyl groups attached to gallium and hydrogen atoms with the exception of P–H are omitted. Selected bond lengths /pm and angles /°: Ga1–Ga1′ 244.11(6), Ga1–O1 193.3(2), Ga1–O2′′ 196.1(2), P–O1 151.9(2), P–O2 151.1(2), O1–P–O2 114.0(1), Ga1′–Ga1–O1 109.97(7), Ga1′–Ga1–O2′′ 114.12(7); Ga1′ generated by –*x*, –*y*, *z*; O2′′ by –*y*, *x*, –*z*.

### *Azodicarbonamide and 1 – Cleavage of the Ga–Ga Bond*

Treatment of the digallium compound **1** with equimolar quantities of azodicarbonamide in THF at room temperature gave cleavage of the Ga–Ga bond [Equation (3)]. CH$_2$(SiMe$_3$)$_2$ as the expected product of substituent exchange reactions could not be detected by NMR spectroscopy. The colorless product **6** precipitated from the concentrated reaction mixture in 70 % yield. A singlet of the GaC*H*Si$_2$ hydrogen atoms at a relatively high field ($\delta$ = –0.58) indicates a coordination number of four at the gallium atoms.[6,9,17] Two resonances were observed for the trimethylsilyl groups in the $^{1}$H, $^{13}$C and $^{29}$Si NMR spectra of **6**. They verify a molecular symmetry with a missing mirror plane bisecting the CSi$_2$ angle. Intact NH$_2$ groups give a broad singlet at $\delta$ = 5.29. Hence, a proton transfer did not occur. Instead, the gallium atoms were oxidized to Ga$^{III}$ by insertion of the diazene unit of the starting aza compound into the Ga–Ga bond, and the N=N double bond was reduced to give a hydrazine moiety with two adjacent carbonyl functions.



(3)

Crystal structure determination (Figure 5) verified the molecular constitution. The gallium atoms have coordination numbers of four and are bonded to two bis(trimethylsilyl)methyl groups, a nitrogen atom of the hydrazine group and the oxygen atom of the carbonyl group. Two five-membered GaCN$_2$O heterocycles result which are annulated via the central N–N bond. The N–N bond lengths (143.1 pm on average) are in the lower range of N–N bonds in hydrazine derivatives,[12] but correspond well to values of dicarbonyl hydrazides.[20] Ga–O (194.6 pm) and Ga–N distances (201.6 pm on average) are in normal ranges. C–O and C–N distances including the carboxyl carbon atoms (129.3 and 132.9 pm on average) reflect a delocalized π-bonding in this part of the molecule (see above) which may influence the relatively short N–N bond lengths by reduction of electron density at the nitrogen atoms. The nitrogen atoms of the hydrazide group and the amido groups as well as the carbon atoms of the carbonyl groups have ideal planar coordination spheres with sums of the angles of 360°. Each NH$_2$ group is coordinated to a DME molecule via hydrogen bonding. The DME molecules are not in plane with the nitrogen and hydrogen atoms, but are bonded in an unsymmetric manner. A short H···O distance results per amido group (H011···O35: 211 pm; H022···O42: 209 pm) which indicates a relatively strong hydrogen bond[16] and represents the main contact between both molecules. The second oxygen atoms of the DME molecules have considerably longer distances to both hydrogen atoms of the amido groups (O32···H 278 and 292 pm, O45···H 276 and 295 pm) indicating a negligible bonding interaction.

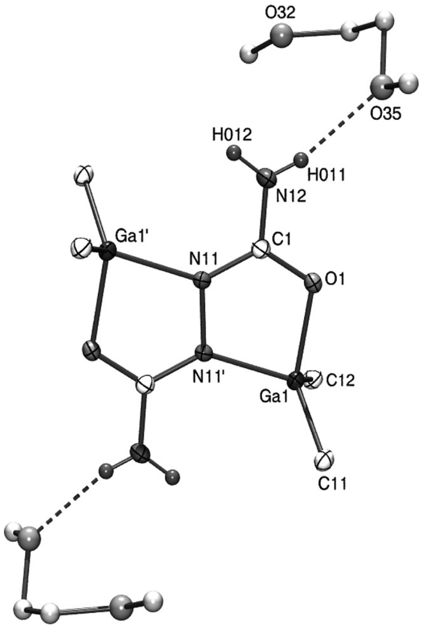


**Figure 5.** Molecular structure and numbering scheme of **6**; the thermal ellipsoids are drawn at the 40 % probability level; trimethylsilyl groups and hydrogen atoms with the exception of NH$_2$ are omitted; atoms of the DME molecules with artificial radii. Selected bond lengths /pm and angles /° (data of the second molecule in square brackets): Ga1–O1 194.5(1) [194.8(1), Ga1–N11′ 201.7(1) [201.5(1)], N11–N11′ 143.0(2) [143.1(2)], C1–N11 132.1(2) [131.9(2)], C1–N12 133.7(2) [134.0(2)], C1–O1 129.2(2) [129.3(2)], N11′–Ga1–O1 80.39(4) [80.44(4)], C1–N11–Ga1′ 136.8(1) [136.8(1)]; Ga1′ and N11′ generated by $-x + 1$, $-y$, $-z$.

## Experimental Section

**General:** All procedures were carried out under an atmosphere of purified argon in dried solvents (THF and dimethoxyethane (DME) over Na/benzophenone). The tetraalkyldigallium compound **1** and 2,6-dichloroisonicotinic acid were obtained according to literature procedures.[1,21] 2-Chlor-6-hydrazineisonicotinic acid hydrazide was obtained according to a modified literature procedure[22] by the treatment of 2,6-dichlorisonicotinic acid with an excess of hydrazine hydrate in ethanol under reflux conditions. It precipitated directly from the reaction mixture in high purity. The starting compounds 4-trifluormethylbenzhydrazide, 2-fuoric acid hydrazide (furan-2-carboxylic acid hydrazide) and 2-chlor-6-hydrazineisonicotinic acid hydrazide and azadicarbonamide (azodicarboxylic acid diamide) were applied as purchased. The assignment of the NMR spectra is based on HSQC, HMBC, H/Si-HMBC, ROESY and DEPT135 data. Only the most intensive masses of a particular molecular fragment are given in the description of the mass spectra; the isotopic patterns were in agreement with the calculated ones.

### *Synthesis*

**Compound 2:** The solid digallium compound **1** (0.242 g, 0.312 mmol) and 4-trifluormethylbenzhydrazide (0.128 g, 0.627 mmol) were dissolved in THF (20 mL) at room temperature. The mixture was stirred for 3 d. Concentration of the solution and cooling to +4 °C afforded colorless crystals of **2**. Two isomers were detected in solution by NMR spectroscopy with an intensity ratio of 1 to 0.4 at room temperature and 1 to 5 at –63 °C (see Results and Discussion). Yield: 0.180 g (62 %; **2**·THF). M.p. (argon, sealed capillary): 183 °C (dec). **$^1$H NMR** (400 MHz, [D$_8$]THF, 298 K): Major component: $\delta$ = 8.18 (d , 4 H, $^3J$(H,H) = 8.2 Hz, *ortho*-H of phenyl), 7.64 (d , 4 H, $^3J_{\mathrm{H,H}}$ = 8.2 Hz, *meta*-H of phenyl), 6.29 and 6.18 (each 2 H, d, $^2J_{\mathrm{H,H}}$ = 12.8 Hz, GaNH$_2$), 0.12 and 0.03 (each 18 H, s, SiMe$_3$), –0.50 (s , 2 H, GaCHSi$_2$); minor component: $\delta$ = 8.14 (d , 4 H, $^3J_{\mathrm{H,H}}$ = 8.2 Hz, *ortho*-H of phenyl), 7.61 (d , 4 H, $^3J_{\mathrm{H,H}}$ = 8.2 Hz, *meta*-H of phenyl), 6.20 (4 H, br., s, NH$_2$), 0.06 and 0.03 (each 18 H, s, SiMe$_3$), –0.49 (s , 2 H, GaCHSi$_2$); the resonance of the NH$_2$ protons gave a typical AB pattern upon cooling to –43 °C: $\delta$ = 6.55 and 6.52;[23] intensity ratio f1,f4 to f2,f3 1:7.3; $^2J_{\mathrm{H,H}}$ = 13.0 Hz. **$^{13}$C NMR** (100 MHz, [D$_8$]THF, 298 K): Major component: $\delta$ = 169.8 (CO), 138.7 (*ipso*-C of phenyl), 132.3 (q, $^2J_{CF}$ = 32.0 Hz, *para*-C of phenyl), 129.4 (*ortho*-C of phenyl), 125.4 (*meta*-C of phenyl), 125.0 (q, $^1J_{CF}$ = 271.4 Hz, $CF_3$), 10.0 ($GaCSi_2$), 4.0 and 3.4 ($SiMe_3$); minor component: $\delta$ = 169.8 (CO), 138.8 (*ipso*-C of phenyl), 132.2 (*para*-C of phenyl, $^2J_{CF}$ = 32.2 Hz), 129.2 (*ortho*-C of phenyl), 125.4 (*meta*-C of phenyl), 125.0 (q, $^1J_{CF}$ = 271.4 Hz, $CF_3$), 10.0 ($GaCSi_2$), 3.8 and 3.5 ($SiMe_3$). **$^{29}$Si NMR** (79.5 MHz, [$D_8$]THF, 298 K): Major component: $\delta$ = –1.30 and –1.35; minor component: $\delta$ = –1.35 and –1.41. **$^{19}$F NMR** ([$D_8$]THF, 376.5 MHz, 298 K): Major component: $\delta$ = –63.5; minor component: $\delta$ = –63.5. **IR** (CsI, paraffin): $\nu$(bar) = 3319 vw, 3279 w, 3183 w $\nu$NH; 2951 vs, 2924 vs, 2853 vs. (paraffin); 1931 m, 1856 vw, 1809 w, 1692 w, 1609 s, 1582 m, 1541 s, 1514 m $\delta$NH, $\nu$C=N, $\nu$C=O, aromatic ring; 1460 vs, 1375 vs. (paraffin); 1323 s, 1248 s $\delta CH_3$; 1169 s, 1134 s, 1105 m, 1067 s, 1045 w $\nu$CC, $\nu$CN, $\nu$CF, $\nu$NN; 1016 s $\delta CHSi_2$; 955 m, 895 w, 843 vs, 762 m $\rho CH_3$(Si); 723 m (paraffin); 671 m νSiC; 588 s, 503 s, 451 s, 401 sh, 388 m, 341 m $\nu$GaC, $\nu$GaO, $\nu$GaN $cm^{-1}$. **MS** (EI, 20 eV, 250 °C): *m*/*z* (%) 860 (4), 862 (6), 863 (3), 864 (3) ($M^+$ of the monomeric formula unit – 2 H); 431 (100), 433 (75) (½$M^+$). **CHN** ($C_{30}H_{50}F_6Ga_2N_4O_2Si_4+OC_4H_8$) (936.6): calcd. C 43.6, H 6.2, N 6.0; found C 43.6, H 6.1, N 6.3 %.

**Compound 3:** The solid digallium compound **1** (0.303 g, 0.391 mmol) and 2-fuoric acid hydrazide (0.099 g, 0.786 mmol) were dissolved in THF (20 mL) at room temperature. The mixture was stirred for 12 h. Concentration of the solution and cooling to +4 °C afforded colorless crystals of **3**, which were washed with of *n*-pentane (10 mL) to remove an unknown impurity. Two isomers were detected in solution by NMR spectroscopy with an intensity ratio of 1 to 0.5 (see Results and Discussion). Yield: 0.230 g (83 %). M.p. (argon, sealed capillary): 198 °C (dec). **$^1$H NMR** (400 MHz, [$D_8$]THF): Major component: $\delta$ = 7.46 (m , 2 H, OC*H*), 6.85 (m , 2 H, OCHCHC*H*), 6.41 (m , 2 H, OCHC*H*), 6.57 and 6.01 (each 2 H, d, $^2J_{H,H}$ = 12.6 Hz, $GaNH_2$), 0.11 and 0.03 (each 18 H, s, $SiMe_3$), –0.54 (s , 2 H, $GaCHSi_2$); minor component: $\delta$ = 7.30 (m , 2 H, OC*H*), 6.70 (m , 2 H, OCHCHC*H*), 6.27 (m , 2 H, OCHC*H*), 6.94 and 6.00 (each 2 H, d, $^2J_{H,H}$ = 12.6 Hz, $GaNH_2$), 0.10 and 0.09 (each 18 H, s, $SiMe_3$), –0.46 (s , 2 H, $GaCHSi_2$). **$^{13}$C NMR** (100 MHz, [$D_8$]THF): Major component: $\delta$ = 164.9 (C=N), 149.8 (*ipso*-C of furyl), 144.8 ((O*C*HCHCH), 113.6 (OCHCH*C*H), 111.5 (OCH*C*HCH), 9.9 ($GaCSi_2$), 4.0 and 3.4 ($SiMe_3$); minor component: $\delta$ = 165.2 (C=N), 149.3 (*ipso*-C of furyl), 144.8 ((O*C*HCHCH), 113.6 (OCHCH*C*H), 111.4 (OCH*C*HCH), 9.4 ($GaCSi_2$), 3.9 and 3.7 ($SiMe_3$). **$^{29}$Si NMR** (79.5 MHz, [$D_8$]THF): Major component: $\delta$ = –1.28 and –1.33; minor component: $\delta$ = –1.06 and –1.24. **$^{15}$*N* NMR** ([$D_8$]THF, 40.5 MHz): Major component: $\delta$ = 220 (C=N), 74.5 ($NH_2$); minor component: $\delta$ = C=N not detected, 75.0 ($NH_2$). **IR** (CsI, paraffin): $\nu$(bar) = 3316 vw, 3275 m, 3244 m, 3113 w $\nu$NH; 2951 vs, 2920 vs, 2853 vs. (paraffin); 1921 w, 1856 vw, 1748 w, 1738 w, 1676 w, 1616 s, 1587 m, 1543 m, 1522 m, 1487 s $\delta$NH, $\nu$C=N, $\nu$C=O, furyl ring; 1464 vs. (paraffin); 1400 s $\delta CH_3$; 1377 vs. (paraffin); 1362 vs, 1246 vs. $\delta CH_3$; 1223 vs, 1204 vs, 1175 s, 1128 m, 1074 m, 1053 s $\nu$CC, $\nu$CN, $\nu$NN; 1011 vs. $\delta CHSi_2$; 952 s, 930 sh, 862 vs, 843 vs, 745 m $\rho CH_3$(Si); 727 s (paraffin); 669 s $\nu_{as}$SiC; 640 vw, 619 s $\nu_s$SiC; 592 s, 577 s, 507 s, 494 s, 426 s $\nu$GaC, $\nu$GaO, $\nu$GaN $cm^{-1}$. **MS** (EI, 20 eV, 160 °C): *m*/*z* (%) 704 (57), 706 (91), 707 (39), 708 (44) ($M^+$ of the monomeric formula unit – 2 H); 579 (37), 581 (60), 582 (23), 583 (30) ($M^+$ – $H_2N$-NC(O)-$C_4H_3O$ (chelating ligand) – 2 H); 547 (22), 549 (29), 551 (13) ($M^+$ – $CH_2(SiMe_3)_2$). **CHN** (solvent free) ($C_{24}H_{48}Ga_2N_4O_4Si_4$) (708.4): calcd. C 40.7, H 6.8, N 7.9; found C 41.2, H 6.9, N 8.2 %.

**Compound 4:** The solid digallium compound **1** (0.321 g, 0.414 mmol) and 2-chloro-6-hydrazinylisonicotinic acid hydrazide (0.167 g, 0.829 mmol) were dissolved in THF (20 mL) at room temperature. The mixture was stirred for 12 h. Concentration of the solution and cooling to –30 °C afforded colorless crystals of **4**, which were treated with *n*-pentane (10 mL) to remove an unknown impurity. Two isomers were detected in solution by NMR spectroscopy with an intensity ratio of 1 to 0.5 at room temperature (see Results and Discussion). Yield: 0.250 g (65 %, **4**·THF). M.p. (argon, sealed capillary): 198 °C (dec). **$^1$H NMR** (400 MHz, [$D_8$]THF): Major component: $\delta$ = 7.28 (s , 2 H, $NH_2NH$ of hydrazinyl), 7.17 (s , 2 H, *ortho*-H of pyridyl, NHCC*H*), 7.04 (s , 2 H, *ortho*-H of pyridyl, ClCC*H*), 6.25 and 6.15 (each 2 H, d, $^2J_{H,H}$ = 13.0 Hz, $GaNH_2$), 3.97 (s , 4 H, $NH_2$ of hydrazinyl), 0.10 und 0.03 (each 18 H, s, $SiMe_3$), –0.53 (s , 2 H, $GaCHSi_2$); minor component: $\delta$ = 7.23 (s , 2 H, $NH_2NH$ of hydrazinyl), 7.14 (s , 2 H, *ortho*-H of pyridyl, NHCC*H*), 7.04 (s , 2 H, *ortho*-H of pyridyl, ClCC*H*), 6.19 and 6.16 (each 2 H, m, covered, $GaNH_2$), 3.97 (s , 4 H, $NH_2$ of hydrazinyl), 0.06 und 0.03 (each 18 H, s, $SiMe_3$), –0.52 (s , 2 H, $GaCHSi_2$). **$^{13}$C NMR** (100 MHz, [$D_8$]THF): Major component: $\delta$ = 169.4 (CO), 163.3 (*meta*-C of pyridyl, $NH_2$NHC), 149.9 (*meta*-C of pyridyl, ClC), 145.9 (*ipso*-C of pyridyl), 110.8 (*ortho*-C of pyridyl, ClC*C*H), 104.7 (*ortho*-C of pyridyl, NHC*C*H), 10.0 ($GaCSi_2$), 4.1 and 3.4 ($SiMe_3$); minor component: $\delta$ = 169.4 (CO), 163.3 (*meta*-C of pyridyl, $NH_2$NHC), 149.9 (*meta*-C of pyridyl, ClC), 146.0 (*ipso*-C of pyridyl), 110.9 (*ortho*-C of pyridyl, ClC*C*H), 104.6 (*ortho*-C of pyridyl, NHC*C*H), 10.0 ($GaCSi_2$), 3.8 and 3.5 ($SiMe_3$). **$^{29}$Si NMR** (79.5 MHz, [$D_8$]THF): Major component: $\delta$ = –1.29 and –1.39; minor component: $\delta$ = –1.39 and –1.43. **IR** (CsI, paraffin): $\nu$(bar) = 3356 w, 3265 s,br. $\nu$NH; 2949 vs, 2922 vs, 2853 vs. (paraffin); 1921 w, 1852 vw, 1688 w, 1653 w, 1605 vs, 1574 m, 1545 s $\delta$NH, $\nu$C=N, $\nu$C=O, aromatic ring; 1462 vs. (paraffin); 1420 s $\delta CH_3$; 1377 vs. (paraffin); 1358 vs, 1294 w, 1248 vs. $\delta CH_3$; 1200 s, 1150 s, 1092 m $\nu$CC, $\nu$CN, $\nu$NN; 1018 s $\delta CHSi_2$; 970 w, 937 s, 864 vs, 843 vs, 772 s, 752 s $\rho CH_3$(Si); 725 s (paraffin); 673 s $\nu_{as}$SiC; 613 m $\nu_s$SiC; 571 m, 540 m, 494 s, 465 w, 430 w, 382 w, 341 w $\nu$GaC, $\nu$GaO, $\nu$GaN $cm^{-1}$. **CHN** ($C_{26}H_{52}Cl_2Ga_2N_{10}O_2Si_4 \cdot OC_4H_8$) (931.5): calcd. C 38.7, H 6.5, N 15.0; found C 39.9, H 6.2, N 15.3 %.

**Compound 5:** The solid digallium compound **1** (0.260 g, 0.335 mmol) and phenylphosphonic acid (0.096 g, 0.676 mmol) were dissolved in THF (20 mL) at room temperature. The mixture was stirred for 12 h. Concentration of the solution and cooling to +4 °C afforded colorless crystals of **5**. Compound **5** decomposes slowly in solution (see Results and Discussion). Yield: 0.165 g (67 %). M.p. (argon, sealed capillary): 215 °C. **$^1$H NMR** (400 MHz, [$D_8$]THF): $\delta$ = 8.06 (d , 4 H, $^1J_{HP}$ = 562.5 Hz, PH), 7.82 (m , 8 H, *ortho*-H of phenyl), 7.60 (m , 4 H, *para*-H of phenyl), 7.53 (m , 8 H, *meta*-H of phenyl), –0.07 and –0.11 (s , 72 H, $SiMe_3$), –0.82 (s , 4 H, $GaCHSi_2$). **$^{13}$C NMR** (100 MHz, [$D_8$]THF): $\delta$ = 134.0 (d, $^1J_{C,P}$ = 145.7 Hz, *ipso*-C of phenyl), 133.3 (*para*-C of phenyl), 130.3 (d, $^2J_{C,P}$ = 14.1 Hz, *ortho*-C of phenyl), 129.4 (d, $^3J_{CP}$ = 14.6 Hz *meta*-C of phenyl), 10.3 ($GaCSi_2$), 3.8 ($SiMe_3$, both resonances coincide). **$^{29}$Si NMR** (79.5 MHz, [$D_8$]THF): $\delta$ = –0.9 and –1.0. **IR** (CsI, paraffin): $\nu$(bar) = 2382 vs. $\nu$PH; 1977 w, 1956 w, 1910 w, 1883 w, 1850 w, 1809 w, 1759 vw, 1663 w, 1593 m phenyl; 1464 vs, 1377 vs. (paraffin); 1329 w, 1304 m, 1292 m, 1240 s $\delta CH_3$; 1179 s, 1132 s, 1055 s $\nu$CC; 1020 s $\delta CHSi_2$; 974 s, 943 vs, 920 vw, 864 s, 847 s, 791 vw, 773 m, 745 s $\rho CH_3$(Si); 711 m (paraffin); 689 s, 667 s $\nu_{as}$SiC; 619 m $\nu_s$SiC; 552 vs, 500 s, 464 vs, 409 m, 351 s $\nu$GaC, $\nu$GaO, $\nu$PO $cm^{-1}$. **MS** (EI, 20 eV, 160 °C): *m*/*z* (%) 1318 (0.2), 1320 (0.3), 1321 (0.2), 1322 (0.2) ($M^+$ – $CH_2(SiMe_3)_2$); 1109 (0.4), 1110 (0.3), 1111 (0.4), 1112 (0.3) ($M^+$ – $GaCH(SiMe_3)_2PHO_2Ph$); 738 (0.6), 740 (1.4), 741 (1.7), 742 (1.1) (½ $M^+$); 369 (100), 370 (22), 371 (75), 372 (17) ($[GaCH(SiMe_3)_2PHO_2Ph]^+$). **CHN** (solvent free) ($C_{52}H_{100}Ga_4O_8P_4Si_8$) (1480.8): calcd. C 42.2, H 6.8; found C 41.9, H 6.8 %.

**Compound 6:** The solid digallium compound **1** (0.311 g, 0.401 mmol) and azodicarbonamide (0.047 g, 0.405 mmol) were dissolved in THF (20 mL) at room temperature. The mixture was stirred for 12 h. The solution was concentrated and cooled to 4 °C to yield colorless crystals of **6**. Alternatively all volatiles were removed in vacuo. The remaining solid was dissolved in DME in an ultrasound bath. Storing of the solution at room temperature gave crystals of **6**. Yield: 0.300 g (70 % of **6**·2DME). M.p. (argon, sealed capillary): 142 °C (dec). **$^1$H NMR** (400 MHz, [D$_8$]THF): $\delta$ = 5.29 (s , 4 H, NH$_2$), 0.10 and 0.18 (each 36 H, s, SiMe$_3$), –0.58 (s , 2 H, GaCHSi$_2$). **$^{13}$C NMR** (100 MHz, [D$_8$]THF): $\delta$ = 160.9 (C=O), 6.9 (GaCSi$_2$), 4.5 and 4.4 (SiMe$_3$). **$^{29}$Si NMR** (79.5 MHz, [D$_8$]THF): $\delta$ = 0.1 and –0.3. **IR** (CsI, paraffin): $\nu$(bar) = 3526 s, 3422 s $\nu$NH; 2949 vs, 2922 vs, 2853 vs. (paraffin); 1607 s, 1537 s $\nu$C=O, $\delta$NH; 1464 vs, 1377 vs. (paraffin); 1364 m, 1294 w, 1242 vs. $\delta$CH$_3$; 1090 m, 1047 w $\nu$NN, $\nu$CN; 1018 vs. $\delta$CHSi$_2$; 966 s, 956 s, 844 vs, 779 m, 756 m $\rho$CH$_3$(Si); 727 m (paraffin); 671 s $\nu_{as}$SiC; 623 m $\nu_s$SiC; 514 s, 484 s, 347 m $\nu$GaC, $\nu$GaN cm$^{-1}$. **MS** (EI, 20 eV, 100 °C): $m/z$ (%): 875 (1.6), 877 (3.2), 878 (1.8), 879 (1.9) (M$^+$ – CH$_3$); 731 (58), 733 (100), 734 (52), 735 (53) (M$^+$ – CH(SiMe$_3$)$_2$); 387 (43), 388 (15), 389 (37) (Ga[CH(SiMe$_3$)$_2$]$_2^+$). **CHN** (solvent free after evacuation) ($C_{30}H_{80}Ga_2N_4O_2Si_8$) (893.1): calcd. C 40.3, H 9.0, N 6.3; found C 40.1, H 8.9, N 6.1 %.

### *Crystal Structure Determinations*

Single crystals were obtained directly from the reaction mixtures (**3**, **5**) or by recrystallization from diethyl ether (**2**) or DME (**6**). Intensity data were collected on a Bruker APEX II diffractometer with monochromated Mo-$K_\alpha$ (**3**, **5**, **6**) or Cu-$K_\alpha$ (**2**) radiation. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final $R$ values are provided in Table 1. The structures were solved by direct methods and refined with the program system SHELXL-97[25] with full-matrix and all independent structure factors ($F^2$). All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}$(C). N–H hydrogen atoms were in all cases found in the Fourier maps after refinement of all heavier atoms and the other hydrogen atoms. But they were refined on ideal positions by using the corresponding HFIX instruction for compounds **2** and **3**; only for **6** they were refined without restrictions. Compound **2** crystallizes with two independent formula units in the asymmetric unit which are connected by hydrogen bonds. Two trifluormethyl groups are disordered (C107 and C307). Their fluorine atoms were refined on split positions (0.59:0.41 and 0.83:0.17, respectively). Two diethyl ether molecules are connected to the dimeric molecules via hydrogen bonds. Compound **3** crystallizes with two independent formula units in the asymmetric unit. In contrast to compound **2** their counterparts connected by hydrogen bonds are generated by the crystallographic center of symmetry. A complete furyl group was disordered (C42). Its atoms were refined on split positions with site occupancy factors of 0.55:0.45. Two THF molecules are coordinated to each dimeric formula unit by hydrogen bonds. Due to the relatively large $U$ values of their atoms they were refined with isotropic displacement factors. The crystals of compound **5** enclose two THF molecules per formula unit. They do not show any close contact to the digallium molecules. Their atoms were refined with isotropic $U$ values. The molecules of compound **6** are located on crystallographic centers of symmetry with two independent molecular halves in the asymmetric unit. Two DME molecules are bonded to each dimer via a hydrogen bridge to one oxygen atom.

The crystallographic data were deposited as supplementary publication no. CCDC-828709 (for **2**·OEt$_2$), -828707 (for **3**·THF), -828708 (for **5**·4THF) and -828710 (for **6**·2DME). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, Great Britain (Fax: +44-1223-336-033; E-mail: deposit@cccd.cam.ac.uk).

## Acknowledgement

We are grateful to the *Deutsche Forschungsgemeinschaft* (IRTG-1444) for generous financial support.

**Table 1.** Crystal data and structure refinement for compounds **2**, **3**, **5**, and **6**.

| | **2**·OEt$_2$ | **3**·THF | **5**·4THF | **6**·2DME |
|---|---|---|---|---|
| Formula | $C_{34}H_{60}F_6Ga_2N_4O_3Si_4$ | $C_{28}H_{56}Ga_2N_4O_5Si_4$ | $C_{68}H_{132}Ga_4O_{12}P_4Si_8$ | $C_{38}H_{100}Ga_2N_4O_6Si_8$ |
| Crystal system | triclinic | triclinic | tetragonal | triclinic |
| Space group[24] | $P\bar{1}$; No. 2 | $P\bar{1}$; No. 2 | $I\bar{4}$; No. 82 | $P\bar{1}$; No. 2 |
| Z | 4 | 4 | 2 | 2 |
| $T$ /K | 153(2) | 153(2) | 153(2) | 153(2) |
| Density (calc) /g·cm$^{-3}$ | 1.317 | 1.262 | 1.177 | 1.157 |
| $a$ /pm | 1465.42(9) | 1251.18(8) | 1874.60(6) | 1240.23(5) |
| $b$ /pm | 1532.8(1) | 1396.45(9) | 1874.60(6) | 1257.10(5) |
| $c$ /pm | 2364.7(2) | 2574.1(2) | 1420.58(9) | 2074.97(8) |
| $\alpha$ /° | 91.959(2) | 86.707(1) | 90 | 88.496(1) |
| $\beta$ /° | 105.001(1) | 89.162(1) | 90 | 87.391(1) |
| $\gamma$ /° | 111.198(1) | 66.185(1) | 90 | 72.469(1) |
| $V$ /nm$^3$ | 4.7351(5) | 4.1075(5) | 4.9921(4) | 3.0814(2) |
| $\mu$ /mm$^{-1}$ | 2.868 | 1.464 | 1.177 | 1.068 |
| Crystal size /mm | 0.24 × 0.20 × 0.02 | 0.29 × 0.27 × 0.16 | 0.43 × 0.20 × 0.15 | 0.23 × 0.11 × 0.08 |
| Radiation | Cu-$K_\alpha$ | Mo-$K_\alpha$ | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| $\Theta$range for data collection /° | 1.95 ≤ 72.63 | 1.58 ≤ 31.86 | 1.54 ≤ 31.68 | 1.70 ≤ 28.04 |
| Independent reflections | 16155 ($R_{int}$ = 0.0483) | 25635 ($R_{int}$ = 0.0274) | 7900 ($R_{int}$ = 0.0237) | 14883 ($R_{int}$ = 0.0201) |
| Parameters | 1026 | 786 | 202 | 563 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0539 (12421) | 0.0517 (16814) | 0.0410 (6934) | 0.0285 (12461) |
| $wR2$ (all data) | 0.1558 | 0.1501 | 0.1304 | 0.0737 |
| Max./ min. residual electron density /10$^{30}$ e·m$^{-3}$ | +1324/–564 | +1850/–969 | +1119/–445 | +383/–242 |

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma [w(F_o^2-F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$

## References

[1] W. Uhl, M. Layh, T. Hildenbrand, *J. Organomet. Chem.* **1989**, *364*, 289.

[2] W. Uhl, *Coord. Chem. Rev.* **1997**, *163*, 1.

[3] W. Uhl, I. Hahn, H. Reuter, *Chem. Ber.* **1996**, *129*, 1425; W. Uhl, H. R. Bock, J. Kösters, M. Voß, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1851.

[4] W. Uhl, H. R. Bock, A. Hepp, F. Rogel, M. Voß, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1255.

[5] W. Uhl, T. Spies, R. Koch, *J. Chem. Soc., Dalton Trans.* **1999**, 2385.

[6] W. Uhl, *Chem. Soc. Rev.* **2000**, *29*, 259; W. Uhl, M. Prött, G. Geiseler, K. Harms, *Z. Naturforsch.* **2002**, *57b*, 141; W. Uhl, L. Cuypers, K. Schüler, T. Spies, C. Strohmann, K. Lehmen, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1526; W. Uhl, T. Spies, W. Saak, *Z. Anorg. Allg. Chem.* **1999**, *625*, 2095; W. Uhl, R. Graupner, I. Hahn, T. Spies, W. Frank, *Eur. J. Inorg. Chem.* **1998**, 355; W. Uhl, I. Hahn, R. Wartchow, *Chem. Ber./Recueil* **1997**, *130*, 417.

[7] W. Uhl, *Z. Naturforsch.* **1988**, *43b*, 1113; W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139.

[8] W. Uhl, R. Graupner, S. Pohl, W. Saak, W. Hiller, M. Neumayer, *Z. Anorg. Allg. Chem.* **1997**, *623*, 883.

[9] W. Uhl, E. Er, *Organometallics* **2006**, *25*, 5832; W. Uhl, A.-C. Fick, T. Spies, G. Geiseler, K. Harms, *Organometallics* **2004**, *23*, 72; W. Uhl, L. Cuypers, M. Prött, K. Harms, *Polyhedron* **2002**, *21*, 511; W. Uhl, T. Spies, D. Haase, R. Winter, W. Kaim, *Organometallics* **2000**, *19*, 1128; W. Uhl, T. Spies, W. Saak, *Eur. J. Inorg. Chem.* **1998**, 1661.

[10] W. Uhl, M. Voß, M. Layh, F. Rogel, *Dalton Trans.* **2010**, *39*, 3160.

[11] W. Uhl, M. Voß, J. Müller, K. Seubert, *Chem. Eur. J.* **2011**, *17*, 7852.

[12] R. Centore, A. Carella, A. Tuzi, A. Capobianco, A. Peluso, *CrystEngComm* **2010**, *12*, 1186; H. Ratajczak, J. Baran, A. J. Barnes, J. Barycki, S. Debrus, Z. Latajka, M. May, A. Pietraszko, *J. Mol. Struct.* **2001**, *596*, 17; E. I. Thiam, A. H. Barry, A. Navaza, P. Retailleau, M. Gaye, A. S. Sall, *Acta Crystallogr., Sect. E* **2009**, *65*, m1014; W. Uhl, M. Layh, B. Rezaeirad, *Inorg. Chem.* **2011**, published online, DOI: 10.1021/ic200572q.

[13] Few examples: C. Tian, *Acta Crystallogr., Sect. E* **2010**, *66*, m71; M. B. Jones, K. I. Hardcastle, C. E. MacBeth, *Polyhedron* **2010**, *29*, 116; S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, *Chem. Eur. J.* **2010**, *16*, 938; L.-K. Liu, F.-T. Luo, L.-C. Hsieh, *Acta Crystallogr., Sect. C* **1994**, *50*, 1333; L. V. Rybin, E. A. Petrovskaya, A. S. Batsanov, Y. T. Struchkov, M. I. Rybinskaya, *J. Organomet. Chem.* **1981**, *212*, 95; K. Vyas, V. M. Rao, H. Manohar, *Acta Crystallogr., Sect. C* **1987**, *43*, 1197.

[14] S. J. Obrey, S. G. Bott, A. R. Barron, *J. Organomet. Chem.* **2002**, *643–644*, 53; P. Jutzi, M. Bangel, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15*, 4559; A. M. Bradford, D. C. Bradley, M. B. Hursthouse, M. Motevalli, *Organometallics* **1992**, *11*, 111; W. Uhl, T. Abel, E. Hagemeier, A. Hepp, M. Layh, B. Rezaeirad, H. Luftmann, *Inorg. Chem.* **2011**, *50*, 325; W. Uhl, T. Abel, J. Kösters, F. Rogel, *Z. Naturforsch.* **2008**, *63b*, 117; W. Uhl, T. Abel, J. Kösters, B. Rezaeirad, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1014.

[15] W. Ziemkowska, R. Anulewicz-Ostrowska, *J. Organomet. Chem.* **2004**, *689*, 2056; L. H. van Poppel, S. G. Bott, A. R. Barron, *Polyhedron* **2002**, *21*, 1877; L. H. Van Poppel, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **2003**, *125*, 11006; A. H. Cowley, S. K. Mehrotra, J. L. Atwood, W. E. Hunter, *Organometallics* **1985**, *4*, 1115.

[16] T. Steiner, *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48; M. Wenger, J. Bernstein, *Angew. Chem.* **2006**, *118*, 8134; *Angew. Chem. Int. Ed.* **2006**, *45*, 7966; R. S. Jebas, B. K. Periyasamy, T. Balasubramanian, *J. Chem. Crystallogr.* **2006**, *36*, 503; M. C. Etter, Z. Urbanczyk-Lipkowska, M. Zia-Ebrahimi, T. W. Panunto, *J. Am. Chem. Soc.* **1990**, *112*, 8415; T. C. Lewis, D. A. Tocher, *Acta Crystallogr., Sect. E* **2005**, *61*, o1023; M. F. Klapdor, H. Willner, W. Poll, D. Mootz, *Angew. Chem.* **1996**, *108*, 336; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 320; A. Dey, M. T. Kirchner, V. R. Vangala, G. R. Desiraju, R. Mondal, J. A. K. Howard, *J. Am. Chem. Soc.* **2005**, *127*, 10545; B. R. Bhogala, V. R. Vangala, P. S. Smith, J. A. K. Howard, G. R. Desiraju, *Cryst. Growth Des.* **2004**, *4*, 647.

[17] W. Uhl, M. Voss, H. Luftmann, *Chem. Commun.* **2009**, 6854; W. Uhl, M. R. Halvagar, M. Layh, *Chem. Commun.* **2009**, 4269; W. Uhl, M. Prött, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2259.

[18] R. M. Issa, M. F. Iskander, M. F. El-Shazly, *Z. Anorg. Allg. Chem.* **1967**, *354*, 98; R. M. Issa, M. F. El-Shazly, M. F. Iskander, *Z. Anorg. Allg. Chem.* **1967**, *354*, 90; M. M. Mostafa, D. Nicholls, *Inorg. Chim. Acta* **1981**, *51*, 35.

[19] T. Svoboda, R. Jambor, A. Ruzicka, Z. Padelkova, M. Erben, L. Dostal, *Eur. J. Inorg. Chem.* **2010**, 5222; R. Pothiraja, S. Shanmugan, M. G. Walawalkar, M. Nethaji, R. J. Butcher, R. Murugavel, *Eur. J. Inorg. Chem.* **2008**, 1834; T. Azais, L. Bonhomme-Coury, J. Vaissermann, P. Bertani, J. Hirschinger, J. Maquet, C. Bonhomme, *Inorg. Chem.* **2002**, *41*, 981; P. Betz, A. Bino, J.-L. Du, L. S.-M. Lo, R. C. Thompson, *Inorg. Chim. Acta* **1990**, *170*, 45.

[20] K. Exner, M. Heizmann, F. Yang, M. Kegel, M. Keller, L. Knothe, B. Großmann, J. Heinze, H. Prinzbach, *Eur. J. Org. Chem.* **2005**, 1311; S. F. Nelsen, S. C. Blackstock, P. A. Petillo, I. Agmon, M. Kaftory, *J. Am. Chem. Soc.* **1987**, *109*, 5724; I. Agmon, M. Kaftory, S. F. Nelsen, S. C. Blackstock, *J. Am. Chem. Soc.* **1986**, *108*, 4477; F.-P. Xiao, L.-F. Jin, *Z. Anorg. Allg. Chem.* **2008**, *634*, 397; Z.-X. Yu, Y.-X. Sun, *Acta Crystallogr., Sect. E* **2006**, *62*, m3521; F. W. B. Einstein, S. Nussbaum, D. Sutton, A. C. Willis, *Organometallics* **1983**, *2*, 1259.

[21] S. A. Malashikhin, K. K. Baldridge, N. S. Finney, *Org. Lett.* **2010**, *12*, 940.

[22] M. Dias, R. Mornet, M. Laloue, *Bioorg. Med. Chem.* **1995**, *3*, 361.

[23] H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, 3rd ed., Wiley-VCH, Weinheim, **1998**.

[24] *International Tables for Crystallography, Space-Group Symmetry*, vol. A (Ed.: T. Hahn), Kluwer Academic Publishers, Dordrecht–Boston–London, **1989**.

[25] *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-RAY Instruments Inc.: Madison,WI, **1990**; G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Structures; Universität Göttingen, **1997**.

Received: June 8, 2011
Published Online: August 31, 2011