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Journal of Organometallic Chemistry 690 (2005) 1529–1539
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Adducts of organogallium chlorides with hydrazines and the formation of dimeric dialkylgallium hydrazides possessing different ring sizes

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Received 13 October 2004; accepted 7 December 2004
Available online 22 January 2005

Abstract

The dialkylgallium chlorides R_2GaCl (R = Me, Et, CMe_3) reacted with hydrazines $H_2N–N(H)R'$ (R′ = CMe_3, C_6H_5) to form the adducts $R_2ClGa \leftarrow NH_2–N(H)R'$ (**1**–**4**), in which the gallium atoms are coordinated by the NH_2 nitrogen atoms of the hydrazine ligands. Treatment of these adducts with *tert*-butyllithium as a base afforded dialkylgallium hydrazides $(R_2Ga–N_2H_2R')_2$ [**5** (R = R′ = CMe_3) and **6** (R = CMe_3, R′ = C_6H_5)] by deprotonation of the hydrazine ligands and precipitation of LiCl in two cases only. The remaining adducts gave a substitution reaction at gallium or an unclear reaction course. The hydrazides **5** and **6** adopt different structures in the solid state. The tri(*tert*-butyl) compound **5** possesses a four-membered Ga_2N_2 heterocycle in its molecular core with two exocyclic N–N bonds, which represents the structural motif usually observed for dialkylgallium hydrazides. **6** has a five-membered Ga_2N_3 heterocycle with one endocyclic and one exocyclic N–N bond. That structure is preserved in solution as clearly shown by NMR spectroscopy. The behaviour of **5** in solution is more complicated, which may be caused by *cis*/*trans* isomerization.

1. Introduction

Alkylgallium hydrazides found considerable interest in recent literature because they may be suitable single source precursors for the generation of gallium nitride GaN [1]. Generally, they were obtained by the treatment of trialkylgallium compounds [2–6] or stable gallium trihydride adducts [7] with different alkylhydrazines, by the reactions of dialkylgallium chlorides with lithium hydrazides [6–8] or by the replacement reaction between a hydrazine derivative and a gallium amide [9]. In some cases, gallium hydrazine adducts could be isolated as stable intermediates [5,6,10]. Furthermore, secondary reactions could be initiated on heating of the gallium hydrazides, which yielded interesting cage compounds by alkane elimination [4,5,7]. Hydrazine N_2H_4 and $GaMe_3$ gave a singular bicyclic compound, $(Me_2Ga)_4(N_2H_2)(NH–NH_2)_2$, in which two five-membered heterocycles are connected by a common N–N bond and in which the $N\text{-}NH_2$ groups occupy exocyclic positions [6]. All remaining dialkylgallium hydrazides published so far contain the same structural motif in their molecular centres consisting of a four-membered Ga_2N_2 heterocycle and two exocyclic N–N bonds. In contrast, the homologous dialkylaluminum hydrazides show a broader variability of structures with four- [2,3,11], five- [12] and six-membered heterocycles [12–14] and none, one, or two endocyclic N–N groups, respectively (Scheme 1). The respective structural motif seems to be determined by the steric demand of the substituents

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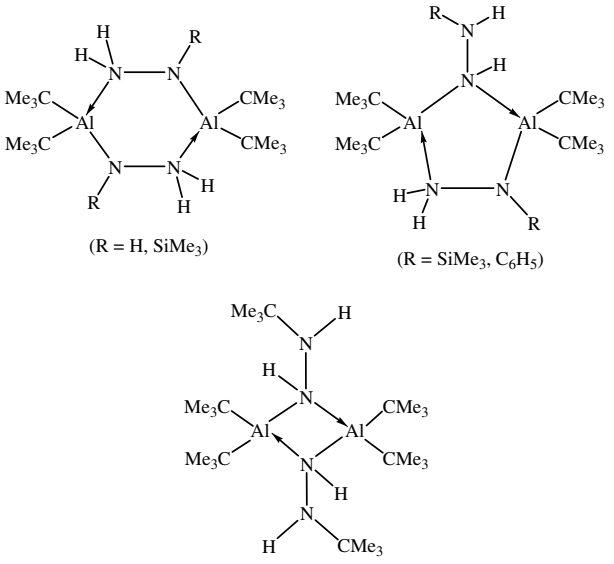
doi:10.1016/j.jorganchem.2004.12.021



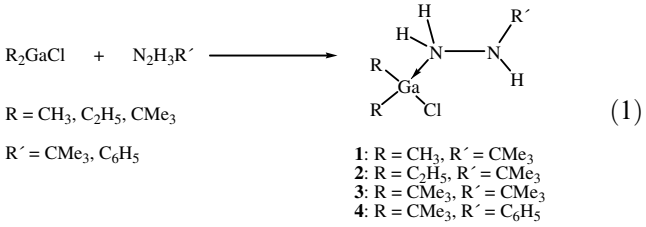
Scheme 1.

attached to aluminum or the hydrazido groups and by the transannular electrostatic repulsion between the ring atoms. Quantum-chemical calculations on the aluminum compounds revealed that the five-membered Al_2N_3 heterocycles are the most favourable ones [12]. While NMR spectroscopic investigations of the aluminum hydrazides verified the preservation of the solid state structures in solution, more complicated spectra were detected with gallium hydrazides, which were interpreted by the occurrence of *cis*/*trans* isomers with respect to the arrangement of the N–N or N–H bonds [2,3,5]. This isomerization process should proceed by the opening of one Ga–N bond in the ring. Here we report on the isolation and characterization of two new dialkylgallium hydrazides, for which different structures were observed in the solid state and in solution.

2. Results and discussion

2.1. Formation of adducts $R_2GaCl \leftarrow NH_2–N(H)R'$

As was shown in preceding investigations of our group [11,12], the treatment of hydrazine adducts of the type $R_2AlCl \leftarrow NH_2–N(H)R'$ with *n*-butyllithium afforded the corresponding dialkylaluminum hydrazides by deprotonation and salt elimination in quite reasonable yields. We hoped to employ this procedure for the synthesis of gallium hydrazides, too. The corresponding gallium hydrazine adducts $R_2GaCl \leftarrow NH_2–N(H)R'$ were easily obtained by the direct treatment of dialkylgallium chlorides (R = Me, Et, CMe_3) with alkyl or aryl hydrazines $H_2N–N(H)R'$ ($R' = CMe_3$, C_6H_5) in moderate to high yields, Eq. (1). All adducts (**1**–**4**) were isolated as colorless solids. They are only sparingly soluble in *n*-hexane, but readily soluble in toluene. A fast exchange of the N–H protons led to the occurrence of only one, generally broad resonance. Only the diethyl compound **2** shows two distinct N–H signals, which are broad and overlap partially. No coupling between the protons of different nitrogen atoms could be resolved.



(1)

The four adducts were characterized by crystal structure determinations (Figs. 1–4). Two polymorphous forms possessing different space groups were observed for compound **1**. Thus, two values of structural parameters are given in the discussion, in all cases the first one refers to the monoclinic cell. Compound **2** has two independent molecules in the asymmetric unit of the unit cell, only one of which is depicted in Fig. 2. All structures consist of adducts formed by the intact

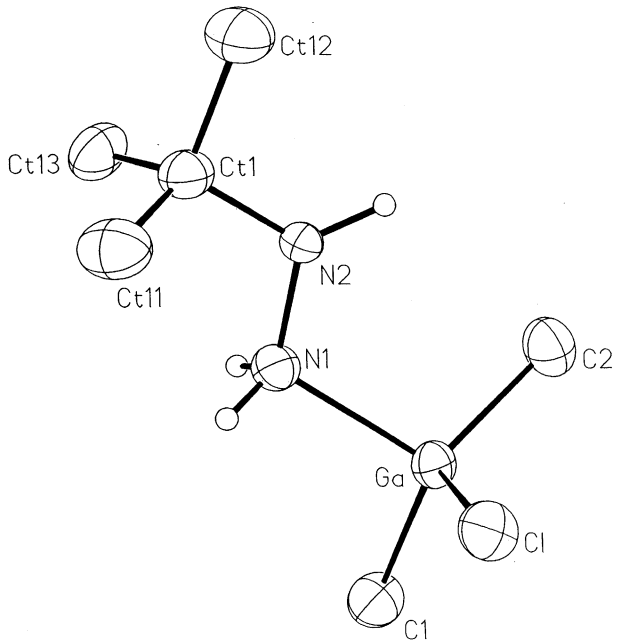


Fig. 1. Molecular structure of **1**. The thermal ellipsoids are drawn at the 40% probability level. Methyl hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): Monoclinic cell: Ga–C1 195.1(4), Ga–C2 195.1(4), Ga–Cl 228.48(9), Ga–N1 206.5(3), N1–N2 145.1(4), C1–Ga–C2 128.8(2), C1–Ga–N1 104.6(1), C2–Ga–N1 107.2(2), C1–Ga–Cl 110.2(1), C2–Ga–Cl 106.8(1), N1–Ga–Cl 93.64(9). Triclinic cell: Ga–C1 196.4(8), Ga–C2 195.6(8), Ga–N1 206.4(6), Ga–Cl 229.1(2), N1–N2 144.9(8), C1–Ga–C2 128.6(4), C1–Ga–N1 103.5(3), C2–Ga–N1 107.3(3), C1–Ga–Cl 110.7(3), C2–Ga–Cl 106.9(3), N1–Ga–Cl 94.3(2).

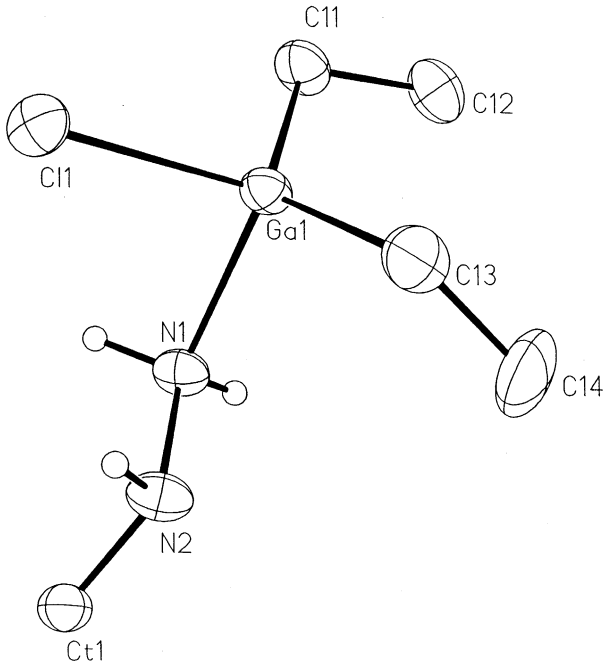


Fig. 2. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups of the *tert*-butyl group and hydrogen atoms of the ethyl groups are omitted. Important bond lengths (pm) and angles (°) (figures of the second molecule in square brackets): Ga1–C11 196.5(3) [196.2(4)], Ga1–C13 195.9(4) [196.3(3)], Ga1Cl1 228,8(1) [228,65(9)], Ga1–N1 206.7(3) [205.8(3)], N1–N2 145.7(4) [146.1(4)], C11–Ga1–C13 126.4(2) [125.9(2)], C11–Ga1–N1 106.7(1) [107.6(2)], C13–Ga1–N1 106.6(2) [106.2(2)], C11–Ga1–Cl1 110.9(1) [109.0(1)], C13–Ga1–Cl1 108.4(2) [110.4(1)], Cl1–Ga1–N1 92.2(1) [92.49(9)].

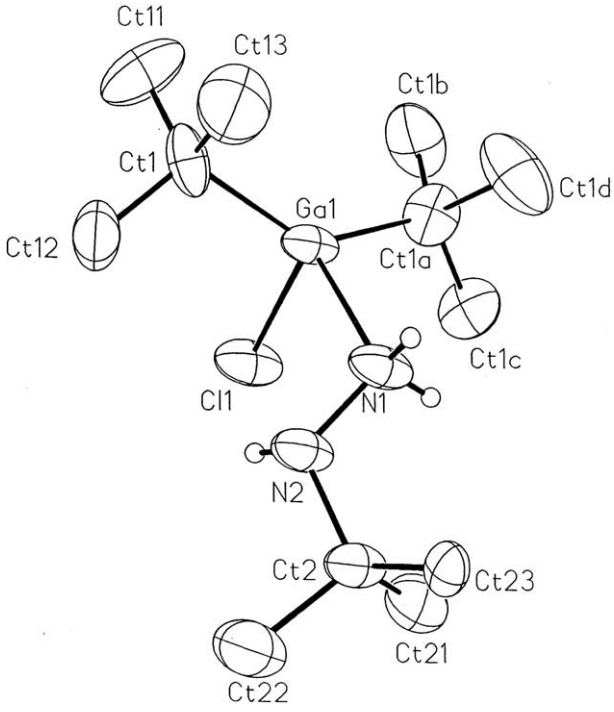


Fig. 3. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms of methyl groups are omitted. Important bond lengths (pm) and angles (°): Ga1–Ct1 198(3), Ga1–N1 210.8(7), Ga1–Cl1 228.7(2), N1–N2 143(2), N1–Ga1–Cl1 92.5(2).

constituents dialkylgallium chloride and hydrazine. While the nitrogen atoms bonded to the *tert*-butyl or phenyl groups are in terminal positions, the NH_2 nitrogen atoms of the hydrazine ligands are attached to the gallium atoms in all compounds, so that coordination numbers of four in a distorted tetrahedral environment result for the central metal atoms. The Ga–C distances to the alkyl groups show a slight, but continuous increase with increasing bulkiness of the substituents [195.1 and 196.0 (**1**, R = Me) to 199.2 pm (**4**, R = CMe_3)]. Same holds for the Ga–N distances, which vary between 206.5/206.4 (**1**) and 212.1 pm (**4**). In contrast, the Ga–Cl bond lengths are almost indistinguishable in all four compounds and deviate only slightly from the average value of 228.7 (±0.4) pm. The N–N distances of the *tert*-butylhydrazine ligands (145.5 pm) are longer than that of the phenylhydrazine ligand (142.9 pm). Compound **3** may not be considered here owing to a severe disorder and the uncertainty of the determined bond lengths and angles. The tricoordinated nitrogen atoms N2 of all compounds **1**–**4** possess a pyramidal environment [sum of the angles 330.8 and 339.0 (**1**), 325.5 and 332.1(**2**), 326.5 (**3**), 338.3 (**4**)]. While in aluminum or indium hydrazine adducts similar to **1**–**4** relatively short H···Cl contacts between the chlorine atoms attached to aluminum or indium and the hydrogen atom of the β-nitrogen atoms may indicate a weak hydrogen bonding [10,15], such an interaction may be

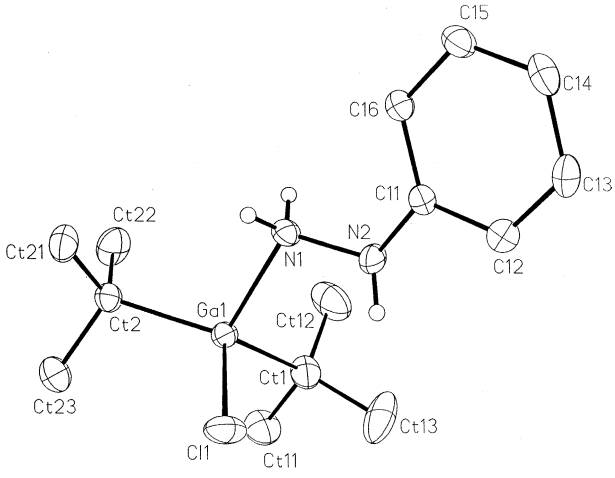


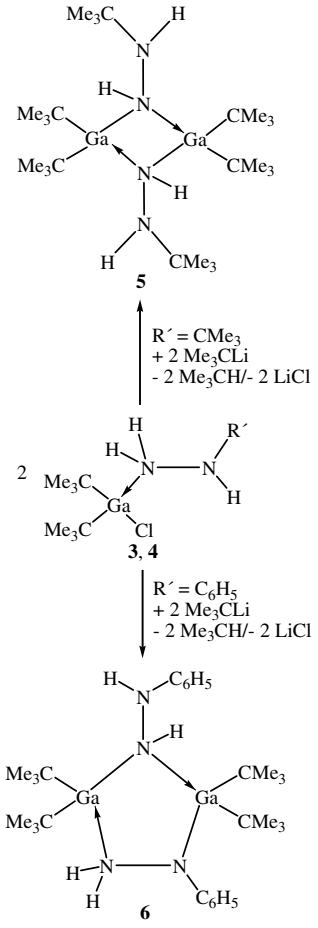
Fig. 4. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms of the phenyl and *tert*-butyl groups are omitted. Important bond lengths (pm) and angles (°): Ga1–Ct1 199.5(3), Ga1–Ct2 198.9(3), Ga1–Cl1 228.30(9), Ga1–N1 212.1(2), N1–N2 142.9(4), Ct1–Ga1–Ct2 127.1(1), Ct1–Ga1–N1 106.4(1), Ct2–Ga1–N1 106.6(1), Ct1–Ga1–Cl1 110.0(1), Ct2–Ga1–Cl1 108.89(9), Cl1–Ga1N1 92.03(8).

excluded for the gallium adducts **1**–**4**. The shortest H···Cl contact (259 pm) was observed for the disordered compound **3**. The longer ones of the remaining compounds [284 (**4**) to 313/321 pm (**1**)] are clearly outside the range of significant interactions. The particular behaviour of the gallium compounds may be caused by the higher electronegativity of gallium compared to that of aluminum or indium and the lower charge separation resulting for the Ga–Cl bonds. Comparable adducts of hydrazines with trialkylgallium compounds [5] or with methylgallium dichloride [6,10] are reported in literature, however, only the last one was characterized by a crystal structure determination.

2.2. Formation of hydrazides $[R_2Ga–N_2H_2R']_2$

Starting with these adducts, we tried to synthesize hydrazides by treatment with butyllithium. However, we were successful in two cases only. The diethyl compound **2** gave the quantitative replacement of the chlorine atom by an *n*-butyl group instead. The adduct $Me_2(nBu)Ga \leftarrow NH_2–N(H)CMe_3$ was formed and clearly identified by NMR spectroscopy [^{1}H NMR: δ = 2.98 (2H, NH_2), 2.53 (1H, NH), 1.73 and 1.59 (each 2H, CH_2 of *n*Bu), 1.44 (6H, Me of Et), 1.10 (Me of *n*Bu), 0.60 (9H, CMe_3), 0.59 (4H, CH_2 of Et); one CH_2 group probably covered]. It was isolated as an oily product, which could not be purified by recrystallization. Distillation succeeded at elevated temperature in vacuum, but partial decomposition occurred as became obvious by an alteration of the integration ratio between alkylgallium and hydrazine residues. Thus, further experimental details are not included here. Clearly, the substitution reaction in that case is favoured by the low steric shielding of the starting compound. The dimethyl compound **1** gave a mixture of unknown products, which could not be separated.

The expected reactions were observed for both di(*tert*-butyl)gallium compounds (**3** and **4**). Treatment with *tert*-butyllithium gave deprotonation and salt elimination, and gallium hydrazides were isolated in moderate yield, Eq. (2). The routine procedures given in the experimental section do not involve the isolation of the intermediate adducts, but the rough products of the adduct formation were directly treated with the alkyllithium derivative. Both hydrazides were isolated as colorless crystals and their constitution was clarified by crystal structure determinations (see below). They adopt different structures in the solid state. A four-membered centrosymmetric Ga_2N_2 heterocycle with two exocyclic N–N bonds was observed for the tri(*tert*-butyl) compound **5**, while for the phenylhydrazide product (**6**) a five-membered Ga_2N_3 ring with one endo- and one exocyclic N–N bond was determined.



(2)

The solution behavior is more complicated. The centrosymmetric structure observed for **5** in the solid state should result in a quite simple ^{1}H NMR spectrum. Instead, four chemically different N–H protons were detected at room temperature. Three resonances in an integration ratio of about 1:2:1 were observed for the *tert*-butyl groups attached to gallium, but only one resonance resulted for the *tert*-butyl group of the hydrazido substituent. The last one splitted into two very narrow resonances upon cooling to 285 K. Upon warming, the signals of the *tert*-butyl groups attached to gallium coincided at about 330 K, those of the N–H protons gave two resonances at about 340 and 350 K, respectively. The activation barrier for the exchange process was estimated [16] to be about 70 kJ/mol, which is similar to values reported before [2,3]. The relative intensities of the NMR signals of the two species at lower temperature (200–320 K) remain constant and verify an almost equimolar distribution (average integration ratio 1–1.2). Thus, the energy difference between both species seems to be rather small. An equilibrium of monomeric and dimeric formula units by partial dissociation can clearly be ruled out, because the determination of the molar mass in benzene by cryoscopy gave the exact value of the dimer. The behavior of **5** is similar to that reported in literature for other dialkylgallium hydrazides [2,3,5]. It

was interpreted in terms of *cis*/*trans* isomerization by the opening of a Ga–N bond in the ring, rotation around the remaining bond, inversion of configuration at nitrogen and ring closure. Monomerization in traces and dimerization of differently oriented monomers may, however, not be excluded. In our case, only one resonance should result for the *tert*-butyl groups attached to the gallium atoms of the *trans*-isomer, while two resonances are to be expected for the *cis*-isomer. This allows the assignment of the different sets of resonances to the respective isomeric forms.

The phenylhydrazido compound **6** only partially shows the expected ^{1}H NMR spectrum at room temperature. The resonances of four chemically different *tert*-butyl groups attached to gallium in equal intensity were observed in accordance with the particular structure containing a five-membered heterocycle. A strong dependency of the relative chemical shifts ($\Delta\delta$) of the outer two signals on temperature was detected. $\Delta\delta$ decreased from 0.70 ppm at 190 K to 0.34 ppm at 370 K. The alteration of the ^{1}H NMR spectra depending on temperature is partially summarized in Fig. 5. As

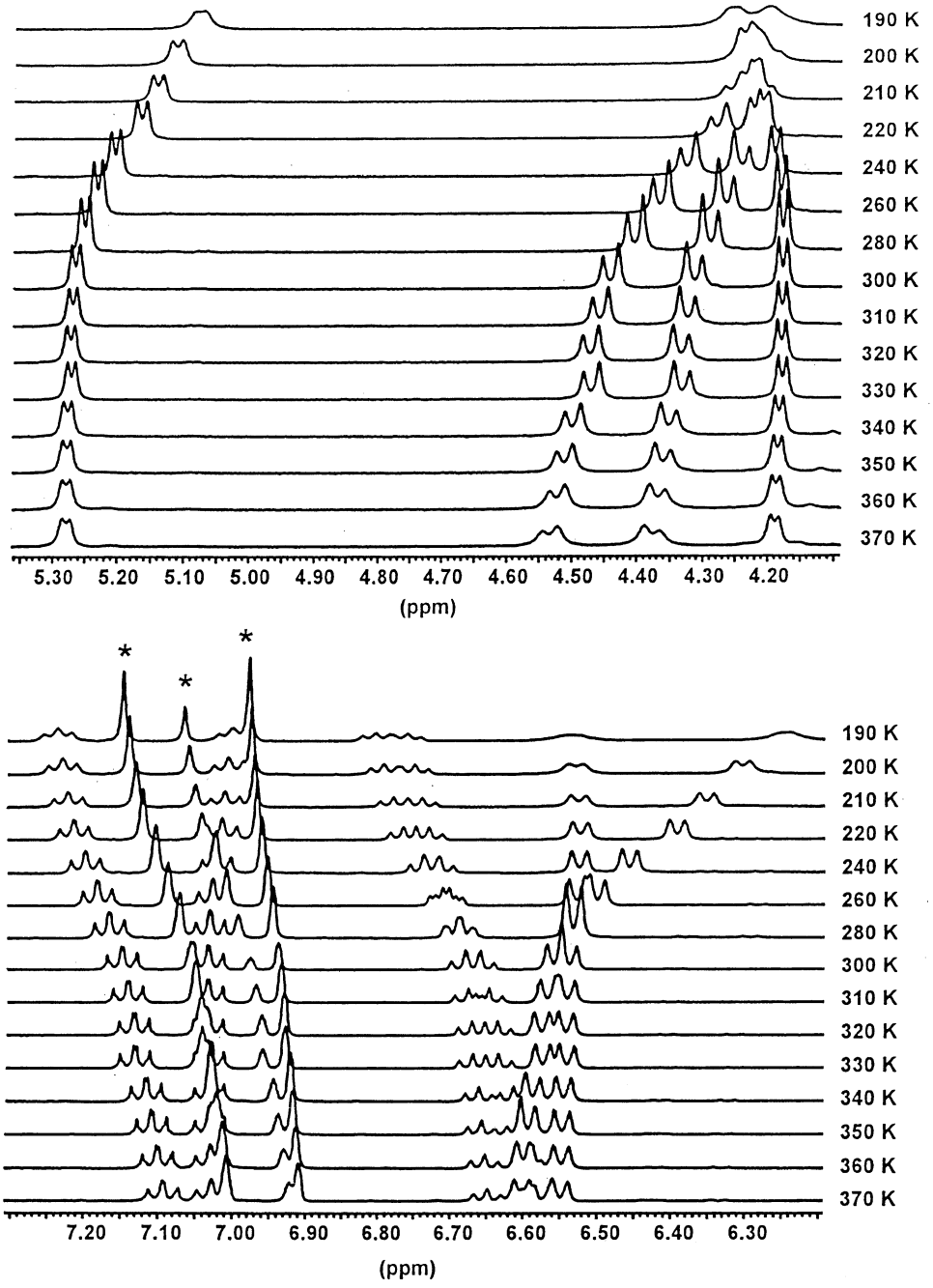


Fig. 5. Temperature dependent ^{1}H NMR spectra of **6**. Details of the NH (top) and phenyl regions (bottom) of the spectra are depicted. Resonances of the solvent toluene are marked by an asterisk.

expected from the molecular structure, also four chemically different N–H protons were observed at room temperature, which showed an equal intensity and a coupling across the N–N bond. One doublet at $\delta = 5.24$ was markedly separated from the remaining three ones at $\delta = 4.39$, 4.28 and 4.17. $\Delta\delta$ was largest at high temperature (370 K), while with decreasing temperature the three high field doublets approached to give a broad, only slightly splitted resonance at 200 K. Most complicated was the phenyl region of the ^{1}H NMR spectrum. Two different phenyl groups are to be expected, one attached to a nitrogen atom of the ring bearing a negative charge and one bonded to the terminal nitrogen atom of the exocyclic N–N bond. Thus, six different resonances of phenyl hydrogen atoms should occur. But only one doublet and three triplets in a strange integration ratio of 2 (t):2 (t):2 (t):4 (d) were observed at 280 K. The triplet at $\delta = 6.68$ deviated most strongly from the ideal shape. At lower temperature that particular triplet and the doublet at $\delta = 6.52$ split into two triplets or doublets, respectively. The two other triplets remained almost unchanged apart from small alterations of their chemical shifts. They approached at higher temperatures. A splitting of the triplet at $\delta = 6.68$ and the doublet at $\delta = 6.52$ was also observed for temperatures above 280 K. The integration ratio of the resulting six resonances is 2:2 (triplets, both *meta*-H, not affected on cooling or warming):1:1 (triplets, both *para*-H, splitting was observed):2:2 (doublets, *ortho*-H, splitting was observed). These values correspond to those expected for the heterocyclic molecule. It seems that by accident a much too simple spectrum was observed at room temperature, while at higher or lower temperatures spectra resulted which were expected by molecular symmetry. A crossing of the resonances at about 280 K is responsible for that particular observation. The strong alterations of the shape of the spectra may be caused by conformational changes of the molecules in solution with respect to the strongly faulted heterocycle observed for the solid state. Or it may depend on the strength of the mesomeric interaction between the phenyl group and the anionic nitrogen atom of the endocyclic hydrazido group.

Fig. 6 shows the molecular structure of the *tert*-butyl hydrazido compound **5**. It possesses a four-membered Ga_2N_2 heterocycle with two exocyclic N–N bonds. The molecules are located on special positions with symmetry 2/*m*. The Ga–C bonds of **5** (202.9 pm) are longer than those of the starting compound **3**, while a shortening of the Ga–N bonds (203.8 pm) was observed compared to the donor-acceptor bond of the adduct **3**. The N–N bond lengths are in the expected range (144.6 pm). The nitrogen atom N1 attached to two gallium atoms has a distorted tetrahedral coordination sphere, while the second, exocyclic nitrogen atom N2 has a pyramidal surrounding (sum of the bond angles

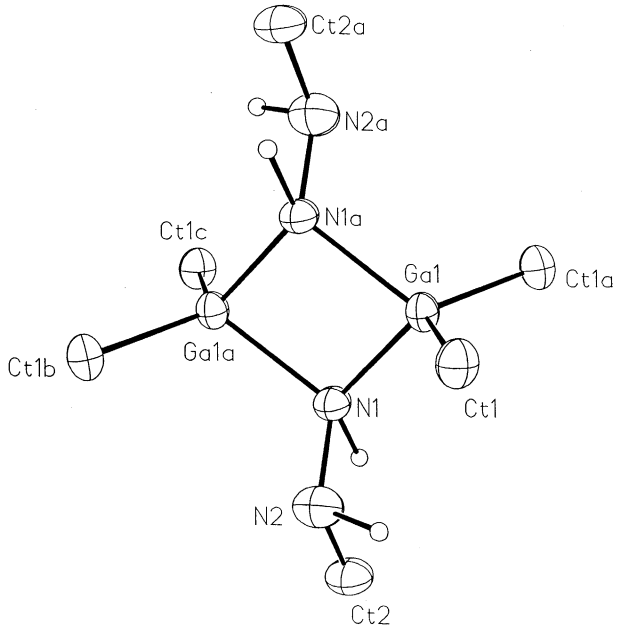


Fig. 6. Molecular structure of **5**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted. Important bond lengths (pm) and angles (°): Ga1–Ct1 202.9(2), Ga1N1 203.8(2), N1–N2 144.6(4), Ct1–Ga1–Ct1a 116.7(2), Ct1–Ga1–N1 114.7(1), Ct1–Ga1–N1a 111.7(1), N1–Ga1–N1a 82.9(1), Ga1–N1–Ga1a 97.1(1); Ct1a generated by $-x, y, -z$; N1a and Ga1a generated by $-x, -y, -z$.

326°, disordered hydrogen atom). The preference of the four-membered heterocycle in that case may be favoured by steric interactions between the bulky substituents. The hydrazine *tert*-butyl groups are bonded to the exocyclic nitrogen atoms and are, thus, in an optimum distance with respect to the *tert*-butyl groups attached to gallium.

In contrast, the phenylhydrazido compound **6** adopts a structure containing a five-membered heterocycle (Fig. 7), which may be favoured by the less steric stress in the molecule owing to the reduced bulkiness of the phenyl ring compared to that of the *tert*-butyl group and by the diminution of transannular electrostatic repulsions [12]. **6** crystallizes with two independent molecules; bond parameters of the second molecule are given in brackets. The endocyclic hydrazide has an NH_2 group (N21), which is attached to Ga2 by a coordinative bond. The amido nitrogen atom (N22) of that hydrazido ligand is bonded to Ga1 and bears the phenyl ring. The second hydrazido group bridges both Ga atoms via its amido nitrogen atom N11, which is further bonded to a hydrogen atom and the second, terminal nitrogen atom N12. The N–N bond is exocyclic, and N12 bears the phenyl ring and the second hydrogen atom. Thus, the hydrazido ligands differ with respect to their bridging positions and the distribution of their hydrogen atoms. The GaN distances depend on the particular bonding mode. The shortest bond lengths on average [198.9 pm (198.3 pm)] were observed for those bonds involving

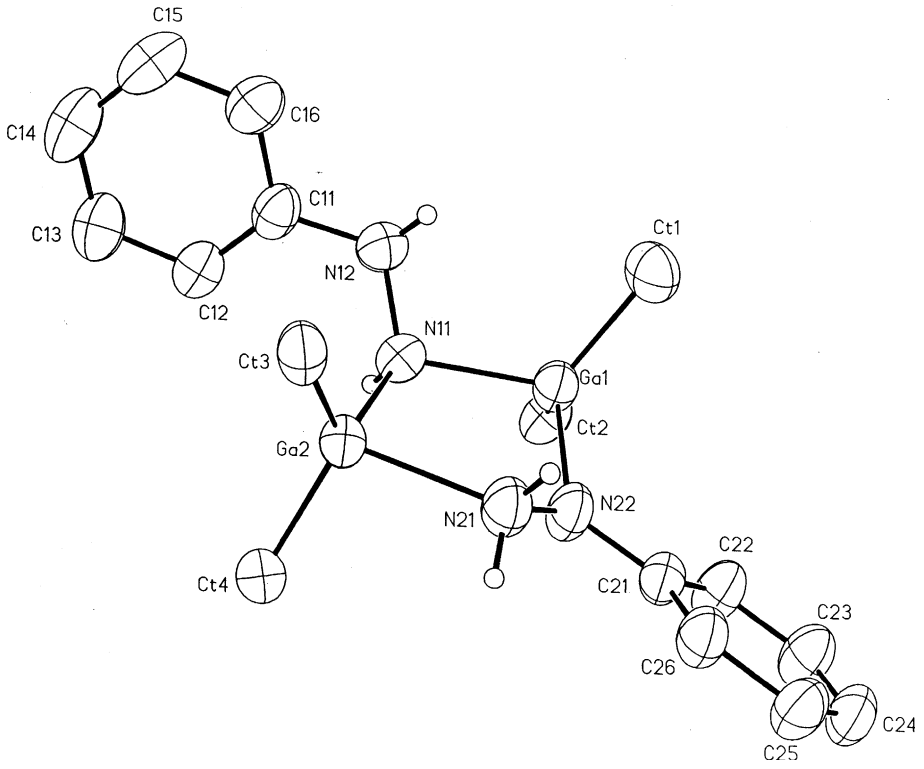


Fig. 7. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms of the phenyl groups are omitted. Two independent molecules were found, structural parameters of the second one are given in square brackets. Important bond lengths (pm) and angles (°): Ga1–N11 207.4(3) [208.5(4)], Ga1–N22 198.9(3) [198.3(3)], Ga2–N21 210.6(3) [209.6(4)], Ga2–N11 199.8(4) [198.9(4)], N11–N12 144.9(5) [143.6(5)], N21–N22 143.5(5) [143.3(5)], Ga1–N11–Ga2 114.9(2) [113.2(2)], N11–Ga1–N22 91.6(1) [92.9(1)], Ga1–N22–N21 115.4(2) [116.1(3)], N22–N21–Ga2 114.3(3) [114.6(3)], N21–Ga2–N11 90.7(1) [92.5(1)].

the amido nitrogen atom N22 of the endocyclic hydrazine. The bridging atom N11 has a short and a long Ga–N distance of 199.8 (198.9) and 207.4 pm (208.5 pm). The longest separations were found for the dative bonds Ga2–N21 [210.6 pm (209.6 pm)]. The N–N bond lengths are quite similar despite the different coordination behaviour of the hydrazido ligands and deviate only slightly from the average value of 143.8 pm. The nitrogen atom N22 has an almost planar coordination sphere [353.1° (355.1°)], which may be caused by a mesomeric stabilization of the negative charge through an interaction of nitrogen lone pairs with the aromatic system of the phenyl rings. This interpretation may also be verified by the coplanar arrangement of the phenyl ring and the further atoms attached to nitrogen [angle between the normals of the planes phenyl versus Ga1, N22, N21, C21 20.3° (15.6°)]. Owing to the uncertainty of the refined hydrogen positions, we refrain from a discussion of structural parameters involving hydrogen atoms. The five-membered heterocycles adopt an envelope conformation. The four atoms N22, Ga1, N11 and Ga2 are almost in a plane with the largest deviation of an atom from that plane of 8.7 pm (7.7 pm). The nitrogen atom N21 of the NH_2 group is located 50.0 pm (45.5 pm) above that plane. Thus, two different structural motifs were determined for the gallium hydrazides reported here similar to the situation of the aluminum hydrazides described in Section 1. Different ring sizes with four-, five- and six-membered heterocycles were also observed for aluminum and gallium hydroxylamides [17].

3. Experimental

All procedures were carried out under purified argon. Toluene was dried over Na/benzophenone, *n*-pentane, *n*-hexane and cyclopentane over $LiAlH_4$. Di(*tert*-butyl)gallium chloride [18], diethylgallium chloride and dimethylgallium chloride [19] were obtained according to literature procedures. Commercially available phenylhydrazine (Aldrich) was degassed and stored over molecular sieves prior to use. MOCHEM GmbH (Marburg) supported us with *tert*-butylhydrazine.

*3.1. Synthesis of (tert-butylhydrazine)dimethylgallium chloride (**1**)*

Dimethylgallium chloride (0.246 g, 1.82 mmol) dissolved in 25 ml of *n*-pentane was treated with 194 μl

(0.160 g, 1.82 mmol) of *tert*-butyl hydrazine at room temperature. The product immediately precipitated as a colorless solid, which is filtered off and dried in vacuum. A second fraction of the product was isolated upon concentration and cooling of the filtrate. Owing to NMR spectroscopic characterization the precipitated product is pure. It may be recrystallized from cyclopentane for further purification. Yield: 0.248 g (61%). M.p. (argon, sealed capillary): 126 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 3.26 (3H, s, br, N–H), 0.51 (9H, s, CMe_3), 0.09 (6H, s, $GaMe_2$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 54.0 (N–C), 25.8 (methyl of *tert*-butyl), −4.0 (GaC). IR (CsBr plates, paraffin, cm^{-1}): 3308 m, 3270 w, 3195 w, 3151 vw νNH; 2955 vs, 2922 vs, 2853 vs, 2700 w, 2639 w (paraffin); 2500 m δNH; 1644 vw, 1592 m δNH_2; 1461 s, 1377 m (paraffin); 1220 w, 1201 m δCH_3; 1125 w, 1051 vw, 1037 vw, 954 w, 928 w, 851 vw δCH, νCN, νNN, νCC; 811 vw ν_{as}NN; 730 m (paraffin); 601 w, 548 vw, 511 w, 464 m, 393 w, 357 w δC_3C, νGaC, νGaN, νGaCl.

3.2. Synthesis of (tert-butylhydrazine)diethylgallium chloride (**2**)

A solution of diethylgallium chloride (0.209 g, 1.28 mmol) in 10 ml of *n*-pentane was added to a cooled (−30 °C) solution of *tert*-butylhydrazine (133 µl, 0.113 g, 1.28 mmol) in 10 ml of the same solvent. After slow warming to room temperature the solvent was removed in vacuum. The colorless residue was recrystallized from cyclopentane (20/−30 °C). Yield: 0.176 g (55%). M.p. (argon, sealed capillary): 92 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 3.21 (1H, s, br, NH); 3.17 (2H, s, br, NH_2), 1.36 (6H, t, $^3J_{H-H}$ = 8.1 Hz, CH_3 of ethyl), 0.68 (4H, q, $^3J_{H-H}$ = 8.1 Hz, CH_2 of ethyl), 0.54 (9H, s, CMe_3). ^{13}C NMR (C_6D_6, 50.3 MHz):δ = 53.9 (N–C), 25.6 (Me of *tert*-butyl), 10.2 (Me of ethyl), 5.9 (GaC). IR (CsBr plates, paraffin, cm^{-1}): 3643 w, 3297 m, 3274 m, 3197 m, 3146 m νNH; 2925 vs, 2856 vs, 2727 w, 2639 w paraffin; 2500 m δNH; 1591 s δNH_2; 1461 vs, 1375 s paraffin; 1280 w, 1219 m, 1201 m δCH_2, δCH_3; 1123 w, 1049 w, 1006 m, 944 m, 850 vw δCH, νCN, νNN, νCC; 814 w ν_{as}NN; 738 w paraffin; 659 m, 567 m, 516 m, 464 w, 390 w, δC_3C, νGaC, νGaN, νGaCl.

3.3. Synthesis of (tert-butylhydrazine)di(tert-butyl)gallium chloride (**3**)

A cooled (−20 °C) suspension of di(*tert*-butyl)gallium chloride (0.156 g, 0.71 mmol) in 10 ml of toluene was treated with 80 µl of *tert*-butylhydrazine (0.063 g, 0.71 mmol). A clear solution was obtained, which was concentrated at room temperature and cooled to −15 °C. The product crystallized as colorless needles. Yield: 0.102 g (47%). Dec. (argon, sealed capillary): 100 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 3.70 (3H, s, br, N–H), 1.29 (18 H, s, Ga–CMe_3), 0.58 (9 H, s, N–CMe_3). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 53.9 (N– C), 30.4 (Me of Ga–CMe_3), 25.5 (Me of N–CMe_3), 24.1 (GaC). IR (CsBr plates, paraffin, cm^{-1}): 3284 m, 3266 m, 3224 w, 3157 w νNH; 2923 vs, 2853 vs (paraffin); 1592 m δNH; 1462 s, 1376 s (paraffin); 1277 w, 1231 w δCH_3; 1216 w, 1197 vw, 1050 w, 1010 w, 949 w δCH, νCN, ν_sNN, νCC; 815 w ν_{as}NN; 733 w (paraffin); 667 w δC_3C; 551 vw, 464 vw, 390 vw νGaC, νGaN, νGaCl.

3.4. Synthesis of (phenylhydrazine)di(tert-butyl)gallium chloride (**4**)

Di(*tert*-butyl)gallium chloride (0.495 g, 2.26 mmol) dissolved in 50 ml of *n*-hexane was treated with 222 µl (0.244 g, 2.56 mmol) of phenylhydrazine at room temperature. The product precipitated as a colorless, voluminous solid, which was filtered off and recrystallized from toluene (20/8 °C). Yield: 0.664 g (90%). Dec. (argon, sealed capillary): 136 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 6.94 (2H, pseudo-t, *meta*-H of phenyl), 6.76 (1H, pseudo-t, *para*-H of phenyl), 6.15 (2H, pseudo-d, *o*-H of phenyl), 4.6 (3H, very broad, N–H), 1.21 (18 H, s, CMe_3). ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 147.7, 129.7, 122.6 and 114.1 (all phenyl), 30.3 (methyl of *tert*-butyl), 24.4 (GaC). IR (CsBr plates, paraffin, cm^{-1}): 3341 w, 3261 w, 3196 w, 3143 w νNH; 2924 vs, 2852 (paraffin); 1934 vw, 1843 vw, 1775 vw, 1711 vw (phenyl); 1590 m δNH, 1588 m, 1500 m, 1496 m (phenyl); 1463 vs, 1377 s (paraffin); 1311 vw, 1264 m δCH_3; 1208 w, 1177 vw, 1153 w, 1110 vw, 1083 w, 1048 vw, 1022 vw, 1010 w, 939 vw, 889 vw, 844 vw δCH, νCN, νNN, νCC; 813 w ν_{as}NN; 764 m, 723 w, 697 vw, 664 m δC_3C, phenyl; 567 w, 493 w, 463 vw, 385 w νGaC, νGaN, νGaCl.

3.5. Synthesis of bis[di(tert-butyl)gallium(tert-butylhydrazide)] (**5**)

Di(*tert*-butyl)gallium chloride (0.313 g, 1.43 mmol) was dissolved in 10 ml of toluene by slight warming and treated with 160 µl of *tert*-butylhydrazine (0.126 g, 1.43 mmol) at room temperature. After stirring for 1 h at room temperature the solution was cooled (−60 °C) and treated with 0.90 ml of a solution of *tert*-butyllithium in *n*-hexane (1.6 M, 1.43 mmol). After slow warming to room temperature and stirring for 3–4 h LiCl was separated by filtration. The filtrate was concentrated in vacuum and cooled to −15 °C to obtain colorless crystals of the product. Yield: 0.123 g (32%); the crystals do not melt until 220 °C; sublimation without decomposition occurred at 140 °C (10^{-2} Torr). ^{1}H NMR (toluene-D_8, 400 MHz, 300 K): δ = (*trans* isomer) 3.61 (1H, s, br, Ga–N–H), 2.85 (1H, s, br, N(H)–C), 1.31 (18H, s, Ga–CMe_3); (*cis* isomer) 3.31 (1H, s, br, Ga–N–H), 2.99 (1H, s, br, N(H)–C), 1.42 and 1.21 (each 9H, s,

Table 1
Crystal data, data collection parameters and structure refinement for **1** (monoclinic), **1** (triclinic), **2**, **3**, **4**, **5** and **6**[a]

	1 (monoclinic)	**1** (triclinic)	**2**	**3**	**4**	**5**	**6**
Formula	$C_6H_{18}ClGaN_2$	$C_6H_{18}ClGaN_2$	$C_8H_{22}ClGaN_2$	$C_{12}H_{30}ClGaN_2$	$C_{14}H_{26}ClGaN_2$	$C_{24}H_{58}Ga_2N_4$	$C_{28}H_{50}Ga_2N_4$
Temperature (K)	193(2)	193(2)	193(2)	193(2)	193(2)	193(2)	193(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group [21]	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	*Pnma* (no. 62)	$P\bar{1}$ (no. 2)	$C2/m$ (no. 12)	$P2_1/c$ (no. 14)
a (pm)	1102.58(6)	608.95(8)	599.34(6)	1993.1(1)	616.86(8)	1662.4(1)	1850.7(1)
b (pm)	609.91(5)	921.8(1)	1265.1(1)	1356.2(1)	868.0(1)	1127.08(9)	1695.89(7)
c (pm)	1672.9(1)	1105.0(1)	1735.3(2)	635.09(5)	1649.4(2)	885.38(5)	2150.3(1)
α (°)	90	113.93(1)	79.19(1)	90	81.67(2)	90	90
β (°)	101.899(5)	90.32(1)	86.41(1)	90	82.31(2)	115.180(4)	114.600(4)
γ (°)	90	101.11(1)	84.43(1)	90	74.13(1)	90	90
V (10^{-30} m^3)	1100.8(1)	553.9(1)	1285.0(2)	1716.7(2)	836.4(2)	1501.2(2)	6136.4(5)
Z	4	2	4	4	2	2	8
D_{calc} (g cm^{-3})	1.348	1.339	1.300	1.190	1.300	1.199	1.260
μ (mm^{-1})	2.688	2.671	2.311	1.741	1.792	1.811	1.777
Crystal size (mm)	$0.50 \times 0.28 \times 0.14$	$0.20 \times 0.12 \times 0.05$	$0.36 \times 0.30 \times 0.24$	$0.32 \times 0.12 \times 0.05$	$0.45 \times 0.09 \times 0.09$	$0.33 \times 0.21 \times 0.15$	$0.20 \times 0.13 \times 0.14$
Radiation	Mo Kα; graphite-monochromator						
Theta range for data collection (°)	$2.04 \leqslant \theta \leqslant 26.19$	$2.03 \leqslant \theta \leqslant 26.04$	$2.64 \leqslant \theta \leqslant 25.88$	$2.04 \leqslant \theta \leqslant 26.04$	$2.46 \leqslant \theta \leqslant 26.01$	$3.62 \leqslant \theta \leqslant 26.10$	$1.59 \leqslant \theta \leqslant 26.30$
Index ranges	$-13 \leqslant h \leqslant 13$	$-7 \leqslant h \leqslant 6$	$-7 \leqslant h \leqslant 7$	$-24 \leqslant h \leqslant 24$	$-7 \leqslant h \leqslant 7$	$-20 \leqslant h \leqslant 20$	$-22 \leqslant h \leqslant 23$
	$7 \leqslant k \leqslant 7$	$-11 \leqslant k \leqslant 11$	$-15 \leqslant k \leqslant 15$	$-16 \leqslant k \leqslant 16$	$-10 \leqslant k \leqslant 10$	$-13 \leqslant k \leqslant 13$	$-21 \leqslant k \leqslant 21$
	$-20 \leqslant l \leqslant 20$	$-13 \leqslant l \leqslant 13$	$-21 \leqslant l \leqslant 21$	$-7 \leqslant l \leqslant 7$	$-20 \leqslant l \leqslant 20$	$-10 \leqslant l \leqslant 10$	$-26 \leqslant l \leqslant 26$
Reflections observed	1974	1797	2518	1388	2417	1505	7443
Independent reflections	2215 (R_{int} = 0.1013)	2187 (R_{int} = 0.0885)	3438 (R_{int} = 0.0473)	1764 (R_{int} = 0.1050)	3077 (R_{int} = 0.0447)	1559 (R_{int} = 0.0519)	12,390 (R_{int} = 0.0786)
Parameters	108	108	251	153	181	85	822
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ [$I > 2\sigma(I)$]	0.0389	0.0695	0.0314	0.0602	0.0333	0.0310	0.0431
$w_2 = \{\sum w(\|F_o\|^2 - \|F_c\|^2)^2 / \sum \|F_o\|^2\}^{1/2}$ (all data)	0.1117	0.1820	0.0813	0.1750	0.0793	0.0907	0.1144
Max./min. residual electron density (10^{30} e m^{-3})	0.564/−1.046	2.841/−0.704	0.388/−0.447	0.764/−1.056	0. 643/−0.894	0.765/−0.369	0.422/0.555

[a] Programme SHELXL-97 [20]; solutions by direct methods, full matrix refinement with all independent structure factors.

Ga–CMe_3); 0.94 (~18H, s, one resonance for N–CMe_3 of both isomers). ^{1}H NMR (toluene-D_8, 400 MHz, 363 K): δ = 3.45 (2H, s, br, Ga–N–H), 2.91 (2H, s, br, N(H)–C), 1.27 (36 H, s, br, Ga–CMe_3), 0.97 (18H, s, N–CMe_3). ^{1}H NMR (toluene-D_8, 400 MHz, 200 K): δ = (*trans* isomer) 3.69 (1H, s, Ga–N–H), 2.85 (1H, s, N(H)–C), 1.42 (18H, s, Ga–CMe_3), 0.87 (9 H, s, N–CMe_3); (*cis* isomer) 3.37 (1H, s, Ga–N–H), 3.07 (1H, s, N(H)–C), 1.58 and 1.30 (each 9H, s, Ga–CMe_3), 0.89 (9H, s, N–CMe_3); the integration ratio between both isomers (about 1:1.2) is almost independent from temperature. ^{13}C NMR (C_6D_6, 100 MHz): δ = 54.4 and 54.2 (N–C), 33.0 (Me of Ga–CMe_3), 27.3 and 27.1 (Me of N–CMe_3), 26.6 and 25.2 (GaC). IR (CsBr plates, paraffin, cm^{-1}): 3282 vw, 3269 vw, 3228 vw, 3156 vw νNH; 2924 vs, 2853 vs (paraffin); 1592 w δNH; 1460 vs, 1376 s (paraffin); 1269 vw, 1245 w δCH_3; 1229 m, 1207 m, 1172 w, 1048 w, 1008 w, 942 w, 918 vw δCH, νCN, νNN, νCC; 812 s, 767 w ν_{as}NN; 730 m (paraffin); 576 w, 534 w, 472 m, 451 m, 399 w, 357 w νGaC, νGaN. Molar mass (in benzene by cryoscopy): Found 540, calc. 542.18.

3.6. Synthesis of bis[di(tert-butyl)gallium(phenylhydrazide)] (6)

Di(*tert*-butyl)gallium chloride (0.295 g, 1.35 mmol) was dissolved in 50 ml of cyclopentane and treated with 132 μl of phenylhydrazine (0.146 g, 1.35 mmol) at room temperature. The intermediate adduct precipitated spontaneously. The suspension was treated with 0.84 ml of a solution of *tert*-butyllithium in *n*-hexane (1.6 M, 1.35 mmol). After filtration and concentration of the filtrate the product crystallized at −15 °C as colorless platelets. Yield: 0.142 g (36%). M.p. (argon, closed capillary): 154 °C. ^{1}H NMR (toluene-D_8, 400 MHz, 370 K): δ = 7.09 and 7.03 (each 2H, pseudo-t, *meta*-H of phenyl), 6.65 (1H, pseudo-t, *para*-H of phenyl), 6.60 (2H, pseudo-d, *ortho*-H of phenyl), 6.58 (1H, pseudo-t, *para*-H of phenyl), 6.55 (2H, pseudo-d, *ortho*-H of phenyl), 5.28 and 4.17 (each 1H, d, $^3J_{H-H}$ = 4.8 Hz, NH), 4.53 and 4.38 (each 1H, d, $^3J_{H-H}$ = 8.7 Hz, NH of the second hydrazine group), 1.22, 1.13, 1.09, and 0.88 (each 9 H, s, CMe_3). ^{1}H NMR (toluene-D_8, 400 MHz, 280 K): δ = 7.16 and 7.06 (each 2H, pseudo-t, *meta*-H of phenyl), 6.68 (2H, pseudo-t, *para*-H of phenyl), 6.52 (4H, pseudo-d, *ortho*-H of phenyl), 5.24 and 4.17 (each 1H, d, $^3J_{H-H}$ = 5.2 Hz, N–H), 4.39 and 4.28 (each 1H, d, $^3J_{H-H}$ = 9.5 Hz, N–H of the second hydrazine group), 1.29, 1.15, 1.10, and 0.85 (each 9H, s, CMe_3). ^{1}H NMR (toluene-D_8, 400 MHz, 200 K): δ = 7.21 and 6.98 (each 2H, pseudo-t, *meta*-H of phenyl), 6.78 and 6.73 (each 1H, pseudo-t, *para*-H of phenyl), 6.51 and 6.28 (each 2H, pseudo-d, *ortho*-H of phenyl), 5.09 (1H, d, $^3J_{H-H}$ = 6.2 Hz, N–H), 4.21 (3H, broad, superposition of the signals of the remaining N–H protons), 1.46, 1.19, 1.08, and 0.77 (each 9H, s, CMe_3). ^{13}C NMR (toluol-D_8, 100 MHz): δ = 155.9, 149.9, 124.5, 117.4, 112.4, and 111.0 (phenyl), 32.9, 31.9, 31.8, and 31.4 (CMe_3), 26.3, 24.2, 23.8, and 22.8 (Ga–C). IR (CsBr plates, paraffin, cm^{-1}): 3388 w, 3222 vw, 3183 vw νNH; 2923 vs, 2853 vs (paraffin); 1599 s δNH; 1577 m, 1568 m, 1492 m (phenyl); 1464 vs, 1377 m (paraffin); 1364 m, 1338 vw, 1305 m, 1270 s, 1245 m δCH_3; 1211 w, 1175 w, 1155 w, 1083 vw, 999 w, 984 m, 936 w, 898 w, 862 w, 848 m, 813 m δCH, νCN, νNN, νCC, δCC; 749 m (paraffin); 692 m, 671 m, 631 w δCC; 529 w, 497 m, 465 w, 399 w νGaC, νGaN.

3.7. Crystal structure determinations of compounds (1–6)

Single crystals of compounds **1**–**6** were obtained on cooling of saturated solutions (**1**-monoclinic: *n*-pentane/−15 °C, **1**-triclinic: cyclopentane/−15 °C, **2**: cyclopentane/−30 °C, **3**, **4** and **6**: cyclopentane/−15 °C, **5**: toluene/−45 °C). The crystallographic data were collected with a STOE IPDS diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 [20] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters and structure refinement details are given in Table 1. Compound **1** crystallizes in two different space groups (monoclinic and triclinic), the results of both structure determinations are included in Table 1. **2** has two independent molecules in the asymmetric unit. The molecules of **3** are disordered over a crystallographic mirror plane. The gallium atom is located on the mirror plane, all remaining atoms are disordered and were refined with occupation factors of 0.5. The molecules of **5** reside on special positions and possess 2/*m* symmetry. Compound **6** crystallizes with two independent molecules in the asymmetric unit. The *tert*-butyl groups of Ct4 and Ct6, Ct7, Ct8 (of the second molecule not drawn in Fig. 7) are disordered over two or three (Ct8) positions; the atoms of the methyl groups were refined with restrictions of bond lengths and bond angles and with site occupation factors of (0.53/0.47), (0.63/0.37), (0.49/0.51), and (0.40/0.30/0.30), respectively.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 235693–235698 for compounds **1**–**6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

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