Hydrazino Derivatives of Gallanes and Indanes − Synthesis and Structures

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Dedicated to Prof. Dr. Marianne Baudler on the occasion of her 80th birthday

Keywords: Gallium / Indium / Cage compounds / Cleavage reactions / Hydrolysis

The reaction of Me_2GaCl with tBuHN–NH_2 proceeds with ligand exchange at the gallium atom leading to $MeCl_2Ga{\cdot}H_2N$–NHtBu (**1**). On the other hand, only one methyl group of the trimethylgallium molecule reacts in refluxing toluene with anhydrous hydrazine in a 4:3 ratio to produce the bicyclic dimethylgallium hydrazide **3**. *N*-Lithio-*N*-trimethylsilyl-*N′*-2-naphthylhydrazine reacts with dimethylgallium chloride, not only by introducing a gallium atom into the hydrazine unit, but also by inducing CH activation at the 1-position of the naphthyl group with methane evolution. The main product isolated is the 2,3-dihydro-1*H*-naphtho[1,2-*d*][1,2,3]diazagallol **4** which proved to be dimeric. A 1:1 $GaMe_3$ adduct of $Li(Me_3Si)N$–NHtBu (**5**) is the unexpected compound in the reaction of Me_2GaCl with $Li(Me_3Si)N$–NHtBu. The expected substitution product $Me_2Ga(Me_3Si)N$–NHtBu is not formed. Compound **5** is a dimer in the solid state. The products obtained from reactions of $Li(Me_3Si)N$–NHtBu with Me_2InCl depend on the solvent. With hexane as a solvent the dimeric trimethylindium adduct of $Li(Me_3Si)N$–NHtBu (**7**), is produced as the main species. In diethyl ether the cage compound **8** is isolated which can be regarded as an $(Me_3SiN{=}InMe)_2$ adduct with $[Li(Me_3Si)N$–NHtBu$]_2$. Moreover, the reaction of Me_2InCl in diethyl ether with the bulky lithium hydrazide $Li[Me_3SiN$–$N(SiMe_3)_2]$ leads not to the substitution product, but to the dimeric adduct **9** of a diindoxane, Me_2In–O–$InMe_2$ with $Li(Me_3Si)N$–$N(SiMe_3)_2$. The formation of this product indicates that ether cleavage or hydrolysis (during crystallization) has occurred.

Introduction

Metal amides have not only become important reagents in synthesis,[1−3] but have also attracted interest due to unique structural patterns.[4−6] More recently, alkali metal hydrazides have been used in the synthesis of new nonmetal hydrazides[7−13] and metal hydrazides.[14−16] Amongst the latter, those of group 13 are considered as being good single-source precursors in MOCVD processes (Metal Organic Chemical Vapor Deposition) for the preparation of AlN, GaN, and InN thin films, which are useful for the production of optoelectronic devices, particularly for light-emitting diodes.[17−23] In comparison to alkali metal organylamides, the molecular structure of the alkali metal hydrazides show additional features, particularly the *side-on* coordination of Li centers to the N−N bond.[13,24−26] The best studied class of group 13 hydrazides are the hydrazinoboranes that feature non-cyclic, cyclic, and cage arrangements as the molecular units.[27−30] Aluminum hydrazides have been reported only recently.[14,24,31−36] Information on hydrazides of gallium and indium is, so far, comparatively scanty.[37−40]

Results

Gallium Hydrazides

Synthesis

Several routes to metallated hydrazines are known, and in this study only two have been employed, the reaction of dimethylgallium and dimethylindium chloride with monolithium hydrazides, and the reaction of trimethylgallium with anhydrous hydrazine.

It was expected that the reaction of dimethylgallium chloride with *tert*-butylhydrazine would first produce a 1:1 addition product followed by methane elimination either to give MeClGa−NH−NHtBu or (ClGa−NH−NtBu$)_n$. However, in toluene solution no gas evolution was observed at ambient temperature. However, this gas evolution set in at 70 °C, and became rapid on heating the solution to reflux. Under these conditions a sparingly soluble product was formed, which showed two signals in the ^1H NMR spectrum in a 1:3 ratio, suggesting the formation of oligomeric (MeGa−NH−NtBu$)_n$ (**2**). From the solution the adduct $MeCl_2Ga{\cdot}H_2N$−NHtBu (**1**) was isolated. This result suggests that under the conditions of the experiment Me_2GaCl is subject to substituent exchange as shown in Equation (1). The Lewis acid $MeGaCl_2$ so formed added to the hydrazine [Equation (2)] while $GaMe_3$ reacted with the hy-

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drazine $H_2N{-}NH\textit{t}Bu$ to produce methane and **2** [Equation (3)].

$$2\,Me_2GaCl \rightarrow Me_3Ga + MeGaCl_2 \qquad (1)$$

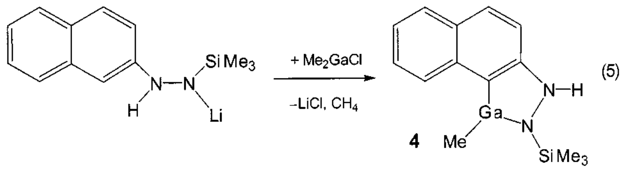
$$MeGaCl_2 + H_2N{-}NH\textit{t}Bu \rightarrow \underset{\mathbf{1}}{MeCl_2Ga{-}NH_2{-}NH\textit{t}Bu} \qquad (2)$$

$$Me_3Ga + H_2N{-}NH\textit{t}Bu \rightarrow \underset{\mathbf{2}}{{}^1/_n\,[MeGa{-}NH{-}N\textit{t}Bu\,]_n} + 2\,CH_4 \qquad (3)$$

$$4\,GaMe_3 + 3\,H_2N{-}NH_2 \xrightarrow{\Delta} \underset{\mathbf{3}}{(Me_2Ga)_4(N_2H_2)(NH{-}NH_2)_2} + 4\,MeH \qquad (4)$$

This result demonstrates the high reactivity of $GaMe_3$. Therefore, hydrazine was allowed to react with $GaMe_3$. In refluxing toluene, practically only compound **3** was formed, containing Me_2Ga and hydrazino units in a ratio of 4:3, irrespective of the molar ratio employed. In **3** there are two different hydrazino groups, one that is doubly metallated, and two hydrazino groups that are singly metallated [see Equation (4)].

Although one might expect that the reaction of Me_2GaCl with a lithiated disubstituted hydrazine would proceed in a more straightforward manner, a surprising reaction occurred between Me_2GaCl and *N*-lithio-*N′*-(2-naphthyl)-*N*-(trimethylsilyl)hydrazine in refluxing toluene, as depicted in Equation (5). The product was the 2,3-dihydro-1*H*-naphtho[1,2-*d*][1,2,3]diazagallol **4**.



In the solid state **4** is present as a dimer (vide infra). Obviously, the hydrogen atom in position 1 of the 2-naphthyl group is more reactive than the hydrogen atom of the NH group of the hydrazide. Taking these results into account it was expected that a more bulky lithium hydrazide such as $Li(Me_3Si)N{-}NH\textit{t}Bu$ might react with Me_2GaCl by simple substitution as shown in Equation (6).

$$Me_2GaCl + LiNSiMe_3{-}NH\textit{t}Bu \rightarrow Me_2Ga{-}N(SiMe_3){-}NH\textit{t}Bu + LiCl \qquad (6)$$

$$2\,Me_2GaCl + 2\,LiN(SiMe_3){-}NH\textit{t}Bu \rightarrow$$
$$\underset{\mathbf{5}}{LiN(SiMe_3){-}NH\textit{t}Bu{\cdot}GaMe_3} + \underset{\mathbf{6}}{MeClGa{-}N(SiMe_3){-}NH\textit{t}Bu} + LiCl \qquad (7)$$

However, only a small amount of LiCl precipitated, and the product obtained was **5**. Obviously, Me_2GaCl again suffers substituent exchange as described by Equation (1), and $GaMe_3$ adds to the lithium hydrazide to form **5**. The second product of the reaction was expected to be $MeClGa{-}N(SiMe_3){-}NH\textit{t}Bu$ (**6**), but this compound could not be isolated.

In summary, none of the reactions described above led to the anticipated product.

X-ray Structure Determinations

Compounds **1** and **3−5** were obtained as single crystals. This allowed the determination of their molecular structures in the solid state, and this knowledge was helpful for the assignment of signals obtained by NMR experiments.

The $MeGaCl_2$ adduct **1** crystallized in the tetragonal system, space group $I4_1/a$ with $Z = 16$. Figure 1 depicts the molecular structure of **1** ascertaining that the compound is the $MeGaCl_2$ adduct of the hydrazine $H_2N{-}NH\textit{t}Bu$. Its Ga−N distance [2.023(7) Å] correlates well with those found for $Cl_3Ga{-}NMe_2SiMe_2NMe_2$ [2.002(9) Å][41]or the dimeric gallium amides $[Me_2Ga{-}N(Ph)SiMe_3]_2$,[42] $[Me(Cl)Ga{-}NHSiMe_3]_2$,[43] and $(\textit{i}Pr_2Ga{-}NHNMe_2)_2$[44] [2.071(2), 2.012(8), and 2.031(2) Å, respectively]. The Ga−C bond in **1** [1.933(7) Å] lies in the range found for several amino(methyl)gallanes having tetracoordinated Ga atoms[33,42,43]. Both N atoms are in a non-planar situation, the coordination site at N1 corresponds with a distorted tetrahedral array (bond angles ranging from 104.3 to 113.8°) and a sum of bond angles of 656.6°, while that of the tricoordinated atom N2 is 320.1° slightly smaller than calculated for a pseudo-tetrahedral array (328.5°). Taking this into account, the N−N bond length of 1.446(9) Å in **1** corresponds with the N−N bond length of hydrazine (1.47 Å)[44] and of the methylhydrazinium cations $MeNH_2NH_2^+$ [1.445(1) Å][45] and $Me_3N{-}NH_2^+$ [1.457(1) Å].[46] The two amino groups are present in a staggered conformation. A *trans* conformation results for the Ga−N−N−C unit (τ = 175.5°).

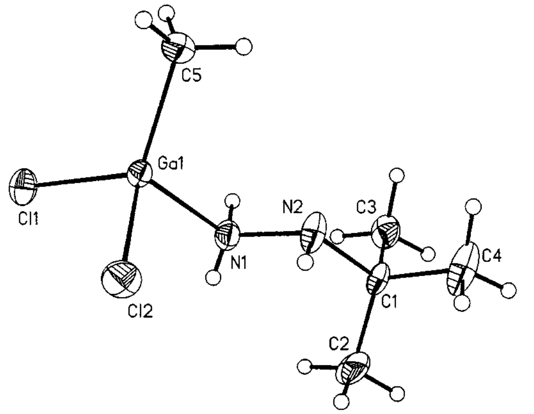


Figure 1. ORTEP representation of **1**; selected bond lengths [Å] and bond angles [°], esd values in parentheses: Ga1−N1 2.023(7), N1−N2 1.446(9), Ga1−C5 1.933(7), Ga1−Cl1 2.202(2), Ga1−Cl2 2.175(2), N1−H1A 0.72, N1−H1B 0.97; N1−Ga1−Cl2 100.8(2), N1−Ga1−C5 112.0(4), Cl1−Ga1−Cl2 105.62(8), Cl1−Ga1−C5 116.4(3), Cl2−Ga1−C5 118.9(3), Ga1−N1−N2 108.3(5), N1−N2−C1 115.4(6), N1−N2−H2 115.4, Cl1···H−N 2.5475(1), Cl2···H−N 2.88(1); angles at hydrogen bonds: N1−H1−Cl2A 160.7, N1−H1B−Cl1B 167.4; Cl···Cl contact: Cl1···Cl1B 3.556

The two Ga−Cl bond lengths differ significantly with Δ = 0.027 Å, and on first sight there is no reason why this should be so. One might suspect that the different Ga−Cl bond lengths arise from different N−H···Cl hydrogen bonding. Hydrogen bonds indeed connect the molecules of **1** in the solid state, and only the H atoms of the NH_2 groups, which have ammonium-type character, are involved in hydrogen bonding, in contrast to the NH group. Bond angles at the H atoms of the bridging N−H···Cl units span a range from 160.7 to 167.4° with H···Cl distances between 2.547 to 2.878 Å. Tetrameric units result by these hydrogen bonds. Figure 2 depicts the association of four molecules of **1** in the crystal.

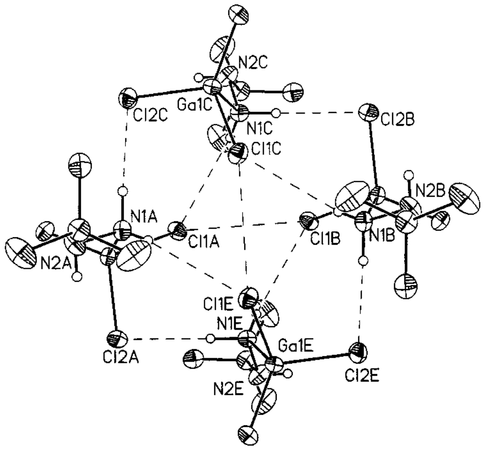


Figure 2. Tetrameric association of **1** formed by hydrogen bonds

The molecular structure of compound **3** is represented in Figure 3, showing a bicyclo[3.3.0]octane skeleton. Compound **3** crystallizes in the triclinic system in space group $P\bar{1}$.[47]The unit cell contains two independent molecules each having a crystallographically imposed center of symmetry lying at the midpoint of the central N−N vector, but these two N atoms are site-disordered with an SOF of 0.5. Therefore, the bicyclic system shows two conformations. In addition, there is a disordered toluene molecule in the unit cell with a center of inversion in the midpoint of the benzene unit. A consequence of this disorder is that the standard deviations particularly for the central N−N bond is fairly large, and this is also true for the *R* indices.

The structure of compound **3** can be considered to be composed of one dimetallated hydrazine unit, $Me_2Ga-NH-NH-GaMe_2$, and two $Me_2Ga-NH-NH_2$ units, which allows all Ga atoms to become tetracoordinated by two Me groups and two N atoms. Because the Ga atoms are part of a five-membered heterocycle the N−Ga−N angles are only 92.8(3) and 92.9(4)° while the C−Ga−C bond angles are 124.1(4)° at Ga1 and 123.8(4)° at Ga2. The Ga1−N2−Ga2 bond angle [107.7(3)°] is closer to the tetrahedral angle than the Ga1−N1−N1A and N1−N1A−Ga2 bond angles [111.7(11) and 111.5(11)°]. The two N−N bond lengths in the molecules with atoms Ga1 and Ga2 are 1.38(2) Å (N−N bridge of the bicycle) and 1.48(8) Å (for the exocyclic N−N bonds). However, these bonds are significantly different in the second independent molecule with 1.51(8) and 1.48(8) Å.

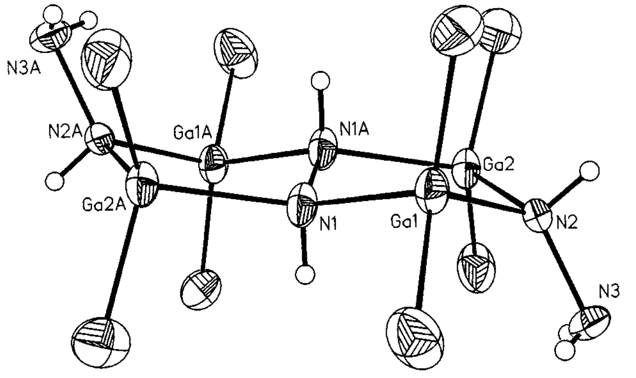


Figure 3. Molecular structure of one of the two independent molecules of **3** in ORTEP representation; *C*-bonded hydrogen atoms omitted; selected bond lengths [Å] and bond angles [°], esd values in parentheses: Ga1−C1 1.947(8), Ga1−C2 1.9478(8), Ga1−C2 1.947(7), Ga2−C3, 1.959(7), Ga1−C4 1.943(8), Ga1−N1 2.03(1), Ga1−N2 1.985(5), Ga2−N1A 2.05(1), Ga2−N2 2.000(5), N1−N1A 1.49(1), N2−N3 1.487(7); C1−Ga1−C2 124.1(4), C3−Ga2−C4 123.8(4), N1−Ga1−N2 92.9(4), N1A−Ga2−N2 96.4(4), Ga1−N2−Ga2 107.7(3), Ga1−N1−N1A 1112(1), Ga2−N1A−N1 112(1), H−N1−N2 104(2), H−N2−N3 106(2); sum of bond angles at N1 655.7, at N2 657.1, at N1A 655.1

While atoms Ga1, N2, Ga2, Ga1A, N2A, Ga2A lie almost in a plane, atom N1 is 0.65 Å apart from the Ga1−N2−Ga2−N1A plane (τ = 8.5°), e.g. the five-membered rings have an envelope conformation. Figure 4 shows the two conformations that result from the site disorder of the central N−N unit. These conformations result in an "up-and-down" arrangement for the central N−N groups.

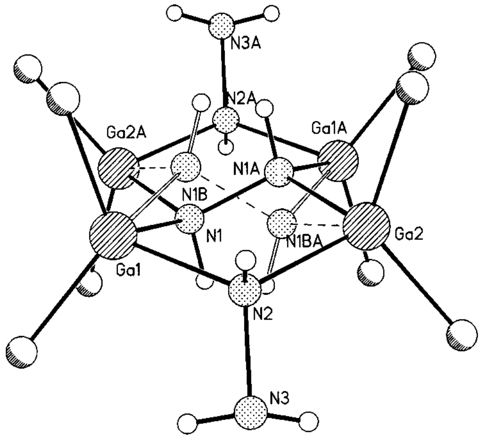


Figure 4. Representation of the disorder of the molecule **3**; methyl hydrogen atoms are removed for clarity

All N atoms in **3** are in a non-planar environment. They can be considered to be sp^3-hybridized. In the solid state, the molecules of **3** are interconnected by NH···N hydrogen bonding. These bridges are formed with the H atoms of the central N_2H_2 units, which bridge to NH_2 groups. This results in chains of interconnected molecules of **3** that extend parallel to the *c* axis of the crystal (Figure 5).

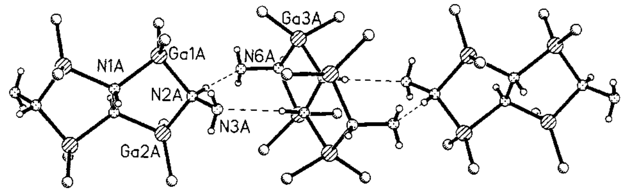


Figure 5. Association of the molecules of **3** in the solid; the chains extend parallel to the *z* axis; note that only N−H···NH_2 bridges are formed; the H atoms of the NH_2 groups are not involved in hydrogen bonds

As indicated, the N−N bond and the corresponding bond angles of **3** could be determined only with large standard deviation and are, therefore, not very accurate due to the indicated disorder.[47] For this reason geometrical data for the molecule were calculated on the B3LYP/6-31* level.[48] The data for the geometry-optimized molecular structure of **3** and frequency analysis are compiled in Table 1 together with the data found in the X-ray structure determination. The calculated data correspond to the energy minimum.

Table 1 shows that the Ga−C distances comply well with the calculated bond lengths, while the calculated Ga−N bond lengths are shorter than the experimental values. More importantly, the calculated central N−N bond length is noticeably longer than the exocyclic N−N bonds. The average experimental value corresponds with the calculated bond length. On the other hand, the experimental bond angles differ by −2.5 to 3.4° from those calculated.

Data for the population analysis and the Wiberg bond orders are summarized in Table 2. These show that the N−N bonds are single bonds. A *trans* conformation for the central N−N unit also results for the calculated structure. In contrast to the experimental structure with its eclipsed conformation for the exocyclic hydrazino moiety (torsion angle Ga−N−N−H 3.9°), a *gauche* conformation results from the calculation as is well known for hydrazine itself[44] (torsion angle 34.7°). This discrepancy, however, can be easily resolved by considering the N−H···N hydrogen bonds that are present in the solid sate.

Table 2. Population analysis and Wiberg bond orders

	Charges	Wiberg bond order	
Ga1	+0.66	N1−N1A	0.99
Ga2	+0.68	N2−N3	1.01
N1	−0.68	Ga1−N1	0.35
N2	−0.72	Ga1−N2	0.36
N3	−0.58	Ga2−N1A	0.35
C1−C4	−0.69	Ga−C	0.69

Yellow crystals of **4** are monoclinic, space group $P2_1/c$ with $Z = 4$ monomeric units; actually, $Z = 2$ because two molecules form a dimer via Ga−N coordinative bonds. The center of the Ga−Ga vector of the four-membered Ga_2N_2 ring coincides with a crystallographic inversion center. The molecular structure of $(\mathbf{4})_2$ is depicted in Figure 6.

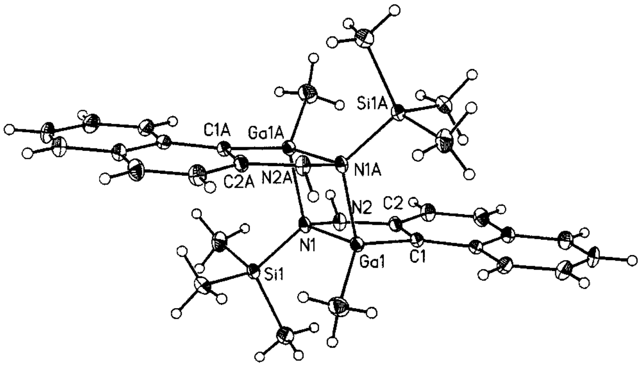


Figure 6. Moleçular structure of dimeric **4** in the crystal; selected bond lengths [Å] and bond angles [°], esd values in parentheses: Ga1−C1 1.947(3), Ga1−C14 1.949(3), Ga1−N1 2.051(2), Ga1−N1A 2.031(2), N1−Si1 1.780(2), N1−N2 1.482(3), N2−C2 1.414(3), C1−C2 1.333(4), C1−C10 1.430(4), C2−C3 1.420(4), C3−C4 1.365(4), C4−C5 1.414(4), C5−C10 1.423(4); C1−Ga1−N1 110.98(9), C1−Ga1−C14 129.2(1), C1−Ga1−N1A 89.25(8), N2−N1−Si1 103.8(2), N2−N1−Ga1 112.5(2), Si1−N1−Ga1 123.5(1); interplanar angles: Ga1,N1,Ga1a,N1a/N1,N2,C1,C2,Ga1 110.1, N1,N2,C1,C2,Ga1/C1−C5,C10 6.5

Table 1. Experimental and calculated structural data for compound **3**

	Exp. values			Calcd. values	
Ga1−C	1.947(8) C1	Ga3−C	1.95(1) C5	C1	1.997
	1.947(7) C2		1.960(1) C6	C2	1.997
Ga2−C	1.959(7) C3	Ga4−C	1.95(1) C7	C3	1.995
	1.943(8) C4		1.95(1) C8	C4	1.995
Ga1−N	2.03(1) N1	Ga3−N	1.96(1) N4A	N1	1.985
	1.985(5) N2		1.997(8) N5	N2	1.972
Ga2−N	2.05(1) N1A	Ga4−N	2.08(1) N4	N1A	1.996
	2.000(5) N2		1.992(7) N5	N2	1.984
N−N	1.49(1) N1	N−N	1.51(3) N4	N1	1.522
	1.481(7) N2		1.476(9)	N2	1.489
N1−Ga1−N2	92.8(3)	N5−Ga3−N4a	96.2(4)		95.3
Ga1−N2−Ga2	107.7(2)	Ga3−N5−Ga4	107.4((3)		108.3
N1−N1A−Ga2	107.3(9)	N4A−N4−Ga4	102(1)		110.7
N1A−N1−Ga1	109.7(9)				107.5

The two Ga−N bond lengths are significantly different, the shorter bond, Ga1−N1 [2.031(2) Å], is found in the five-membered ring, the longer one, Ga1−N1A [2.051(2) Å], in the four-membered ring. Inspection of the Ga−C bond lengths reveals an interesting and somewhat unusual feature, both are of equal lengths [Ga1−C1 1.949(3), Ga1−C14 1.947(3) Å] although C1 is of sp^2-type hybridization, and this should result in a shorter Ga−C distance as compared to the Ga1−C14 bond with an sp^3-C atom. Due to the situation that the Ga atom is both part of a four- and a five-membered ring system, the tetracoordinated Ga atom shows strong deviations from the tetrahedral bond angle. Even the C1−Ga1−N1 bond angle of the five-membered ring is only 87.4°, a consequence of the longer Ga1−C1 and Ga1−N1 bonds.

The molecular structure of **4** was of importance to unequivocally demonstrate that the Ga metallation of the naphthyl group occurred at the 1-position. An almost planar Ga−N−N−C−C five-membered ring is present with atoms N2 and C2 being 0.064 and −0.082 Å away from the best plane. The ring is almost coplanar with the naphthalene moiety, the angle between the two planes being only 7.2°. The Ga_2N_2 four-membered ring forms an angle of 113.6° with the five-membered GaN_2C_2 ring. Because both N atoms of the hydrazine moiety in compound **5** are sp^3-hybridized (sum of bond angles at N2 338.4°), a comparatively long N−N bond can be expected. The distance [1.482(3) Å], however, is typical for a simple hydrazine unit.

The needles of **5** proved to be monoclinic, space group $P2_1/n$ with $Z = 2$. Figure 7 shows that the molecule is dimeric. There is a crystallographic inversion center situated in the center of the six-membered Li_2N_4 ring. The $GaMe_3$ units are attached at the deprotonated side of the hydrazide units. Moreover, it can be noted that the hydrazine *t*BuNH−NHSiMe$_3$ is metallated at the silyl-group-carrying nitrogen atom. Both Li atoms of the Li_2N_4 ring are coordinated to two nitrogen atoms and, in addition, each one shows Li···H−C contacts with CH hydrogen atoms of the $GaMe_3$ units that add to the steric shielding of the Li centers [Li−H 2.20(1), 2.21(1) Å]. The Li−N bond lengths are found in the expected ranges,[49] actually both can be considered to be of equal length. Moreover, it should be noted that the Ga−N bond length is shorter than the Li−N distances.

It can be seen from Figure 7 that the Me groups are arranged in such a manner that a staggered orientation results, minimizing intramolecular repulsion of the methyl groups. Although the ring adopts no true chair conformation, the ring is, nevertheless, not planar. Bond angles for the ring atoms are: Li1−N2−N1 98.1(2), N1−N2−Li1A 108.6(2), and N2−Li1−N1A 124.8(2)°. The bond angles N2−N1−Si1 and N2−N1−Ga1 [119.5(1)° and 116.6(1)°, respectively] are wider than expected for a tetrahedral moiety at nitrogen atoms N1 and N2, and the angle Ga1−N1−Li1A is sharp with 80.5(1)°.

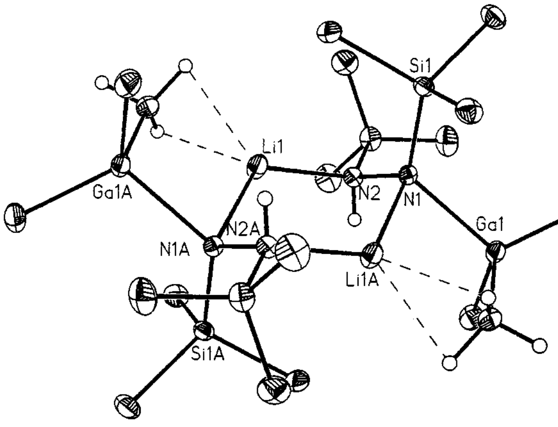


Figure 7. Molecular structure of **5** in the crystal; CH hydrogen atoms are omitted; selected atom distances [Å] and bond angles [°], esd values in parentheses: Ga1−N1 2.053(2), Ga1−C8 1.998(3), Ga1−C9 2.084(3), Ga1−C10 1.985(3), Li1−N1 2.093(4), Li1−N2 2.010(4), Li1···C9 2.234(4), N1−N2 1.496(2), N2−C4 1.514(3), N1−Si1 1.743(2), Li1···H9A 2.20(1); Li1···H9B 2.21(1); N1−Ga1−C8 108.7(1), N1−Ga1−C9 102.83(9), N1−Ga1−C10 113.0(1), N1A−Li1−C9 95.5(2), N2−Li1−N1A 124.8(2), N2−N1−Ga1 116.6(1), N2−N1−Si1 119.5(1), N2−N1−Li1A 108.6(2), N1−N2−Li1 98.1(2), Ga1−N1−Li1A 80.5(19); torsion angles: Li1A−N1−Ga1−C9 16.0, Li1−N2−N1−Li1A 49.0; sum of bond angles at N1 331.8, at N2 324.9

Two of the Ga−C bond lengths are almost of equal lengths considering the 3σ criterion. However, the Ga1−C9 distance is noticeably elongated; it is this atom of the CH_3 group that is involved in Li···H−C interactions. Consequently, the Li−C distance is short, 2.234(4) Å, a distance that is typical for organolithium compounds.[49,50] The N−N bond in **5** is fairly long, 1.496(2) Å. All N atoms are tetracoordinated.

NMR Spectra

As expected, the ^{1}H and ^{13}C NMR spectra of the adduct **1** is simple. There are three signals of each kind. Those of the ^{1}H resonances are observed at δ = 0.33 (GaMe), 0.65 (CMe), and 4.15 (broad, NH) in a 1:3:1 ratio, while the ^{13}C signals are located at δ = −3.1 (GaMe), 25.6 (C*Me*), and 55.3 (*C*Me$_3$). It is well known that the shielding of the Ga*Me* group resonances depends on the nature of the substituents, the more electronegative the substituents the stronger the deshielding. For example, while the ^{1}H signal of $(Me_2GaCl)_2$ is found at δ = 0.12, it is observed for $(Me_2Ga{-}NMe_2)_2$ at δ = −0.4. The NH resonance signal is broad and not resolved, indicating rapid exchange of these protons.

In contrast, the signal for the *N*-bonded hydrogen atoms in the bicyclic compound **3** are well resolved. There are three signals at δ = 2.24, 2.35, and 2.72 in the correct intensity ratio. On the other hand, seven signals were observed in the region from δ = −0.4 to −0.1 for the Me groups attached to the Ga atoms. Complementary results were obtained in the ^{13}C NMR spectrum, which reveals 7 signals in the range δ = −11.2 to −7.1. The double envelope conformation of compound **3** should lead to four pairs of chemically equivalent methyl groups. In case of inversion at the N atoms two sets of four signals may results. That inversion takes place is ascertained by coalescence of the ^{13}C resonances at 80 °C. Using the Eyring equation[51] the calculated activation energy is $\Delta G^* = 72.3$ kJ/mol. This corresponds with the activation energy of 73.9 kJ/mol[52] found for the six-membered hydrazinoalane $[Me_2Al-NSiMe_3-NCMe_3]_2$.[16]

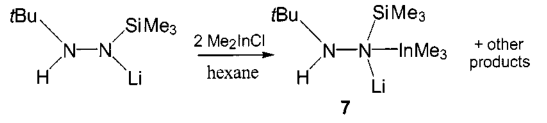
Knowing the structure of compound **4**, only a single ^{29}Si resonance was expected and found at $\delta = -0.17$, apart from the ^1H and ^{13}C resonances of the $SiMe_3$ group. On the other hand, six ^1H signals for the naphthyl group were found, and this corresponds with a metallation of the naphthyl group at the 1-position, excluding the possibility of metallation at the 3-position. For this latter case, only three signals should be observable.

The ^1H and ^{13}C NMR spectra of compound **5** are in agreement with the X-ray structure. The GaMe protons are fairly well shielded with $\delta^1H = -0.08$. With $\delta = 7.00$ the ^{29}Si nucleus is better shielded compared with $\delta^{29}Si = 13.6$ for compound **4**, and this is most likely due to the negative charge at the Si bearing nitrogen atom of compound **5**.

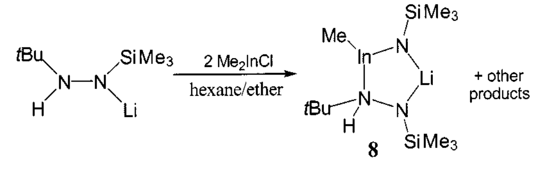
Indium Hydrazides

Synthesis

In order to test whether Me_2InCl is also liable to substituent exchange on reactions with lithium hydrazides this indium chloride was allowed to react with $Li(Me_3Si)N-NH\mathit{t}Bu$ in a 1:1 molar ratio in hexane. The indium homologue **7** of the gallium complex **5** was indeed formed as indicated in Equation (8).



(8)



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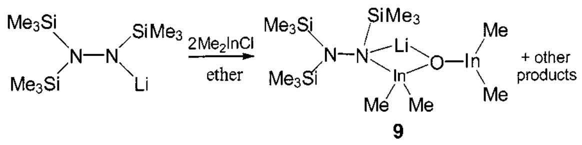


(10)

However, when the same reaction was performed in an ether/hexane mixture the reaction took a different course, as depicted in Equation (9). Only compound **8** and no byproducts could be isolated and characterized. This would have been important to obtain an idea on the course of the redox reaction involved in the formation of compound **8**, which can be considered to be composed of the iminoindane $MeIn{=}NSiMe_3$ added to the lithium hydrazide used as a starting material. Assuming that the first step in the reaction is the expected substitution to give $Me_2In-N(SiMe_3)-NH\mathit{t}Bu$, a methyl transfer to produce the amine $NHMe(\mathit{t}Bu)$ may formally lead to the iminoindane. A similar reaction has not been observed in our experiments with gallium.

One might expect that by employing a sterically better shielded lithium hydrazide than $Li(Me_3Si)N-NH\mathit{t}Bu$ could lead to anticipated products. For this reason Me_2InCl was treated with $Li(Me_3Si)N-N(SiMe_3)_2$. In nonpolar solvents such as hexane or toluene, the NMR spectra pointed to a very complex reaction, e.g. fifteen ^{29}Si NMR signals were detected in the range $\delta = 5.0-19.5$. However, when ether was employed as a solvent the situation changed drastically because compound **9** was formed as the main product. This compound was isolated and fully characterized. Nevertheless, it is once again an unexpected product, as shown in Equation (10). Compound **9** can be regarded as the adduct of a bis(dimethylindium) oxide (diindoxane) with lithium tris(trimethylsilyl)hydrazide. The X-ray structure determination shows that **9** is actually a dimer in the solid state.

Structures

Compound **7** crystallizes, like the trimethylgallane adduct **5**, in the monoclinic system, space group $P2_1/n$ (no figure is given because the structure of **7** is very similar to the structure of **5**). The molecular parameters for both compounds are listed in Table 3. The unit cells differ particularly with respect to the angle β. As far as the molecular parameters are concerned, there are no great differences except, of course, for the In−N and In−C bond lengths. The molecular symmetry is C_i. The equatorial positions of the chair-type six-membered ring are occupied by the *tert*-butyl and Me_3In groups while the Me_3Si groups are in axial positions. Li··H contacts complete the coordination sphere of the Li atom by two H atoms. The Li···C contact of Li1 to C10A [2.278(8) Å] is 0.04 Å longer than in compound **5**. This difference is probably due to the fact that there is only one Li···H contact while there are two Li···H contacts in compound **5**. The bond angles N2−N1−Si1 (120.4°) and N2−N1−In1 (116.0°) are quite open. This indicates that the Li−N bonds are highly polar.

Compound **8** is present as a dimer in the monoclinic crystal, space group $C2/m$. The molecular symmetry is, crystallographically imposed, C_2. Figure 8 shows the molecular structure with its cage-like arrangement of the core atoms. While we have previously discussed the compound as a formal adduct of an iminoindane with a lithium hydrazide, we now see that it is an adduct of a dimeric, tub-shaped six-membered lithium hydrazide with a four-membered 1,3,2,4-diazadiindetidine. The NH hydrogen atoms are present in axial positions, while the Me_3Si and MeIn groups are in equatorial positions. The four-membered In_2N_2 ring is only slightly bent (folding angle 13°) with endocyclic angles close to 90°. Due to the different atomic radii, one observes trapezoidal InN_2Li fragments. All indium atoms are tetracoordinated while the Li atoms are tricoordinated. The N atoms reside in a distorted tetrahedral environment.

The most interesting structural features are the In−N distances. These are short for the four-membered In_2N_2 ring [2.145, 2.178(4) Å], while those to the lithium hydrazide units are 2.223(3) Å. This latter bond length compares well with those found for $(Me_2N-InMe_2)_2$ (2.255 Å),[53]

Table 3. Structural parameters of the Me_3E adducts of $Li(Me_3Si)N-NH\textit{t}Bu$ (E = Ga, In); atom distances in Å, bond angles in °; standard deviations in parentheses

	E = Ga (**5**)	E = In (**7**)		E = Ga (**5**)	E = In (**7**)
E−N	2.053(2)	2.281(3)	N1−E−C10	102.83(9)	97.3(1)
E−C	1.998(3) C8	2.189(4) C8	N1−E−C8	113.0(1)	105.4(2)
	1.985(3) C10	2.242(3) C10	N1−E−C9	108.7(1)	112.9(1)
	2.048(3) C9	2.169(4) C9	N2−N1−E	116.6(1)	116.0(2)
N−N	1.492(2)	1.495(4)	N1−N2−Si	119.5(1)	120.4(2)
N−C	1.514(2)	1.503(5)	N2−Li1−Li1A	108.6(2)	109.9(3)
N−Li	2.093(4) N1	2.087(7)	N1−N2−Li1	98.1(2)	94.2(3)
	2.010(4) N2	2.008(6)	N1−Li1A−C10	95.5(3)	102.0(3)
N−Si	1.743(2)	1.744(3)			

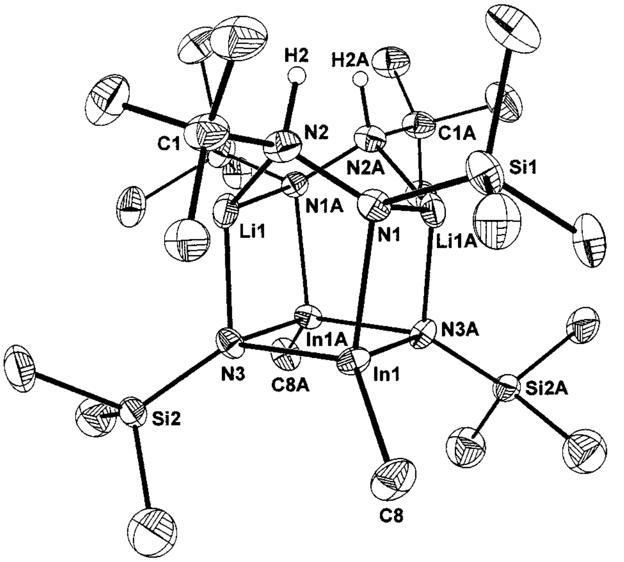


Figure 8. Molecular structure of **8**; hydrogen atoms are removed for clarity; selected atom distances [Å] and bond angles [°], esd values in parentheses: In1−N1 2.323(3), In1−N3 2.145(4), In1−N3A 2.178(3), Li1−N1A 2.165(8), Li1−N2 1.983(9), N1−N2 1.472(5), In1−C8 2.157(4), N1−Si1 1.752(7), N3−Si3 1.733(5); N3−In1−N3A 88.1(1), N3−In1−N1 99.8(1), In1−N1−Li1A 79.3(2), In1−N1−N2 1135.5(2), N2−N1−Li1A 107.3(3), N2−Li1−N3 114.1(4), N2−Li1−N1A 112.9(4), N3−Li1−N1A 101.9(3), N1−N2−Li1 103.0(3), Li1−N2−In1A 84.9(2), In1−N3−In1A 91.9(1), Li1−N3−In1 95.1(3); sum of bond angle at Li1 328.9, at N2 333.2

$(\textit{i}Pr_2In-NH\textit{t}Bu)_2$ (2.231 Å),[54] and various other aryl or Me_3Si substituted dimeric aminoindanes (up to 2.305 Å).[55,56] Shorter In−N bonds are observed for $[Me_2In-N=CMe_3]_2$ (2.195 Å)[57] or $[Cl_2In-N=CPh_2]_2$ (2.112 Å).[58] These latter distances fall into the range for the In_2N_2 unit of **8**.

The monoclinic compound **9**, which crystallizes in space group $P2_1/c$, displays a spirocyclic system (as depicted in Figure 9) featuring a central four-membered In_2O_2 ring. Its center coincides with a crystallographic inversion center. The interplanar angle between this ring and the neighboring LiN_2In ring is 67.1°, the latter ring is almost planar as demonstrated by an Li−N−In−N torsion angle of 4.3°. Both In atoms are tetra-coordinated with a very open C−In−C angle of 126.6(2)° at In1 and 131.4(2)° at In2.

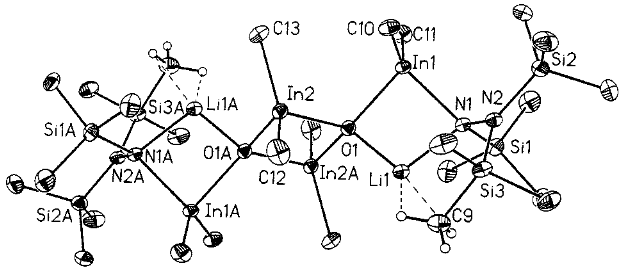


Figure 9. ORTEP plot of the molecular structure of **9**; selected atom distances [Å] and bond angles [°], esd values in parentheses: In1−N1 2.201(3), N1−N2 1.508(4), In1−O1 2.168(3), In2−O1 2.144(3), In2−O1A 2.162(3), N1−Si1 1.738(3), N2−Si2 1.738(4), N2−Si3 1.742(4), In1−C12 2.143(5), In1−C13 2.166(5), Li1−N1 2.036(9), Li1−O1 1.837(8), Li···H 2.03(1), 2.23(1);− O1−In1−N1 87.98(1), O1−In2−O1A 84.8(1), C11−In1−C12 126.6(2), C1−In2−C13 131.4(2), O1−Li1−N1 102.9(4), N1−Li1−C9 90.6(3), In2−O1In1 112.4(1)

The Li ions are formally two-coordinated with bonds to one O and one N atom, but the next shortest distances (2.03 and 2.23 Å) are found to H atoms of the Me_3Si groups. The N−N bond length is 1.508(4) Å. The sum of bond angles at atom N2 is 360°, and from this point of view, one has to regard the N−N bond as comparatively long. Once again, we take this as evidence for polar Li−N interactions due to a high negative charge at N2. The compound can be regarded an addition product of lithium tris(trimethylsilyl)hydrazide with bis(dimethylindium) oxide.

NMR Spectra

NMR spectroscopic data recorded for compound **7** are similar to those found for compound **5**. However, the ^1H and ^{13}C resonances for **7** are at slightly higher field due to the lower electronegativity of In. The ^{29}Si resonance is found at δ = 6.4, shifted only by 0.6 ppm to higher field compared to **5**. On the other hand, the ^7Li chemical shift at δ = −1.0 is the same as found for **5**.

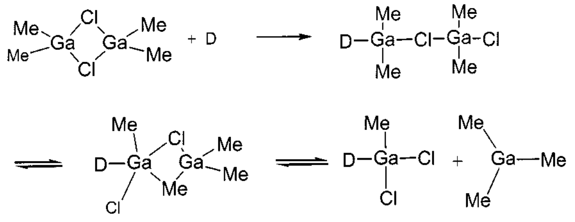
Knowing the structure of compound **8**, it is not surprising to find its NMR spectroscopic data are close to those of **7**. Even $\delta^7Li = -0.9$ is almost the same. As expected, there are two ^{29}Si NMR signals, while the NH protons result in a broad signal.

In agreement with the structure of **9** there are four ^{1}H and ^{13}C signals in the NMR spectra for the MeIn groups and two signals each for the Me_3Si group in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. However, not having had available the X-ray structure result it would have been difficult to guess the presence of a bis(dimethylindium) oxide unit in the molecule.

Discussion

This study demonstrates that the reactions of Me_2GaCl with organylhydrazines and lithium organylhydrazides are characterized by a substituent exchange at Me_2GaCl, leading to $MeGaCl_2$ and $GaMe_3$. Most likely, the substituent exchange is induced by the base as depicted in Equation (11). Such exchange reactions are well know in the chemistry of organyl compounds of the heavier group 13 elements.[59] Nevertheless, reactions of lithium amides with dialkylaluminium chlorides or dialkylgallium chlorides lead to the expected dialkylmetal amides without ligand exchange.[60] However, reaction of $t\mathrm{Bu}_2AlCl$ with $Li_2N_2(SiMe_3)_2$ produced $[t\mathrm{BuAl}{-}N(SiMe_3){-}N(SiMe_3)]_2$, indicating a similar ligand exchange at the metal atom as reported here.[14] Moreover, Uhl et al. found that the reaction of $t\mathrm{Bu}_2AlCl$ with $H_2NNHSiMe_3$ produced $t\mathrm{BuCl}_2Al{\cdot}NH_2{-}NHSiMe_3$, a compound that is analogous to compound **1**.[61]

It is interesting that the *tert*-butylhydrazine removes $MeGaCl_2$ from the equilibrium in Equation (1) while the lithium hydrazide $Li(Me_3Si)N{-}NH{-}t\mathrm{Bu}$ adds to trimethylgallium and not to a methylgallium chloride molecule. This can be rationalized as follows. The hydrazide is expected to be a stronger base than the hydrazine, and binds, therefore, to Me_3Ga because one can expect that $MeGaCl_2$ formed in the ligand exchange reaction has (most likely) reacted rapidly with the hydrazide by substitution as indicated in Equation (7).



(11)

Trimethylgallium reacts with hydrazine (N_2H_4) readily with CH_4 evolution to produce a bicyclic compound **3** that may be a precursor for MOCVD of GaN. As far as we are aware, no such structure has been observed so far for group 13 hydrazides. So, in contrast, the reaction of $t\mathrm{Bu}_2AlH$ with N_2H_4 leads, in a first step, to the six-membered $(t\mathrm{Bu}_2Al{-}NH{-}NH_2)_2$, and in a second step to $(t\mathrm{Bu}_2Al{-}NH{-}NH{-}Alt\mathrm{Bu}_2)_2$ with retention of the six-membered ring structure.[62]

C-Metallation by Ga results when the reaction of Me_2GaCl with $Li(Me_3Si)N{-}NH(naphth)$ is performed in refluxing toluene. The product **4** is a 2,3-dihydro-1*H*-naphtho[1,2-*d*][1,2,3]diazagallol, which dimerizes via Ga−N bonds generating a centrosymmetric Ga_2N_2 ring system. As far as we know, this is the first example of the gallation of a naphthalene ring.

Interestingly, Me_2InCl behaves in a manner similar to Me_2GaCl in its reactions with lithium organylhydrazides. However, the solvent seems to play a more important role than in the reactions with Me_2GaCl. Therefore, an unprecedented type of redox reaction occurs in the formation of compound **8**. And even the reaction shown in Equation (10) is unusual in the sense that the bulky $Li(Me_3Si)N{-}N(SiMe_3)_2$ is retained if the reaction is performed in ether. Whether dimethylindium chloride induces double ether cleavage or the formation of the diindoxane unit is a result of unintended slow hydrolyses during the crystallization process was not investigated. Ether cleavage by strong Lewis acidic group 13 halides is not unusual, but the cleavage reaction usually stops after the first step leading to alkoxides X_2EOR of group 13 compounds.[63] In−O−In structural units are well known e.g. in organylindium alkoxide or OH-bridged diorganylindium carboxylates.[64−66]

Experimental Section

General: All experiments were conducted using Schlenk techniques under a blanket of nitrogen or argon. Solvents used were rendered anhydrous by conventional methods and stored under nitrogen. NMR spectra were recorded using JEOL 270 and 400 instruments. X-ray diffraction data were obtained with a Siemens P4 instrument equipped with a CCD area detector and a low-temperature device LT2. Data collection was performed using Mo-K_{α} radiation. Commercial products were Me_2GaCl (1 M in hexane, checked for purity by NMR), $GaMe_3$ (neat), BuLi (1.5 M in hexane). Hydrazine hydrate was made anhydrous with activated BaO. The trimethylsilylhydrazines were prepared according to the literature.[67] Reaction with BuLi in hexane afforded the *N*-lithio derivatives. Me_2InCl was prepared from $InCl_3$ by methylation with an ether solution of MeLi in a 1:2 ratio. The sublimed product had a m.p. of 221−222 °C (ref. 222−225 °C[68]). ^{1}H NMR (C_6D_6): $\delta = 0.23$.

***tert*-Butylhydrazine−Dichloro(methyl)gallane (1):** To a stirred solution of $t\mathrm{BuHN}{-}NH_2$ (1.24 g, 14.1 mmol), dissolved in toluene (30 mL), was added a solution of Me_2GaCl (1.91 g, 14.1 mmol) in 5 mL of toluene. No gas evolution occurred, which set in slowly at 70 °C and became rapid on heating the mixture to reflux for 3 h. A solid had formed that was removed by filtration and the filtrate was cooled to −20 °C. Within a few days crystals of **1** separated from the filtrate. These crystals were suitable for X-ray crystallography. Yield: 0.83 g (24%), m.p. 51−53 °C. The solid on dissolving in hot toluene showed ^{1}H NMR resonances in a 1:3 ratio for MeGa and *t*Bu protons. This product, assumed to be **2**, was not further characterized. Yield: 0.84 g. NMR of **1** (C_6D_6): $\delta^{1}H = 0.33$ (s, 3 H, GaMe), 0.65 (s, 9 H, *t*Bu), 4.15 (br., NH); $\delta^{13}C = -3.1$ (Ga*Me*), 25.6, 55.3 (*t*Bu). $C_5H_{15}Cl_2GaN_2$ (243.81): calcd. C 24.63, H 6.20, N 11.49; found C 24.21, H 6.12, N 11.51.

3,7-Diamino-2,2,4,4,6,6,8,8-octamethyl-1,3,5,7-tetrazonia-2,4,6,8-tetragallatabicyclo[3.3.0]octane (3): $GaMe_3$ (5.85 g, 50.9 mmol) was condensed into a three-necked flask at −78 °C. It was diluted with toluene (40 mL). While stirring a solution of toluene (20 mL) containing N_2H_4 (1.63 g, 50.8 mmol), was added droppwise at −50 °C to the $GaMe_3$ solution. After slowly warming the reaction mixture to room temperature, gas evolution set in quickly and was rapid on heating the resulting suspension to reflux (2 h). The solid (5.68 g) that had formed was isolated by filtration and proved to be principally compound **3** (NMR). Single crystals separated from the filtrate kept at −20 °C. Yield after crystallization from toluene: 4.86 g of **3** (65% calcd. for $GaMe_3$), m.p. 62−63 °C. No explosive decomposition was observed on heating, but one should be careful in handling this compound because methylaluminium hydrazides are reported to be explosive. NMR (C_6D_6): δ^1H = 0.38 to −0.09 (7 signals, 24 H, Ga*Me*), 2.24 (br., 2 H, NH), 2.34 (br., 4 H, NH), 2.74 (br., 2 H, NH); at 80 °C: δ^1H = −0.32 (br. s, 24 H, Ga*Me*), 2.40 (br. s, 6 H, NH), 2.64 (br. s, 2 H, NH); $\delta^{13}C$ = −11.5, −10.6, −9.4, −7.3, −6.4, −5.9, −7.1 (Ga*Me*); at 80 °C: $\delta^{13}C$ = −9.0 (br., Ga*Me*). IR (hostaflon): $\tilde{\nu}$ = 3161 (br., νNH), 1613, 1601 cm^{-1} (δNH_2). $C_{15}H_{40}Ga_4N_6$ (583.40): calcd. C 30.88, H 6.91, N 14.41; found C 30.73, H 6.87, N 14.28.

1-Methyl-2-trimethylsilyl-2,3-dihydro-1*H*-naphtho[1,2-*d*]-[1,2,3]diazagallol (4): A stirred solution of naphth(H)N−$NHSiMe_3$ (2.01 g, 8.7 mmol) in toluene (40 mL) was metallated with a hexane solution of butyllithium (5.6 mL, 1.56 M, 8.7 mmol). After heating to reflux for 2 h, the solution was cooled to −30 °C. Then, a solution of Me_2GaCl (1.18 g, 8.7 mmol) in toluene (20 mL) was added dropwise. After addition, the suspension was allowed to attain room temperature. On heating to reflux for 2 h some gas evolution was noted. The solid that had formed was removed by filtration and the solvents evaporated in vacuo. The remaining oil was treated with hexane (10 mL) and the solution stored at −20 °C. Light yellow crystals separated within a few weeks. Yield: 1.56 g of **4** (57%), m.p. 113−115 °C. NMR (C_6D_6): δ^1H = −0.17 (s, 3 H, Ga*Me*), 0.30 (s, 9 H, *Me*Si), 5.71 (s, 1 H, NH), 6.7−7.8 (m, 6 H, naph*H*); $\delta^{13}C$ = −8.6 (Ga*Me*), 1.4 (Si*Me*), 114.8, 123.1, 126.9, 128.8, 130.0, 130.5, 130.8, 135.7, 139.9, 155.3 (arom. C); $\delta^{29}Si$ = 13.6. $C_{14}H_{19}GaN_2Si$ (313.12): calcd. C 53.70, H 6.12, N 8.95; found C 53.55, H 6.09, N 8.89.

Lithium *N'*-*tert*-Butyl-*N*-trimethylsilylhydrazide−Trimethylgallium (5): $Me_3Si(H)N-NH\mathit{t}Bu$ (1.76 g, 11.0 mmol), dissolved in hexane (40 mL), was metallated by adding to the stirred solution BuLi in hexane (7.05 mL, 1.56 M, 11 mmol). The metallation was completed by heating to reflux for 2 h, followed by cooling to −40 °C. Addition of Me_2GaCl (1.54 g, 11.0 mmol), dissolved in hexane (20 mL), led to the formation of a precipitate that was removed by filtration after the suspension had been stirred for 12 h at ambient temperature. Cooling the filtrate to −78 °C yielded colorless needles of **5**, which separated within three weeks. Yield: 1.05 g (34%), m.p. 64−65 °C (dec.). NMR (C_6D_6): δ^1H = −0.08 (s, 9 H, Ga*Me*), 0.21 (s, 9 H, Si*Me*), 1.05 (br. s, 9 H, C*Me₃*), 3.6 (br. s, 1 H, NH); $\delta^{13}C$ = −2.7 (GaMe), 2.7 (SiMe), 29.0 ($C\mathit{Me}_3$); $\delta^{29}Si$ = 7.0; δ^7Li = −1.0 ($h_{1/2}$ = 19 Hz). $C_{10}H_{28}GaLiN_2Si$ (281.09): calcd. C 42.73, H 10.04, N 9.97; found C 41.85, H 9.87, N 9.73.

Lithium *N'*-*tert*-Butyl-*N*-trimethylsilylhydrazide−Trimethylindium (7): A stirred solution of $Me_3Si(H)N-NH\mathit{t}Bu$ (1.68 g, 10.5 mmol) in 30 mL of toluene was treated with a 1.56 M solution of BuLi (6.7 mL, 10.5 mmol) in hexane. After heating to reflux for 4 h and cooling to ambient temperature, the solution was added dropwise to a stirred suspension of Me_2InCl (1.89 g, 10.5 mmol) in toluene (40 mL), kept at −60 °C. After addition, the mixture was allowed to attain room temperature followed by heating the orange mixture to reflux for 2.5 h. Then, the solids (0.15 g) were removed by filtration and the filtrate stored at −20 °C. Within three weeks small crystals had settled, suitable for X-ray diffraction analysis. Yield: 1.33 g of **6** (39%), m.p. 70−71 °C (dec.). NMR ([D₈]toluene): δ^1H = −0.18 (s, 9 H, InMe), 0.22 (s, 9 H, $SiMe_3$), 0.98 (s, 9 H, *t*Bu),3.4 (s br., 1 H, NH); $\delta^{13}C$ = −5.9 (InMe), 3.3 ($SiMe_3$), 28.3 (*t*Bu), 55.1 (*t*Bu); $\delta^{29}Si$ = 6.4; δ^7Li = −1.0 ($h_{1/2}$ = 18 Hz). $C_{10}H_{28}InLiN_2Si$ (326.19): calcd. C 36.82, H 8.65; N 8.59; found C 35.45, H 8.12, N 8.43.

Dimeric Lithium *N'*-*tert*-Butyl-*N*-trimethylsilylhydrazide−(Methylindyl)(trimethylsilyl)imide (8): A stirred solution of $Me_3Si(H)N-NH\mathit{t}Bu$ (1.75 g, 10.9 mmol) in diethyl ether (40 mL) was deprotonated by adding a hexane solution of BuLi (1.56 M, 7.0 mL, 10.9 mmol). To complete the reaction the mixture was kept at reflux for 2 h. After cooling to ambient temperature, Me_2InCl (1.97 g, 10.9 mmol), dissolved in 40 mL of diethyl ether, was added. Small amounts of a solid were filtered off after 12 h. Then the solvents were removed from the filtrate in vacuo and the solid residue treated with hexane (40 mL). The solution was stored at −25 °C. Crystals of **8** separated within four weeks. Yield: 0.92 g of **8** (55%), m.p. 104−105 °C (dec.). NMR (C_6D_6 or [D₈]toluene): δ^1H = −0.10 (s, 3 H, InMe), 0.21 (s, 9 H, $SiMe_3$), 0.25 (s, 9 H, $SiMe_3$), 1.03 (s, 9 H, *t*Bu), 3.3 (br. s, 1 H, NH); $\delta^{13}C$ = −6.0 (InMe), 3.2 ($SiMe_3$), 4.4 ($SiMe_3$), 28.8 (*t*Bu), 55.2 (*t*Bu); $\delta^{29}Si$ = 3.5 ($NSiMe_3$), 6.5 ($NNSiMe_3$); δ^7Li = −0.9 ($\Delta h_{1/2}$ = 18 Hz). $C_{11}H_{31}InLiN_3Si_2$ (383.33): calcd. C 34.46, H 8.15, N 10.96; found C 33.98, H 7.85, N 11.21.

Lithium Tris(trimethylsilyl)hydrazide−Bis(dimethylindium) Oxide Dimer (9): To a stirred solution of Me_2InCl (0.83 g, 4.6 mmol) in ether (40 mL) was added a solution of $(Me_3Si)_2N-NLi(SiMe_3)$ (1.16 g, 4.6 mmol) in diethyl ether (20 mL). After 12 h, the insoluble material (0.10 g, 2.4 mmol LiCl) was removed by filtration. After all volatile components had been stripped off from the filtrate in vacuo, recrystallization of the residue from toluene produced colorless crystals of **9** within 2 weeks. Yield: 0.73 g (57%), m.p. 165 °C. NMR (C_6D_6): δ^1H = −0.03 (s, 3 H, InMe), 0.03 (s, 3 H, $SiMe_3$), 0.04 (s, 3 H, InMe), 0.08 (s, 3 H, InMe), 0.10 (s, 9 H, $SiMe_3$), 0.13 (s, 18 H, $SiMe_3$); $\delta^{13}C$ = −5.4, −3.4, −2.9, −0.6 (InMe), 0.9, 1.4 ($SiMe_3$); $\delta^{29}Si$ = 6.6, 12.1. $C_{13}H_{39}In_2LiN_2OSi_3$(560.30): calcd. C 27.87, H 7.02, N 5.00; found C 27.79, H 7.05, N 4.98.

Crystal Structure Determinations: Single crystals were covered with a perfluoroether oil and a specimen selected, placed on the tip of a glass fiber and then mounted on the goniometer head. The crystal was then cooled to −80 °C. After alignment, the dimensions of the unit cell were determined from reflections on 5 sets of 15 frames each. Data were collected with the SMART program[69] in the hemisphere mode. An exposure time of 5 s/frames was chosen. Δφ was changed by 0.3° between two frames. Data on a total of 1240 frames were collected and reduced with the program SAINT[70] Absorption correction was employed (SADABS[71]). The structures were solved by direct methods and refined by using the programs SHELXTL and SHELX97.[72] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated position and included in the final cycles of refinement as riding on the respective carbon atom. Table 4 contains relevant crystallographic data and data related to structure solution and refinement.[73] Thermal ellipsoids in the figures are depicted on a 25% probability level.

Table 4. Crystal data and data collection parameters

Compound	**1**	**3**	**4**	**5**	**7**	**8**	**9**
Empirical formula	$C_5H_{15}Cl_2GaN_2$	$C_{15}H_{40}Ga_4N_6$	$C_{14}H_{19}GaN_2Si$	$C_{10}H_{28}GaLiN_2Si$	$C_{10}H_{28}InLiN_2Si$	$C_{11}H_{31}InLiN_3Si_2$	$C_{13}H_{39}In_2LiN_2OSi_3$
Formula mass	243.81	583.41	313.12	281.09	326.19	383.33	560.31
Crystal size [mm]	0.20×0.30×0.50	0.20×0.30×0.40	0.09×0.10×0.20	0.10×0.10×0.30	0.07×0.1×0.3	0.1×0.2×0.3	0.10×0.20×0.20
Crystal system	tetragonal	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$I4(1)/a$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/c$
a [Å]	21.0004(3)	9.831(5)	11.033(3)	8.9742(1)	12.453(4)	20.731(7)	18.111(4)
b [Å]	21.0004(3)	9.846(4)	13.678(4)	16.3792(2)	9.116(4)	10.066(3)	9.342(2)
c [Å]	9.9230(1)	14.862(5)	10.141(3)	10.7599(1)	14.648(5)	20.193(5)	15.539(3)
α [°]	90	98.08(1)	90	90	90	90	90
β [°]	90	98.40(1)	100.63(1)	97.877(1)	106.49(1)	115.63(1)	105.35(1)
γ [°]	90	111.552(9)	90	90	90	90	90
V [Å^3]	4376.2(1)	1293.7(9)	1504.0(7)	1566.68(3)	1594.5(10)	3798.9(19)	2535.3(9)
Z	16	2	4	4	4	8	4
ρ(calcd.) [Mg/m^3]	1.480	1.498	1.383	1.192	1.359	1.340	1.468
μ [mm^{-1}]	2.948	4.130	1.894	1.809	1.534	1.360	1.962
F(000)	1984	592	648	600	672	1584	1128
Index ranges	$-14 \le h \le 23$ $-23 \le k \le 23$ $-11 \le l \le 11$	$-11 \le h \le 11$ $-11 \le k \le 11$ $-17 \le l \le 13$	$-12 \le h \le 11$ $-16 \le k \le 16$ $-11 \le l \le 11$	$-11 \le h \le 10$ $-20 \le k \le 20$ $-12 \le l \le 13$	$-14 \le h \le 14$ $-10 \le k \le 10$ $-17 \le l \le 17$	$-25 \le h \le 25$ $-12 \le k \le 12$ $-21 \le l \le 23$	$-23 \le h \le 23$ $-11 \le k \le 11$ $-14 \le l \le 21$
2θ [°]	46.52	49.42	49.42	58.56	49.42	51.34	58.88
T [K]	193	193	193	193	193	193	193
Refl. collected	8870	6483	7090	8721	7607	9685	14106
Refl. unique	1503	3403	2251	3062	2205	2912	4362
Refl. observed (4σ)	1446	2500	1913	2676	1931	2554	3737
R(int.)	0.0245	0.0244	0.0259	0.0215	0.0261	0.0230	0.0279
No. of variables	107	253	171	248	171	257	223
Weighting scheme[a] x/y	0.0446/57.0488	0.1017/1.8549	0.0252/0.9647	0.0636/0.4699	0.0319/1.1868	0.0287/14.4461	0.0481/0.8766
GOOF	1.208	1.044	1.071	1.051	1.102	1.070	1.219
Final R(4σ)	0.0544	0.0608	0.0262	0.0321	0.0267	0.0306	0.0326
Final $wR2$	0.1378	0.1545	0.0577	0.0802	0.0599	0.0713	0.0771
Largest residual peak [e/Å^3]	1.154	0.736	0.256	0.736	0.419	1.065	0.479

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

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[1] L. Fieser, *Reagents for Organic Synthesis*, John Wiley, Interscience Publ., New York, **1990**.

[2] K. W. Henderson, *Chem. Eur. J.* **2001**, *7*, 3430−3437.

[3] J. C. Stowell, *Carbanions in Organic Synthesis*, J. Wiley, Interscience Publ., New York, **1979**.

[4] *Lithium Chemistry* (Eds.: A. Sapse, P. von Rague-Schleyer), John Wiley & Sons, Inc., New York, Chichester, Brisbane, Toronto, Singapore, **1995**, chapter 5.

[5] R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167−209.

[6] K. Gregory, P. von Rague-Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 48−142.

[7] N. Wiberg, M. Veith, *Chem. Ber.* **1971**, *104*, 3176−3190.

[8] C. Drost, U. Klingebiel, *Chem. Ber.* **1993**, *126*, 1413−1416.

[9] K. Bode, U. Klingebiel, M. Noltemeyer, H. Witte-Abel, *Z. Anorg. Allg. Chem.* **1995**, *421*, 500−505.

[10] W. Uhl, J. Molter, W. Saak, *Z. Anorg. Allg. Chem.* **1999**, *625*, 231−328.

[11] A. Heine, D. Stalke, *Angew. Chem.* **1992**, *104*, 941−942; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 854−855.

[12] H. Hommer, H. Nöth, H. Sachdev, M. Schmidt, H. Schwenk, *Chem. Ber.* **1995**, *128*, 1187−1194;.

[13] R. J. Wehmschulte, P. P. Power, *Inorg. Chem.* **1996**, *35*, 2717−2718.

[14] W. Uhl, J. Molter, R. Koch, *Eur. J. Inorg. Chem.* **1999**, 2021−2028.

[15] D. A. Neumayer, A. H. Cowley, A. Decken, R. A. Jones, V. Lakkotia, J. G. Ekerdt, *Inorg. Chem.* **1995**, *14*, 4698−4700.

[16] H. Nöth, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1931−1938.

[17] D. A. Neumayer, J. G. Ekerdt, *Chem. Mater.* **1996**, *8*, 9−25.

[18] V. Lakkotia, D. A. Neumayer, A. H. Cowley, R. A. Jones, J. G. Ekerdt, *Chem. Mater.* **1995**, *7*, 546−552.

[19] D. C. Boyd, R. T. Haasch, D. R. Mantell, R. K. Schulze, J. F. Evans, W. L. Gladfelter, *Chem. Mater.* **1989**, *1*, 119−124.

[20] A. Devi, W. Rogge, R. A. Fischer, F. Stowasser, H. Sussek, H. W. Becker, J. Wolfrum, *J. Phys. IV* **1999**, *9*, 589.

[21] M. A. Munoz-Hernandez, D. Rutherford, H. Tiaminen, D. A. Atwood, *J. Organomet. Chem.* **1999**, *582*, 103.

[22] J. McMurran, D. Dai, K. Balasubramanian, C. Steffek, J. Koutsetakis, J. L. Hubbard, *Inorg. Chem.* **1999**, *37*, 6638.

[23] A. Devi, H. Sussek, H. Pritzkow, M. Winter, R. A. Fischer, *Eur. J. Inorg. Chem.* **1999**, 2127−2134.

[24] N. Metzler, H. Nöth, H. Sachdev, *Angew. Chem.* **1994**, *106*, 1837−1839; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1746−1748.

[25] C. Drost, C. Jäger, U. Klingebiel, M. Noltemeyer, G. M. Sheldrick, *Chem. Ber.* **1994**, *621*, 290−847.

[26] B. Gemünd, H. Nöth, H. Sachdev, M. Schmidt, *Chem. Ber.* **1996**, *129*, 1335−1344.

[27] H. Nöth, W. Regnet, H. Rihl, R. Standfest, *Chem. Ber.* **1971**, *104*, 722−733.

[28] H. Fußstetter, H. Nöth, *Liebigs Ann. Chem.* **1981**, 633−641.

[29] S. Diemer, H. Nöth, W. Storch, *Eur. J. Inorg. Chem.* **1999**, 1765−1779.

[30] *Gmelin, Handbuch der Anorganischen Chemie, Ergänzungswerk zur 8. Auflage*, **1975**, vol. 22, pp. 249−257.

[31] N. R. Fetter, A. Bartocha, *Canad. J. Chem.* **1961**, *39*, 2001−2008.

[32] Y. Kim, J. H. Kim, J. E. Park, H. Hyunjoon, J. T. Park, *J. Organomet. Chem.* **1997**, 545−546, 99−103.

[33] D. W. Peters, M. P. Power, E. D. Bourret, J. Arnold, *Chem. Commun.* **1998**, 753−754.

[34] J. S. Silverman, C. D. Abernethy, R. A. Jones, A. H. Cowley, *Chem. Commun.* **1999**, 1645−1646.

[35] H. Nöth, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1931−1938.

[36] W. Uhl, J. Molter, R. Koch, *Eur. J. Inorg. Chem.* **2000**, 2255−2262.

[37] D. W. Peters, E. D. Bourret, M. P. Power, J. Arnold, *J. Organomet. Chem.* **1999**, *582*, 108−115.

[38] D. A. Neumayer, A. H. Cowley, A. Decker, R. A. Jones, V. Lakhotia, J. Eckerdt, *Inorg. Chem.* **1995**, *34*, 4698−4700.

[39] D. W. Peters, M. P. Power, E. D. Blurret, J. Arnold, *Chem. Commun.* **1998**, 753−754.

[40] W. Uhl, F. Hannemann, *Eur. J. Inorg. Chem.* **1999**, 201−207.

[41] W. R. Null, J. S. Blanton, A. M. Boccanluso, L. A. Silks III, A. R. Garber, J. D. Odom, *Inorg. Chem.* **1991**, *30*, 4136.

[42] S. D. Waezsada, C. Rennekamp, H. W. Roesky, C. Röpken, E. Parsini, *Z. Anorg. Allg. Chem.* **1998**, *624*, 987−990.

[43] W. R. Nutt, R. E. Stimson, M. F. Leopold, B. H. Rubin, *Inorg. Chem.* **1982**, *21*, 1909−1921.

[44] A. Yamaguchi, I. Ichishima, T. Shimanouchi, S.-I. Mizushima, *J. Chem. Phys.* **1959**, *31*, 843

[45] T. M. Klapötke, H. Nöth, H. Schwenk-Kircher, W.-H. Walther, G. Holl, *Polyhehedron* **1999**, *18*, 717−719.

[46] T. Habereder, A. Hammerl, G. Holl, T. M. Klapötke, J. Knizek, H. Nöth, *Eur. J. Inorg. Chem.* **1999**, 849−852.

[47] The structural data are given for the triclinic unit cell, space group "$P\bar{1}$", The structure of **3** could also be solved in the monoclinic system, space group *C*2/*m.* In this case, two independent molecules were also found. However, the central N atom occupies a special position. This results in planar heterocycles. The model could be better refined by choosing split positions for this atom, however, the disorder for the toluene molecule could not be refined. Therefore the data are given here for a triclinic space group.

[48] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh, PA, **1998**.

[49] *Lithium Chemistry* (Eds.: M.-A. Sapse, P. von Rague-Schleyer), J. Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, **1995**.

[50] W. N. Setzer, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353−449.

[51] M. Hesse, H. Meier, B. Zech, *Spektroskopische Methoden in der organischen Chemie*, 4th ed., Georg Thieme, Stuttgart, New York, **1991**.

[52] T. Seifert, PhD Thesis, University of Munich, **2000**, p. 40.

[53] K. Mertz, W. Schwarz, F. Zettler, H.-D. Hausen, *Z. Naturforsch., Part B* **1975**, *30*, 159−161.

[54] B. Neumüller, *Chem. Ber.* **1989**, *122*, 2283−2287.

[55] O. T. Beachley, C. Bueno, M. R. Churchill, R. B. Hallock, R. G. Simmons, *Inorg. Chem.* **1981**, *20*, 2423−2428.

[56] K. Aitchison, J. D. J. Backer-Dirks, D. C. Bradley, M. Fator, D. M. Frigo, M. B. Hursthouse, B. Hussain, *J. Organomet. Chem.* **1989**, *366*, 11−23.

[57] F. Weller, U. Müller, *Chem. Ber.* **1979**, *112*, 2039−2044.

[58] H. W. Roesky, U. Seseke, M. Noltemeyer, G. M. Sheldrick, *Z. Naturforsch., Part B* **1988**, *43*, 1130−1136.

[59] J. R. Rice, J. P. Oliver, *J. Organomet. Chem.* **1977**, *133*, 183−188.

[60] M. R. Kopp, T. Kräuter, A. Dashti-Mommerz, B. Neumüller, *Z. Naturforsch., Teil B* **1999**, *54*, 627−631.

[61] W. Uhl, J. Molter, W. Saak, *Z. Anorg. Allg. Chem.* **1999**, *625*, 321−328.

[62] W. Uhl, J. Molter, B. Neumüller, *Inorg. Chem.* **2001**, *40*, 2011−2014.

[63] H. Reinheckel, K. Haage, D. Jahnke, *Organomet. Chem. Rev. A* **1969**, *4*, 47.

[64] U. Dembrowski, T. Pape, R. Herbst-Irmer, E. Pohl, H. W. Roesky, *Acta. Crystallogr., Sect.C* **1993**, *49*, 1309−1311.

[65] M. Häißlein, H.-D. Hausen, K. W. Klinkhammer, J. Weidlein, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1608−1618.

[66] W. Uhl, R. Graupner, I. Hahn, *Z. Anorg. Allg. Chem.* **1997**, *623*, 565−572.

[67] K. B. Starowieyski, A. Bekalska, A. Okni′nski, *J. Organomet. Chem.* **1985**, *293*, 7.

[68] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, 3rd ed., F. Enke, Stuttgart, **1990**, vol. 2.

[69] *SMART*, Siemens Analtyic Instruments, Madison, Version 5, **1996.**

[70] *SAINT*, Siemens Analytical Instruments, Madison, Version 5, **1996.**

[71] G. M. Sheldrick, *SADABS, A program for absorption correction for data obtained by the hemisphere mode, implemented in SAINTS*, Bruker Analytical Instruments, Madison, **1999**, version 6.05.

[72] G. M. Sheldrick, *SHELX97, programs for structure solution, refinement*, Göttingen, **1997**.

[73] Crystallographic Data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Cenre as supplementary publication no. CCDC-165817 to -165823. Copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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