DOI: 10.1002/ejic.200700954

Different Reactivity Patterns in the Reactions of the Homologous Trimethylelement Compounds EMe_3 (E = Al, Ga, In) with Methylhydrazine

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Keywords: Aluminum / Gallium / Indium / Hydrazides / Heterocycles

The trimethylelement compounds EMe_3 (E = Al, Ga, In) followed three different reaction courses upon treatment with methylhydrazine, $H_2N–N(H)Me$. $AlMe_3$ reacted at room temperature by releasing 1.5 equiv. methane to yield the sesquihydrazide $(Me_2Al)_3[\mu\text{-}NH–N(H)Me]_6Al$ (**1**), which in the solid state has a hexacoordinate central aluminum atom and six hydrazido groups in the bridging positions to the three terminally arranged $AlMe_2$ groups. Dissociation occurred upon dissolution, and the dialuminum compound $Me_2Al[\mu\text{-}NH–N(H)Me]_2Al(Me)[NH–N(H)Me]$ (**2**), containing one terminal hydrazido group, was identified unambiguously by NMR spectroscopy. $GaMe_3$ gave a simple adduct, $Me_3Ga\leftarrow N(H)Me–NH_2$ (**3**), under the same reaction conditions. Boiling toluene was required to initiate a secondary reaction with the release of methane. A bicyclic tetragallium compound, **4**, in which a twofold deprotonated hydrazide, $[HN–NMe]^{2–}$, bridges four gallium atoms, was the result. Each pair of gallium atoms on both sides of the central hydrazinediide ligand is further bridged by the monoanionic hydrazide $[HN–N(H)Me]^–$ to yield two annelated, five-membered Ga_2N_3 heterocycles. A similar compound, **5**, was directly obtained from the reaction of $InMe_3$ with methylhydrazine at room temperature.

Introduction

The synthesis of organoaluminum, -gallium, and -indium hydrazides found some interest in recent research, because these compounds may be applicable in material chemistry as molecular precursors for the deposition of the corresponding nitrides.[1] Another important aspect is the interesting coordination behavior of hydrazido ligands, which is caused by two directly connected donor nitrogen atoms and has afforded a broad variety of different structural motifs in former investigations.[2] Simple adducts between hydrazines and trialkylelement compounds or alkylelement halides resulted from donor–acceptor interactions without secondary reactions.[3–9] Hydrazides obtained by the release of hydrogen, alkanes, or lithium halides were monomeric in a few cases only owing to steric shielding[10] or through the coordinative saturation of the central atoms by a side-on coordination of the hydrazido group through both nitrogen atoms.[11,12] Most compounds gave dimeric formula units with four-, five-, or six-membered heterocycles and 1,1- (geminal) or 1,2-bridging (vicinal) functions of the N–N bonds.[5,7,9,12–23] Oligomers possessing a cage-like arrangement of metal and nitrogen atoms or oligocyclic derivatives are known to a lesser extent.[3,6,16,17,24–26] The synthesis of these hydrazides was accomplished essentially by four procedures: (i) Reactions of trialkylelement compounds or dialkylelement hydrides with hydrazines by the release of alkanes or elemental hydrogen; (ii) salt elimination by the treatment of dialkylelement halides with lithium hydrazides, or, quite similarly, by the reaction of hydrazine adducts of element chlorides with butyllithium; (iii) amide replacement by the treatment of aminoalanes with hydrazines; (iv) addition of Al–H bonds to the C=N double bonds of 2,3-diazabutadienes or diazenes (hydroalumination). The last method involved aluminum trihydride as a starting reagent and afforded very interesting and unprecedented oligomeric hydrazides possessing singular heterocyclic or cage-type structures,[26] but it could not be transferred to dialkylaluminum hydrides or any gallium hydride.[27] With few exceptions only, most reactions involving hydrogen or alkane elimination afforded the monoanionic hydrazido ligand. From our former experience, we know that a second deprotonation to yield the corresponding dianion cannot be realized even under more drastic reaction conditions in most cases, because the cleavage of the N–N bond is the favored reaction at elevated temperatures. Such reactions were observed for small substituents attached to gallium, such as hydrogen atoms or methyl groups.[16,17,23] In order to generate dianionic hydrazides and to systematically investigate their coordination properties, we therefore treated the compounds EMe_3 (E = Al, Ga, In) with methylhydrazine, which, to the

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best of our knowledge, has not been employed for the syntheses of gallium or indium hydrazides before. We hoped to isolate metal-rich hydrazides possessing unprecedented configurations and bridging situations of the hydrazido ligand.

Results and Discussion

Reaction of Trimethylaluminum with Methylhydrazine

The reaction of the starting compounds in an equimolar ratio at room temperature afforded a colorless precipitate, which dissolved immediately with gas evolution. In accordance with the corresponding reaction of trimethylgallium, we suppose that an adduct of both components had formed intermediately, which was consumed by the release of methane in a fast secondary reaction. The reaction was finished after a relatively short period of one minute only. After concentration and cooling of the solution to –30 °C, colorless crystals of product **1** precipitated. Crystal structure determination (see below) revealed that the expected dimeric hydrazide, $[Me_2Al–N(H)–N(H)Me]_2$, had not formed. Instead, a tetraaluminum compound resulted, which had six methyl groups and six bridging hydrazido ligands (Scheme 1). The specific reaction of the components in a molar ratio of 4:6 $[AlMe_3/H_2N–N(H)Me]$ afforded crystals of sesquihydrazide **1** in an almost quantitative yield of 91%.

The constitution of **1** was clarified by crystal structure determination and elemental analysis. The mass spectrum showed the molecular peak minus one N–Me fragment, which is a reasonable decomposition pathway for these hydrazides.[6] However, the results of the NMR spectroscopic characterization in solution did not agree with the relatively symmetrical molecular structure. We observed resonances of three chemically different hydrazido ligands in an equivalent ratio and three different methyl groups attached to aluminum. Molar mass determination by cryoscopy in benzene gave clear evidence that the tetraaluminum compound did not exist in solution. We found an excellent agreement with a dialuminum species, $Al_2Me_3[N(H)–N(H)Me]_3$ (**2**), which corresponds to half the molar mass of the tetraaluminum compound. The equilibrium between compounds **1** and **2** is represented in Scheme 1. The occurrence of three different resonances of the methyl groups attached to aluminum is caused by the molecular symmetry of **2**: one methyl group of the $AlMe_2$ moiety is in a *cis* position to the terminally arranged hydrazido ligand, while the other one is *cis* to the methyl substituent of the second aluminum atom. The observation of three chemically different hydrazido groups may indicate a *trans* arrangement for the bridging hydrazides, so that only one of the inner N–H bonds neighbors the terminal hydrazido group. This configuration corresponds to the one usually observed for dimeric dialkylaluminum, -gallium, or –indium hydrazides containing four-membered E_2N_2 heterocycles (see Introduction).

Crystal structure determination verified the occurrence of an unusual tetraaluminum sesquihydrazide, $Al[\mu\text{-}N(H)–N(H)Me]_6(AlMe_2)_3$ (Figure 1).[28] This represents a singular structural motif for hydrazides containing heavier group 13 elements. The inner aluminum atom is octahedrally coordinated by six nitrogen atoms of different hydrazido ligands. The Al–N distances to that aluminum atom are close to the average value of 203.2 pm. The angles N–Al–N deviate only

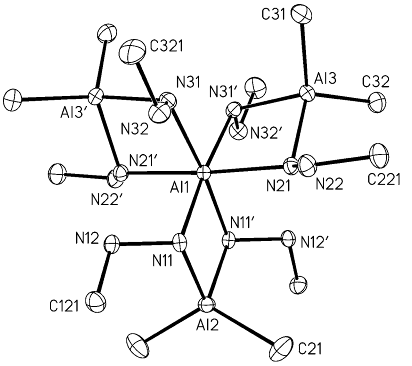
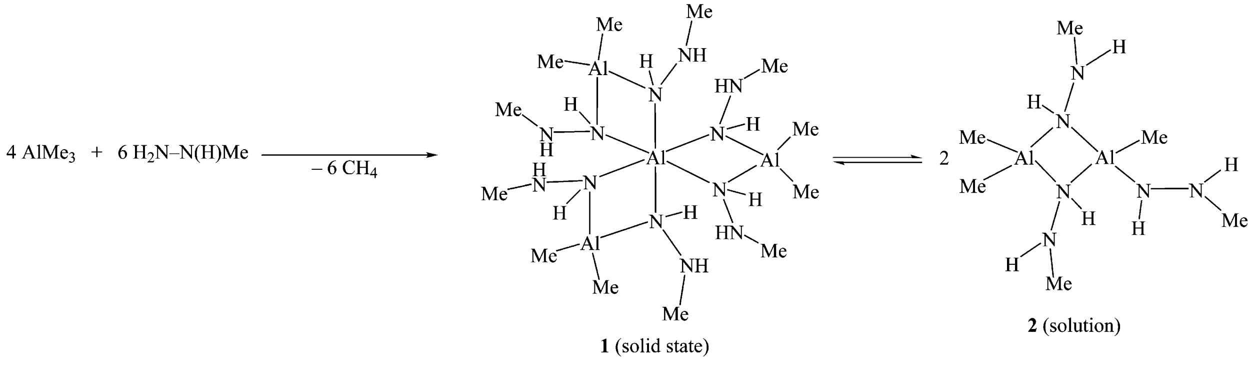


Figure 1. Molecular structure and numbering scheme of **1**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [°]: Al1–N11 202.8(1), Al1–N21 202.5(1), Al1–N31 204.5(1), Al2–N11 193.7(1), Al3–N21 193.7(1), Al3–N31′ 193.9(1), N11–N12 146.0(2), N21–N22 145.5(2), N31–N32 146.2(2), N11–Al1–N11′ 83.87(7), N21–Al1–N31′ 82.17(5), N11–Al2–N11′ 88.76(7), N21–Al3–N31′ 87.25(5), Al1–N11–Al2 93.69(5), Al1–N21–Al3 94.38(5), Al1–N31–Al3′ 93.69(5); Al3′, N11′, and N31′ generated by –*x*, *y*, –*z* + 0.5.



Scheme 1.

slightly from the ideal angles of 90 and 180°. As expected, the strongest deviations are observed for the four-membered Al_2N_2 heterocycles (82.7° on average), which result from the bridging function of all hydrazido ligands between the inner aluminum atom and the terminal $AlMe_2$ groups. Thus, each of these rings has two exocyclic N–N bonds. The Al–N distances to the terminal $AlMe_2$ groups containing tetrahedrally coordinated aluminum atoms are considerably shorter (193.8 pm on average) than those to the central hexacoordinate aluminum atom. The N–N distances (145.9 pm) correspond to standard values.

Reactions of Trimethylgallium with Methylhydrazine

The reaction of equimolar quantities of trimethylgallium and methylhydrazine afforded an oily product in quantitative yield, which was identified as the adduct $Me_3Ga{\leftarrow}N(H)Me{-}NH_2$ (**3**) by the characteristic ratio of the signal intensities in the ^1H NMR spectrum (Scheme 2). Those adducts are expected to be formed in the first step of all reactions of hydrazines with alkylelement compounds (E = Al, Ga, In). Secondary reactions may afford the hydrazides by the release of hydrogen or alkanes either spontaneously or upon heating. As mentioned in the Introduction, some adducts could be isolated in previous studies and were characterized by crystal structure determinations. Interestingly, in the reactions of methylhydrazine described here, only the adduct of trimethylgallium was stable enough to be identified and characterized unambiguously by standard methods.

3

Scheme 2.

Dissolution of the oily product in cyclopentane and cooling to –30 °C afforded colorless crystals of **3**, which were rather sensitive towards air and melted below room temperature. Nevertheless, we were able to prepare and handle a single crystal at low temperature and to determine its crystal structure (Figure 2). The result verifies the formation of an adduct. The gallium atom has a distorted tetrahedral coordination sphere. The Ga–N bond (211.4 pm) is expectedly longer than that in gallium hydrazides, in which a negatively charged nitrogen atom is bonded to gallium. As is usual for neutral hydrazines, the N–N distance (144.5 pm) is in the lower range of N–N bond lengths. Interestingly, it is observed for the first time that the hydrazine ligand bonds through the nitrogen atom that bears the alkyl group. Methylamine is a stronger base than ammonia by the negative inductive effect of the methyl group.[29] Thus, the nitrogen atom attached to the methyl group may be the most basic center of methylhydrazine, and the constitution of **3** may therefore be the generally favored one. Steric repulsion between the alkyl groups of the hydrazine ligands and the alkyl groups attached to the aluminum or gallium atoms may compensate for the stronger basicity, and usually the coordination occurs through the sterically less shielded NH_2 nitrogen atom.[3–9]

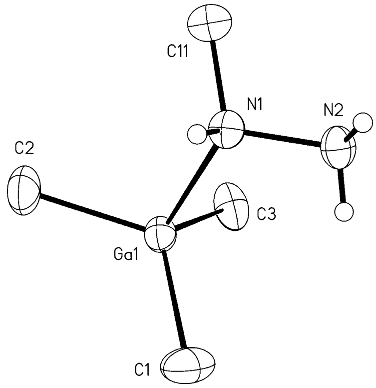
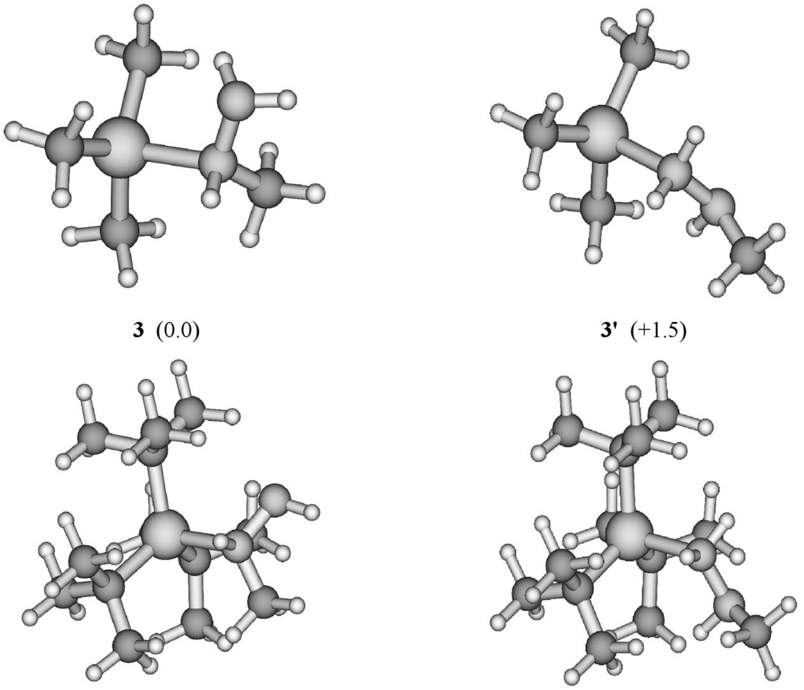


Figure 2. Molecular structure and numbering scheme of **3**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of hydrazine hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [°]: Ga1–N1 211.4(2), N1–N2 144.5(3), Ga1–N1–N2 110.6(2).

To understand its unusual coordination mode, compound **3** was investigated by quantum chemical methods. The corresponding tri(*tert*-butyl)gallium methylhydrazine adduct was included in order to test the influence of steric shielding. Different conformers with respect to the rotation around the N–N bond were considered and optimized. SCS-MP2 single-point calculations were conducted for the energetically most favored structures of both trialkylgallium derivatives. Figure 3 presents the lowest energy conformers of each isomer and the relative energies of isomer pairs with respect to the coordination of the hydrazine ligand. Obviously, in the most stable adduct of trimethylgallium with methylhydrazine, the hydrazine ligand is coordinated by the methylated nitrogen atom (cf. **3** and **3′**). The result does not depend on the quantum chemical method used (the values obtained with PBE-D differ by less than 0.7 kcal mol^{-1} from the corresponding SCS-MP2 values). This observation is in accordance with the intuitive prediction that the basicity of the nitrogen atom is enhanced by alkyl substitution. In contrast, the coordination of methylhydrazine through the NH_2 nitrogen atom is more favored for the tris(*tert*-butyl)gallium adducts (**3a** and **3a′**). Clearly, these calculations confirm the influence of steric interactions between the alkyl groups attached to the gallium atoms and to the hydrazine ligands. Only trimethylgallium seems to be small enough to allow for the intrinsically favored coordination of the alkyl-substituted nitrogen atom.

Solutions of adduct **3** in toluene could be stirred at room temperature for several days without any hint of decomposition or a secondary reaction. Gas evolution started only upon heating these solutions to 90 °C, and completion of the thermolysis reaction required stirring in boiling toluene

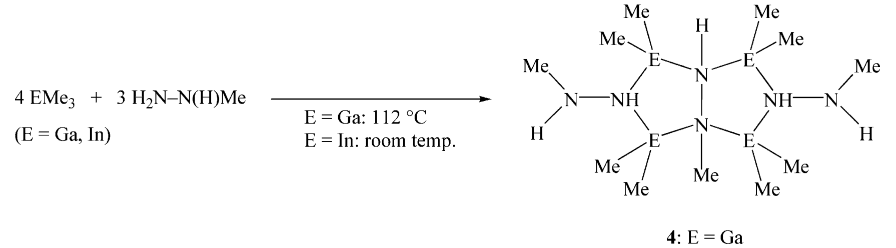


3 (0.0) **3'** (+1.5)

3a (+1.8) **3a'** (0.0)

Figure 3. Optimized geometries of the trimethylgallium methylhydrazine adduct **3**, its isomer **3′**, and the corresponding tris(*tert*-butyl)gallium compounds **3a** and **3a′** [PBE-D/TZV(d,p)]. Relative energies [SCS-MP2/TZV(2df,2dp)] of the isomer pairs in kcal mol^{-1}.

for 2 h. An amorphous colorless powder precipitated from the reaction mixture after concentration and cooling to –30 °C. Recrystallization from cyclopentane afforded the crystalline compound **4**. Crystal structure determination revealed a bicyclic structure containing four gallium atoms and a doubly deprotonated hydrazinediide ligand in the bridging position. The molecular structure is given in Scheme 3. Optimization of the stoichiometric ratio of the starting compounds to the ideal one according to Scheme 3 resulted in compound **4** in 74% yield. The ^{1}H NMR spectroscopic characterization proved to be rather difficult, and more resonances than expected were observed. At room temperature we could separate two similar sets of resonances for different molecular species (see Experimental Section). In both cases, their assignment is in agreement with the bicyclic structure of **4**. Any suggestion for the respective constitution in solution is rather speculative. The differences may result from frozen conformations or from compounds having a second endocyclic N–N bond to form a six-membered heterocycle. Similar compounds possessing Al_2N_4 rings including two N–N bonds and exclusively monoanionic hydrazides were obtained in our group several years ago.[13,20,23] Two further resonances occurred in the Ga–CH_3 range of the spectrum (^{1}H NMR: δ = –0.03 and –0.21 ppm, ^{13}C NMR: δ = –2.7 and –6.2 ppm; in each case, the second resonance has the highest intensity). Also these resonances seem to be involved in the equilibrium at room temperature, and their intensity changed with temperature. Upon heating of the sample to 370 K, the ^{1}H NMR spectrum showed the expected shape with four resonances of equal intensity for the four chemically different methyl groups attached to gallium (δ = –0.10, –0.29, –0.33, and –0.37 ppm). All signals were still relatively broad at that temperature, which prevented an unambiguous assignment, in particular for N–H resonances. A peak corresponding to the molar mass of **4** was detected in the mass spectrum. Its isotopic pattern was in excellent accordance with a calculated one.



4: E = Ga
5: E = In

Scheme 3.

The bicyclic structure of compound **4** was confirmed by a crystal structure determination (Figure 4). Two five-membered Ga_2N_3 heterocycles are annelated by a common H–N–N–Me moiety. This situation resembles the bicyclic backbone of the hydrocarbon [3.3.0]-octane. Thus, one hydrazine molecule is twofold deprotonated. Each nitrogen atom of that inner group is bonded to two gallium atoms. A very interesting structural motif results, in which a hydrazido ligand bridges four atoms of a group 13 metal. Both dimethylgallium groups on each side of the inner N–N bond are further bridged by a nitrogen atom of an exocyclic hydrazido ligand to complete the five-membered rings. These rings have an envelope conformation in which the inner nitrogen atoms, N32 (or N3A) are 74 and 81 pm above the planes spanned by the atoms Ga1, N11, Ga2, N31, and Ga4, N21, Ga3, N31, respectively (76 and 78 pm for the second position of the disordered hydrazinediide moiety). The hydrogen atom and the methyl group of the central hydrazinediide are in a *trans* arrangement across the N–N bond. In contrast, both terminally arranged exocyclic N–N bonds are on the same side of the bicyclic ring system. The result of this particular molecular symmetry is four chemically different methyl groups attached to gallium, while the monoanionic exocyclic hydrazido groups have an identical chemical environment. Owing to the disorder of the central hydrazinediido ligand, we abstain from a discussion of the N–N bond lengths. The angles N–Ga–N in the heterocycles are close to 95°. A similar compound was obtained by the reaction of trimethylgallium with hydrazine, $H_2N–NH_2$, without reference to the formation of an intermediate adduct.[22]

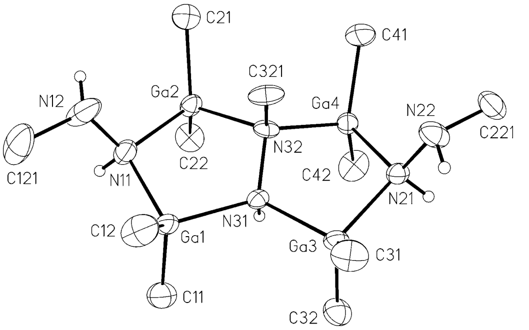


Figure 4. Molecular structure and numbering scheme of **4**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the hydrazine hydrogen atoms are omitted for clarity. N3A and N3B are from the disordered inner hydrazine ligand; N3A is attached to the methyl group. Important bond lengths [pm] and angles [°]: Ga1–N11 200.1(3), Ga1–N31 205.2(8), Ga1–N3A 201.9(7), Ga2–N11 200.8(3), Ga2–N32 205.6(9), Ga2–N3B 203.0(6), Ga3–N21 201.6(3), Ga3–N31 201.5(8), Ga3–N3A 206.0(6), Ga4–N21 200.2(3), Ga4–N32 200.3(9), Ga4–N3B 203.0(6), N11–N12 143.6(5), N21–N22 144.5(5), N31–N32 151(2), N3A–N3B 149(1), N11–Ga1–N31 95.2(2), N11–Ga1–N3A 95.1(2), Ga1–N11–Ga2 108.9(2), N11–Ga2–N32 96.5(3), N11–Ga2–N3B 94.3(2), Ga2–N32–Ga4 117.3(4), Ga2–N32–N31 104.7(7), Ga4–N32–N31 104.6(8), Ga2–N3B–Ga4 117.3(3), Ga2–N3B–N3A 112.7(5), Ga4–N3B–N3A 114.6(5), N32–Ga4–N21 94.2(3), N3B–Ga4–N21 95.8(2), Ga4–N21–Ga3 107.0(1), N21–Ga3–N31 94.9(2), N21–Ga3–N3A 94.9(2), Ga3–N31–N32 112.3(6), Ga3–N31–Ga1 117.6(4), Ga1–N31–N32 113.6(7), Ga3–N3A–N3B 104.1(5), Ga3–N3A–Ga1 117.0(3), Ga1–N3A–N3B 105.5(6).

Reaction of Trimethylindium with Methylhydrazine

The formation of an adduct similar to the gallium compound **3** was not observed for the corresponding reaction of trimethylindium and methylhydrazine. Instead, slow gas evolution started immediately after the addition of the hydrazine to a solution of trimethylindium in *n*-pentane at room temperature. The reaction required 14 h to be completed (Scheme 3). A colorless solid precipitated, which was insoluble in common organic solvents (cyclopentane to chloroform) and was removed by filtration. Its constitution is unknown. Concentration of the filtrate and cooling to –30 °C yielded colorless crystals of compound **5** in 71% yield (based on the optimized stoichiometric ratio given in Scheme 3). According to the results of a crystal structure determination, compound **5** is isostructural to the tetragallium compound **4** described before. In contrast to **4**, the NMR spectroscopic characterization of **5** gave the expected resonances already at room temperature without any sign of an equilibrium of different forms in solution. Four singlets were obtained for the four chemically different methyl groups attached to indium. The methyl groups attached to the exocyclic N–N bonds gave one doublet caused by the coupling to the hydrogen atom bonded to the same nitrogen atom. Expectedly, a quartet was detected for this proton. H–H coupling across the N–N bond was observed for few compounds only. Accordingly, the N–H protons of these hydrazido ligands gave a singlet, which is broadened as a result of the quadrupole moment of the nitrogen atoms. Two further resonances occur for the methyl group and the hydrogen atom of the doubly deprotonated hydrazinediide. The integration ratio is in accordance with the calculated one. According to these results, trimethylindium seems to be more reactive than the corresponding gallium compound with respect to the deprotonation of hydrazines by methane elimination.

The molecular structure of **5** is depicted in Figure 5. The tetraindium derivative is isostructural to compound **4**. It consists of two five-membered In_2N_3 heterocycles annelated by a twofold deprotonated hydrazine. Each nitrogen atom of that hydrazine coordinates two indium atoms, and an exocyclic hydrazide bridges pairs of indium atoms on the same side of the central N–N bond. Once again, the molecule has an approximate mirror plane across the atoms H21, N21, N22 and C221. The central group does not show a disorder similar to **4**, which allows for a discussion of the gradual increase of the N–N bond lengths on going from the monoanionic exocyclic to the dianionic endocyclic hydrazine groups (146.1 pm on average vs. 148.2 pm). This increase has been observed before[2] and may be caused by the stronger electrostatic repulsion between both negatively charged nitrogen atoms in the formally dianionic ligand. The smallest distances were usually determined for neutral hydrazines, however, the differences become smaller and an overlap of the respective ranges of distances force a cautious interpretation. An envelope form results once again for both five-membered heterocycles with the inner nitrogen atom N22 73 and 84 pm above the average planes of the remaining atoms. The normals to the planes of the four coplanar atoms in each heterocycle include an angle of 22°. All In–N distances are in a narrow range between 221.7 and 226.5 pm and do not show any dependency on the charge of the hydrazine ligand.

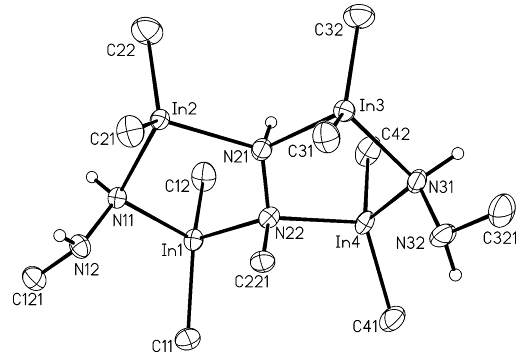


Figure 5. Molecular structure and numbering scheme of **5**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the hydrazine hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [°]: In1–N11 221.7(3), In1–N22 224.4(3), In2–N11 221.7(3), In2–N21 221.7(3), In3–N21 226.5(3), In3–N31 221.8(3), In4–N22 222.6(3), In4–N31 222.5(3), N11–N12 145.9(4), N21–N22 148.2(4), N31–N32 146.2(4), N11–In1–N22 92.2(1), In1–N11–In2 108.0(1), N11–In2–N21 94.1(1), In2–N21–In3 113.2(1), In2–N21–N22 115.4(2), In3–N21–N22 114.6(2), N21–In3–N31 92.4(1), In3–N31–In4 106.9(1), N31–In4–N22 92.7(1), In1–N22–In4 115.5(1), In1–N22–N21 109.8(2), In4–N22–N21 105.2(2).

Conclusion

A surprising variability of reaction courses was observed upon treatment of the compounds EMe_3 (E = Al, Ga, In) with methylhydrazine. A sesqui compound $Al_2Me_3[NH–N(H)Me]_3$ (**2**) or its dimer **1** resulted with trimethylaluminum. It was formed by the release of 1.5 equiv. methane per formula unit of the starting trialkylaluminum compound. A double deprotonation of hydrazine did not occur. The starting point of all reactions may be the formation of adducts by an interaction of a nitrogen lone pair with the coordinatively unsaturated aluminum, gallium, or indium atoms. However, only in the case of trimethylgallium were we able to unambiguously identify and isolate such an adduct, namely compound **3**. The secondary reaction by the release of methane required boiling toluene for completion. Twofold deprotonation occurred, and in bicyclic product **4**, a formally dianionic H–N–N–Me group bridges four gallium atoms. Trimethylindium afforded the corresponding product, **5**, directly at room temperature. These differences may depend on the strongly differing polarity of the E–C bonds. The lowest polarity is expected for the Ga–C bond. Accordingly, a persistent adduct is formed, and drastic conditions are required to release methane. The higher polarity of the In–C bond and hence the stronger basicity of the methyl group favor the attack on methylhydrazine already at room temperature. Trimethylaluminum is the most reactive compound possessing the most basic methyl groups in this series. However, twofold deprotonation of the hydrazine did not occur under the given conditions. The considerable charge transfer to the hydrazide ligands caused by the relatively low electronegativity of aluminum may reduce the acidity of the remaining N–H bonds.

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-pentane and cyclopentane over $LiAlH_4$, toluene over Na/benzophenone). $InMe_3$ was obtained according to a literature procedure.[30] Commercially available methylhydrazine was distilled prior to use and stored under argon. MOCHEM GmbH (Marburg, Germany) kindly supported us with donations of $AlMe_3$ and $GaMe_3$. The assignment of the resonances in the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Reaction of Trimethylaluminum with Methylhydrazine; Synthesis of 1: Trimethylaluminum (0.51 g, 7.08 mmol) was dissolved in *n*-pentane (30 mL) and treated with methylhydrazine (0.56 mL, 0.49 g, 10.65 mmol) at room temperature. A colorless solid precipitated, which dissolved completely after a few seconds to yield a clear solution. The dissolution process was accompanied by gas evolution. The mixture was stirred for 0.5 h and subsequently concentrated in vacuo. Colorless crystals of compound **1** precipitated upon cooling of the solution to –30 °C. Yield: 0.75 g (91%), m.p. (argon, sealed capillary): above 105 °C, gas evolution, gray solid at 300 °C. Tetraaluminum compound **1** dissociated in solution to give the dialuminum derivative **2**. Thus, the NMR spectroscopic characterization is based on **2**. ^1H NMR ($[D_8]$toluene, 400 MHz, 300 K): $\delta = -0.39$, -0.44, and -0.45 (s, each 3 H, $AlMe_2$ and AlMe); 2.31 (s, 3 H, terminal NHNH*Me*), 2.38 (d, $^3J_{H-H} = 6.4$ Hz, 3 H, μ-NHNH*Me*), 2.42 (d, $^3J_{H-H} = 6.0$ Hz, 3 H, μ-NHNH*Me*), 2.53, 2.54, and 2.55 (s, br., each 1 H, N*H*NHMe); 4.47 (s, 1 H, terminal NHN*H*Me), 4.64 (q, $^3J_{H-H} = 6.4$ Hz, 1 H) and 4.92 (q, $^3J_{H-H} = 6.0$ Hz, 1 H, both μ-NHN*H*Me) ppm. ^{13}C NMR ($[D_8]$toluene, 100 MHz, 300 K): $\delta = -8.8$ and -9.8 (AlMe, two resonances coincide at 9.8); 42.4 (Me of both bridging NHNHMe groups), 42.8 (Me of terminal NHNHMe) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 3410 (vw), 3247 (m), 3213 (m), 3142 [w, ν(NH)], 2921 (vs), 2853 (vs), 2786 (sh, paraffin), 1455 (vs), 1376 (vs, paraffin), 1187 [m, $\delta(CH_3)$], 1133 (w), 1080 (m), 1015 (w), 976 (w), 940 (vw), 893 [w, ν(CN), ν_s(NN)], 851 (vw), 816 [vw, ν_{as}(NN)], 724 (vw, paraffin), 658 (vw), 521 (w), 415 (m), 400 (m), 382 (m), 317 [s, ν(AlC), ν(AlN)] cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 457 (1) $[M - (N–Me)]^+$, 407 (9) $[M - 2\,(NH–Me) - H]^+$, 377 (100) $[M - 3\,(NH–Me) - H]^+$. $C_{12}H_{48}Al_4N_{12}$ (468.5): calcd. C 30.8, H 10.3, Al 23.0, N 35.9; found C 31.1, H 10.8, Al 23.1, N 35.4. Molar mass in solution (cryoscopy, benzene): calcd. 234.3 $g\,mol^{-1}$ for the dialuminum compound **2**; found: 242 $g\,mol^{-1}$.

Reaction of Trimethylgallium with Methylhydrazine; Synthesis of Adduct 3: Trimethylgallium (1.42 g, 12.4 mmol) was dissolved in *n*-pentane (30 mL) and treated with methylhydrazine (0.66 mL, 0.57 g, 12.4 mmol) at room temperature. The mixture was stirred for 0.5 h, and the solvent was removed in vacuo. A colorless, highly viscous liquid consisting of pure adduct **3** remained in an almost quantitative yield (1.94 g, 98%). Purification by distillation failed because of decomposition. Recrystallization from cyclopentane (20/–30 °C) yielded colorless crystals, which immediately melted upon warming to room temperature. ^{1}H NMR ([D$_8$]toluene, 400 MHz, 240 K): δ = –0.27 (s, 9 H, GaMe$_3$), 1.72 (d, $^3J_{H–H}$ = 6.2 Hz, 3 H, NMe), 2.35 (d, $^3J_{H–H}$ = 4.8 Hz, 2 H, NH$_2$), 2.63 (m, 1 H, N*H*Me) ppm. ^{13}C NMR ([D$_8$]toluene, 100 MHz, 240 K): δ = –6.9 (GaMe), 40.7 (NMe) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 3345 (w), 3287 (w), 3224 [w, ν(NH)], 2938 (vs), 2854 (sh, paraffin), 1607 [s, δ(NH)], 1451 (s), 1377 (s, paraffin), 1305 (vw), 1189 [s, δ(CH$_3$)], 1140 (w), 1110 (w), 1080 (m), 1014 (m, br.), 859 [m, ν(CN), ν_s(NN)], 727 [vs, ν_{as}(NN)], 677 (w), 603 (w), 546 (vs), 522 [w, ν(GaC), ν(GaN)] cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 145 (11), 147 (8) [M – Me]$^+$; 99 (100), 101 (84) [GaMe$_2$]$^+$. $C_4H_{15}GaN_2$ (160.9): calcd. C 29.9, H 9.4, Ga 43.3, N 17.4; found C 29.0, H 8.8, Ga 44.1, N 18.0.

Thermal Decomposition of the Adduct 3; Synthesis of 4: Trimethylgallium (2.31 g, 20.1 mmol) was dissolved in toluene (25 mL) and treated with methylhydrazine (0.80 mL, 0.70 g, 15.2 mmol) at room temperature. The mixture was slowly heated. Gas evolution started at about 90 °C. After 2 h under reflux, the solution was cooled to room temperature, concentrated and stored at –30 °C. Compound **4** precipitated as a colorless amorphous solid. It was recrystallized from cyclopentane for further purification. Yield: 1.97 g (74%), m.p. (argon, sealed capillary): 87 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 300 K): Isomer I (see Results and Discussion): δ = 0.08, –0.16, –0.18, and –0.31 (s, each 6 H, GaMe); 1.71 {s, 2 H, H–NGa$_2$ of [N(H)–N(H)–Me]$^-$}, 2.05 {d, $^3J_{H–H}$ = 6.5 Hz, 6 H, *Me–N*–H of [N(H)–N(H)–Me]$^-$}, 2.63 {q, $^3J_{H–H}$ = 6.5 Hz, 2 H, *H–N*–Me of [N(H)–N(H)–Me]$^-$}, 2.78 [s, 1 H, H–NGa$_2$ of the dianion $^-$N(H)–N(Me)$^-$], 2.88 [s, 3 H, Me–NGa$_2$ of the dianion $^-$N(H)–N(Me)$^-$] ppm; Isomer II: δ = 0.04, –0.19, –0.23, and –0.28 (s, each 6 H, GaMe); 2.09 {d, $^3J_{H–H}$ = 6.5 Hz, 6 H, *Me–N*–H of [N(H)–N(H)–Me]$^-$}, 2.39 {q, $^3J_{H–H}$ = 6.5 Hz, 2 H, *H–N*–Me of [N(H)–N(H)–Me]$^-$}, 2.59 [s, 3 H, Me–NGa$_2$ of the dianion $^-$N(H)–N(Me)$^-$], 3.00 [s, 1 H, H–NGa$_2$ of the dianion $^-$N(H)–N(Me)$^-$] (H–NGa$_2$ of the monoanionic ligand [N(H)–N(H)–Me]$^-$ was not observed) ppm. ^{13}C NMR (C$_6$D$_6$, 100 MHz, 300 K): Isomer I: δ = –5.4, –7.4, –9.1, and –9.9 (GaMe); 41.1 [$^-$N(H)–N(Me)$^-$], 42.6 {[N(H)–N(H)–Me]$^-$} ppm; Isomer II: δ = –5.6, –7.4, –8.3, and –10.0 (GaMe); 41.4 [$^-$N(H)–N(Me)$^-$], 42.6 {[N(H)–N(H)–Me]$^-$} ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 3617 (m, br.), 3564 (sh), 3292 (s), 3238 (s), 3177 [s, ν(NH)], 2953 (vs), 2916 (vs), 2857 (vs), 2792 (sh, paraffin), 1884 (m, br.), 1846 (m), 1767 (sh), 1736 [m, δ(NH)], 1468 (vs), 1366 (vs, paraffin), 1204 [vs, δ(CH$_3$)], 1067 (s), 1018 (s), 961 (s), 932 [sh, ν(CN), ν_s(NN)], 856 (s), 820 (s), 731 [vs, br., ν_{as}(NN)], 579 (s), 527 (s), 478 [m, ν(GaN), ν(GaC)] cm^{-1}. MS (EI, 70 eV, only the most intensive peaks are given, the isotopic patterns are in complete agreement with the calculated ones): *m*/*z* (%) 530 (5), 532 (12), 534 (13), 536 (5) [M]$^+$; 515 (13), 517 (35), 519 (34), 521 (16) [M – Me]$^+$. $C_{11}H_{38}Ga_4N_6$ (533.3): calcd. C 24.8, H 7.2, Ga 52.3, N 15.8; found C 25.4, H 7.3, Ga 51.5, N 15.5.

Reaction of Trimethylindium with Methylhydrazine; Synthesis of 5: Trimethylindium (1.71 g, 10.7 mmol) was dissolved in *n*-pentane (80 mL), treated with methylhydrazine (0.43 mL, 0.37 g, 8.04 mmol), and stirred at room temperature for 12 h. Immediately after addition of the hydrazine, a colorless solid of unknown constitution precipitated, and gas evolution was observed. The solid was removed by filtration, it is insoluble in common organic solvents. After concentration of the filtrate and cooling to –30 °C, colorless crystals of hydrazide **5** precipitated. Yield: 1.36 g (71%), m.p. (argon, sealed capillary): 70 °C. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 300 K): δ = –0.13, –0.12, –0.11, and 0.11 (s, each 6 H, InMe); 1.71 {s, 2 H,

Table 1. Crystal data and structure refinement for the compounds **1**, **3**, **4**, and **5**.[a,b]

	1	**3**	**4**	**5**
Formula	$C_{12}H_{48}Al_4N_{12}$	$C_4H_{15}GaN_2$	$C_{11}H_{38}Ga_4N_6$	$C_{11}H_{38}In_4N_6$
Temperature [K]	153(2)	153(2)	153(2)	153(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group[31]	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [pm]	1375.3(2)	795.9(2)	1309.5(1)	1015.64(7)
b [pm]	1193.1(2)	726.6(1)	1470.7(1)	2047.7(1)
c [pm]	1651.6(3)	1434.2(3)	1252.3(1)	1137.73(7)
α [°]	90	90	90	90
β [°]	98.078(4)	98.920(4)	111.388(2)	91.919(1)
γ [°]	90	90	90	90
V [10^{-30} m^3]	2683.2(8)	819.3(3)	2245.6(3)	2364.8(3)
Z	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.160	1.304	1.578	2.005
μ [mm^{-1}]	0.197	3.268	4.750	3.854
Crystal size [mm]	0.20 x 0.15 × 0.09	0.46 × 0.30 × 0.21	0.16 × 0.13 × 0.09	0.32 × 0.26 × 0.24
Radiation	Mo-K_α; graphite monochromator			
Theta range for data collection [°]	$2.27 \le \theta \le 30.05$	$2.59 \le \theta \le 31.05$	$1.67 \le \theta \le 27.56$	$1.99 \le \theta \le 30.00$
Index ranges	$–19 \le h \le 19$	$–11 \le h \le 11$	$–16 \le h \le 17$	$–14 \le h \le 14$
	$–16 \le k \le 16$	$–10 \le k \le 10$	$–19 \le k \le 19$	$–28 \le k \le 28$
	$–23 \le l \le 23$	$–20 \le l \le 20$	$–16 \le l \le 16$	$–15 \le l \le 15$
Independent reflections	3932 [R_{int} = 0.0398]	2488 [R_{int} = 0.0437]	5173 [R_{int} = 0.0545]	6858 [R_{int} = 0.0362]
Parameters	158	80	238	221
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$ [$I > 2\sigma(I)$]	0.0430 (3274)	0.0402 (1993)	0.0404 (3687)	0.0290 (6165)
$wR_2 = \{\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2/\Sigma\lvert F_o\rvert^2\}^{1/2}$ (all data)	0.1093	0.0965	0.0989	0.1019
Max./min. residual electron density [10^{30} e m^{-3}]	0.398/–0.225	0.943/–0.662	1.121/–0.635	0.982/–0.884

[a] Program: SHELXL-97;[32] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] See ref.[33] for CCDC reference numbers.

H–NIn$_2$ of [N(H)–N(H)–Me]$^-$}, 2.07 {d, $^3J_{H-H}$ = 6.2 Hz, 6 H, *Me–N*–H of [N(H)–N(H)–Me]$^-$}, 2.43 {q, $^3J_{H-H}$ = 6.2 Hz, 2 H, Me–*N–H* of [N(H)–N(H)–Me]$^-$}, 2.82 [s, 3 H, Me–NIn$_2$ of the dianion $^-$N(H)–N(Me)$^-$], 2.97 [s, 1 H, H–NIn$_2$ of the dianion $^-$N(H)–N-(Me)$^-$] ppm. ^{13}C NMR (C_6D_6, 100 MHz, 300 K): δ = –9.6, –9.2, –8.8, and –6.1 (InMe); 44.3 (NHMe), 45.4 (Me–NIn$_2$) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 3379 (vw), 3269 (w), 3217 (m), 3156 [m, ν(NH)], 2955 (vs), 2920 (vs), 2857 (vs), 2774 (s, paraffin), 1634 (w), 1593 [w, δ(NH)], 1462 (vs, paraffin), 1445 (vs), 1406 (w), 1377 [w, δ(CH$_3$)], 1341 (s, paraffin), 1240 [m, δ(CH$_3$)], 1165 (vs), 1070 (m), 1026 (vs), 941 [s, ν(CN), ν_s(NN)], 866 (s), 797 (m), 689 [vs, br., ν_{as}(NN)], 554 (vw), 507 (m), 471 [w, ν(InN), ν(InC)] cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 714 (2) [M]$^+$; 699 [M – Me]$^+$ (3); 552 (5), 554 (37), 555 (4) [M – InMe$_2$ – Me]$^+$. $C_{11}H_{38}In_6N_6$ (713.7): calcd. C 18.5, H 5.4, In 64.4, N 11.8; found C 18.7, H 5.8, In 63.7, N 12.6.

Crystal Structure Determinations: Single crystals of compounds **1** and **5** were obtained from the reaction mixtures in *n*-pentane upon cooling to –30 °C, crystals of **3** and **4** from cyclopentane at –30 °C. The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Table 1. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}$(C). With the exception of **4**, the positions of the hydrazine hydrogen atoms were taken from difference Fourier maps and refined without restrictions. The molecules of **1** reside on crystallographic twofold rotation axes. Compound **4** showed a disorder of the central H–N–N–Me group. Its nitrogen and carbon atoms were refined on split positions with occupancy factors of 0.44 and 0.56. Only in this case, the hydrazine hydrogen atoms were considered in fixed positions.

Quantum Chemical Calculations: Wave function (SCS-MP2)[34] and density functional theory (DFT) calculations have been performed with slightly modified versions of the TURBOMOLE suite of programs.[35] In all treatments, the RI approximation[36] for the two-electron integrals has been used. The geometries were optimized with the PBE functional[37] together with an empirical dispersion correction (PBE-D).[38] As AO basis, the triple-zeta (TZV) sets of Ahlrichs et al.[39] have been employed. For the structural optimizations, we used one additional polarization function on all atoms [TZV(d,p)], while for SCS-MP2 single-point energy calculations, a set of three polarization functions [TZV(2df,2dp)] was employed.

Acknowledgments

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

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Received: September 12, 2007