Inorganic Chemistry

FORUM ARTICLE

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Aluminum, Gallium, and Indium Hydrazides and the Generation of Oligonuclear Element-Nitrogen Cages: Molecular Intermediates on the Way to Element Nitrides

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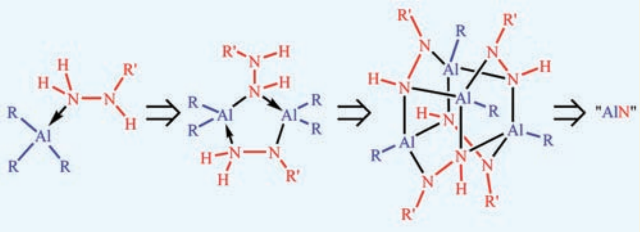
ABSTRACT: Organoelement aluminum, gallium, and indium hydrazides, $[R_2ENHN(H)R']_2$ (E = Al, Ga, In), are easily available from the corresponding trialkylelement compounds, ER_3, and hydrazines, $H_2NN(H)R'$, via elimination of the respective hydrocarbons. Their diverse molecular structures are derived from four-, five-, or six-membered element-nitrogen heterocycles. Their stepwise thermolysis under carefully controlled conditions was shown to proceed along one of several different well-defined routes. Cleavage of the N−N bonds afforded aluminum or gallium imides, $[REN(H)]_n$, with up to eight metal atoms in a single molecule, while preservation of the N−N bonds led to interesting cages in which intact N−N bonds of formally dianionic hydrazinediides bridge the metal atoms via their two adjacent donor atoms. Further thermolysis yielded the amorphous element nitrides via the gradual degradation of the hydrazinediide groups. Several intermediates have been isolated and provided insight in the course of these reactions. A particularly interesting compound was one that features a hydrazinetetraide unit, $[N{-}N]^{4-}$, that is stabilized by coordination to six gallium atoms.



INTRODUCTION

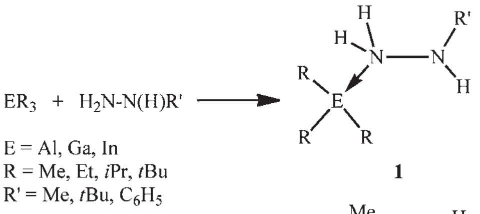
Hydrazines and their deprotonated derivatives represent a fascinating class of ligands that are suitable to form coordination compounds with a large variety of main-group and transition-metal elements. Their specific ligand properties are a result of their two adjacent donor atoms. This arrangement favors the formation of small heterocycles with a single metal atom by a quasi side-on coordination of the ligand or the bridging of several metal atoms that leads to the formation of cycles or cages. A similar coordination behavior is reported for the partially or completely deprotonated isoelectronic compounds hydroxylamine[1] and hydrogen peroxide.[2] Over and above this unique structural chemistry, these metal hydrazides exhibit remarkable chemical and physical properties, which are of interest in a wide area of research. Transition-metal hydrazides,[3] for instance, are believed to play an important role as intermediates in the biological and laboratory-based reduction of dinitrogen to ammonia[4] and are of interest in the context of N−C bond formation starting from hydrazines and unsaturated substrates.[5] Aluminum, gallium, and indium hydrazides have been explored as molecular precursors for the synthesis of element nitrides via metal−organic chemical vapor deposition and related procedures.[6] The starting materials for these reactions are generally hydrazine derivatives and trialkylelement compounds. It is widely believed that the first step is the formation of the corresponding adducts, but the true mechanism of the degradation processes to the nitrides is still unknown. Its understanding is, however, crucial for an optimization of these procedures with respect to the substitution pattern of the starting materials and physical parameters of thermolysis such as temperature, aggregation state (solid, liquid, solution, and gas phases), byproducts, or the purity and phase of the isolated products (amorphous and crystalline). In the past decade, we have conducted systematic investigations in this field,[7] and we have synthesized many adducts, $R_3E{\leftarrow}NH_2N(H)R'$ (E = Al, Ga, In), and studied their decomposition behavior. We have isolated many intermediates that suggest a range of possible decomposition pathways and are of interest not only in view of potential applications but also, in particular, with respect to their highly interesting structural chemistry. This article is mainly focused on reactions starting with trialkylelement derivatives and neutral hydrazines because these reactions were found to be superior to other methods, affording hydrazides in high yields with only volatile byproducts and avoiding the formation and cumbersome separation of inorganic salts.

ADDUCTS

The treatment of trialkylelement compounds ER_3 (E = Al, Ga, In) with hydrazines afforded adducts of the type $R_3E{\leftarrow}NH_2N(H)R'$ (eq 1; **1** and **2**) in which a nitrogen atom of the hydrazine ligand is bonded to the metal atoms of the organometallic compounds.[8−18] Relatively long E−N distances (Al←N about 205 pm; Ga←N 215 pm; In←N 239 pm) are typical for these donor−acceptor interactions. Many of these adducts have been isolated and characterized by crystal structure determination despite their reactivity and tendency to spontaneously eliminate

Received: March 21, 2011
Published: May 03, 2011

the corresponding hydrocarbons already at low temperatures. These secondary processes are favored by polar E—C bonds and small alkyl groups at the metal atom (e.g., $AlMe_3$). The formation of adducts is expected to be the initial reaction step even in cases where their isolation or identification by NMR spectroscopy was unsuccessful. The sterically less shielded NH_2 nitrogen atoms of the hydrazine ligands are, with only one exception (**2**),[10] bound to the metal atoms, while the more basic nitrogen atoms bearing alkyl substituents are in the terminal positions. Steric repulsion between the alkyl groups of the hydrazine moieties and the alkyl groups attached to the metal atoms may compensate for the higher basicity and may favor coordination via the NH_2 groups. Quantum-chemical calculations (DFT and SCS-MP2) for $Me_3Ga{\leftarrow}N(Me)HNH_2$ (**2**), the sterically congested *tert*-butyl derivative $(Me_3C)_3Ga{\leftarrow}NH_2N(H)Me$ and their isomeric forms, are in agreement with the experimentally observed coordination modes.[10] The $GaMe_3$ adduct (**2**) with the more basic N(H)Me group bound to gallium was calculated to be thermodynamically more stable (by 1.8 kcal/mol) than its isomeric form, $Me_3Ga{\leftarrow}NH_2N(H)Me$, hereby confirming the expected preference for coordination of the hydrazine via the *N*-alkyl nitrogen atom. The reverse situation is found for the $Ga(CMe_3)_3$ adduct for which $(Me_3C)_3Ga{\leftarrow}NH_2{-}N(Me)H$ was calculated to be the more stable form (1.5 kcal/mol). These calculations support the influence of steric interactions for the stability of the different structures, although packing effects or hydrogen bonding (present in **2** but not in **1**) may also play a role.



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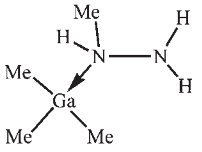
(1)

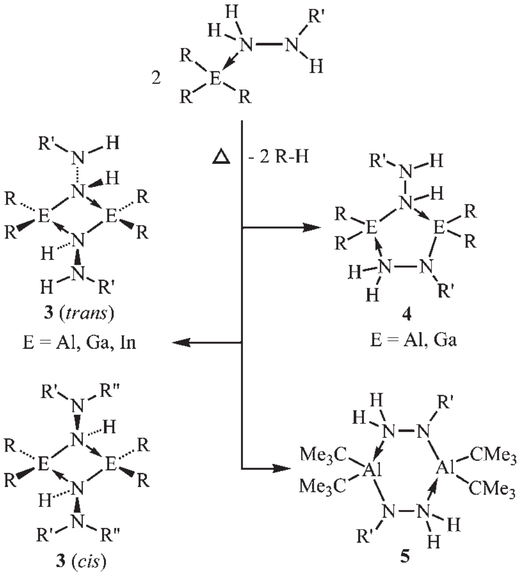


2

Other adducts reported in the literature such as $(Me_3C)_2ClAl{\leftarrow}NH_2N(H)SiMe_3$ and $MeCl_2Ga{\leftarrow}NH_2N(H)CMe_3$ contain dialkyl- or monoalkylelement halides coordinated by hydrazine ligands.[19−24] As a consequence of the relatively large covalent radius of indium, only the corresponding dialkylindium chloride adducts, $R_2InCl{\leftarrow}NH_2N(H)R'$, have coordination numbers larger than 4 at the metal atoms. These result in unusual oligomeric or polymeric structures in the solid state with bridging chlorine and hydrazine ligands.[24] A unique coordination pattern is observed for the polymeric structure of $Me_2ClIn{\leftarrow}NH_2N(H)CMe_3$ in which each nitrogen atom of the neutral hydrazine ligand is coordinated to a metal atom.[24]

HYDRAZIDES WITH THE MONOANIONIC HYDRAZIDE LIGAND $[N(H)N(R')H]^-$

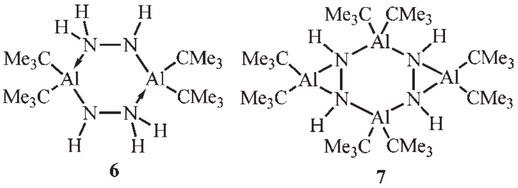
The hydrazine adducts (**1** and **2**) generally eliminate below room temperature or upon slight warming spontaneously 1 equiv of the corresponding alkane. The products are monoanionic hydrazides, $[N(H)N(H)R']^-$ (eq 2), which in solution and the solid state have dimeric structures with bridging metal atoms.[11−14,17,18,25−31] Dissociation to the monomeric formula unit required the addition of ether or tetrahydrofuran.[32] Alternative methods for the synthesis of these hydrazides comprise the reaction of dialkylelement halides with lithium hydrazides,[22,32,33] the treatment of adducts, $R_2ClE{\leftarrow}NH_2N(H)R'$, with butyllithium,[21,23,34] the reaction of dialkylelement hydrides with hydrazines,[20,35−37] an amine—hydrazide exchange reaction,[38] and the reduction of diazene with a gallium(I) compound.[39] The reactions of trialkylelement derivatives with hydrazines are clearly superior to other methods because the synthesis of the starting organoelement compounds requires additional steps, the reactions are less selective, the products form complexes with lithium,[22,32] and, in some cases, inorganic salts are formed as side products. The approximately 30 documented crystal structures of the dimeric group 13 element hydrazides have revealed three different structural motifs (eq 2). By far the most frequently observed structures are four-membered E_2N_2 heterocycles (**3**), which have two exocyclic N—N bonds and the anionic nitrogen atoms of the hydrazido ligands in bridging positions between both metal atoms. Five-membered (**4**)[13,23,29,34] and especially six-membered heterocycles (**5**)[32,34,36] with one or two endocyclic N—N bonds are less common. They have one or two donor—acceptor bonds between the metal atoms and the NH_2 groups. The conversion of a six-membered heterocycle into a five-membered heterocycle has only been observed once.[34]



(2)

Quantum-chemical calculations [B3LYP/6-31G and SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)] for two aluminum hydrazides, $[Me_2AlN_2H_2SiMe_3]_2$[34] and $[(Me_3C)_2AlN_2H_2Me]_2$,[29] show the five-membered Al_2N_3 heterocycle to be thermodynamically favored in comparison to the four-membered Al_2N_2 rings. This is in good agreement with the experimentally determined molecular structures. The energetic differences between both forms are, however, relatively small (about 3 kcal/mol). It is, therefore, interesting that the four-membered Ga_2N_2 heterocycle with both hydrazide ligands in an exocyclic arrangement was found in the crystal structure of the corresponding gallium compound $[(Me_3C)_2GaN_2H_2Me]_2$.[29] In this case, conversion of the four-membered ring system into the five-membered ring system was calculated to be endothermic by 0.7 kcal/mol. This leads to the conclusion that the observed structure of these hydrazides depends on at least two factors:

Scheme 1



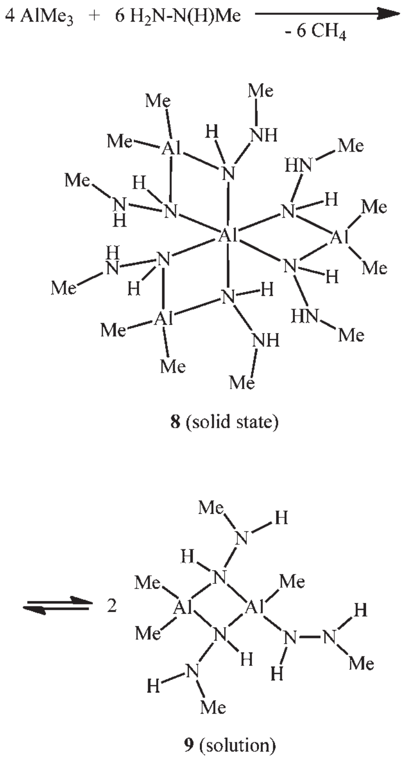
6 7

Caused by the electronegativity differences of the metal and nitrogen atoms, relatively high partial charges are located at the respective atoms. These favor the direct E—N bonding interactions in the four-membered rings with significant ionic contributions but result in a high transannular electrostatic repulsion between both nitrogen and aluminum atoms. These repulsive interactions are smaller in larger rings and, therefore, favor the formation of the five-membered heterocycles. Steric interactions constitute the second relevant contribution. Most important is the close contact between the substituents attached to the nitrogen atoms and the alkyl groups bonded to the metal atoms that disfavors the five-membered rings. The distance between both groups is largest in the most common four-membered E_2N_2 cycles in which the alkyl groups exclusively occupy positions at the terminal nitrogen atoms. Hence, the final observed structures are determined by a subtle balance between electrostatic attraction and repulsion on the one side and steric interactions on the other. The different structures of the compounds $[(Me_3C)_2EN_2H_3Me]_2$ (E = Al, Ga) may be rationalized by these arguments.[29] The small methyl groups of the hydrazine ligands do not seriously hinder a direct Al—N(Me) or Ga—N(Me) bond. The charges at the metal and nitrogen atoms are calculated to be higher in the aluminum compound (+2.0 vs +1.7 on E and −1.1 vs −1.0 on N).[29] The Ga—N distances are, in addition, slightly longer than the Al—N bonds and that leads to longer transannular E—E and N—N distances for the gallium compound (313 and 276 vs 302 and 268 pm). Both effects result in a smaller electrostatic repulsion between atoms of the same type in the gallium derivative and allow formation of the four-membered rings.

The compounds with four-membered E_2N_2 heterocycles and two exocyclic N—N bonds exist in two isomeric forms. One isomer has a 2-fold rotation axis perpendicular to the central ring and both hydrazide groups on the same side (cis), and the other possesses a center of symmetry with the N—N bonds on different sides of the E_2N_2 heterocycle (trans). Calculations on $[(Me_3C)_2EN(H)N(H)Me]_2$ (E = Al, Ga) have shown the cis isomer to be thermodynamically slightly more stable (1.8 vs 1.1 kcal/mol) than the trans isomer.[29] The latter isomer was found to be present in the solid-state structure of the aluminum compound featuring a planar Al_2N_2 ring.[29] The cis form with a puckered central ring has so far only been verified in the compounds $[Me_2InN(H)N(H)CMe_3]_2$ and $[Et_2AlN(H)NC_4H_4]_2$.[17,35] The high prevalence of the trans form may be a result of the better packing of the planar molecules in the solid state. Probably because of the small energy differences, many of the hydrazides exist in solution as an equilibrium mixture of the two isomers[13,17,18,23,26,28,29,35] and, in some cases, a five-membered ring.[13,29] This has complicated the characterization of these compounds by NMR spectroscopy. The mechanism of isomerization may include partial monomerization.

We have carried out only a very few experiments with the unsubstituted hydrazine N_2H_4. The reaction with equimolar quantities of di-*tert*-butylaluminum hydride afforded a six-membered Al_2N_4 heterocycle (**6**; Scheme 1).[36] An excess of the hydride yielded the unique tricyclic compound **7** (Scheme 1), in which both N—N bonds of the Al_2N_4 ring are bridged by di-*tert*-butylaluminum groups.[36] Both compounds are thermally quite stable. In contrast, dangerously explosive materials were obtained from other reactions. This observation is in accordance with reports in the literature.[15,40] Reactions with N_2H_4 should therefore be carried out with the greatest care.

A unique course of reaction was observed in the case of the sterically less shielded reactants $AlMe_3$ and $H_2NN(H)Me$. A total of 1.5 equiv of the hydrazine was required to completely consume the aluminum compound (eq 3).[10] A colorless substance precipitated after a short reaction time and then rapidly redissolved under gas evolution. This may indicate the intermediate formation of an adduct that could, however, not be isolated or identified by NMR spectroscopy. An unprecedented sesquihydrazide (**8**) was isolated that in the solid state possesses a tetranuclear structure, $Al[N(H)N(H)Me]_6(AlMe_2)_3$. The central aluminum atom is coordinated in an octahedral fashion by six nitrogen atoms of the hydrazide ligands. The nitrogen atoms form bridges to the aluminum atoms of the terminal $AlMe_2$ groups, resulting in three Al_2N_2 heterocycles. **8** dissociates in solution quantitatively to the dinuclear compound **9**, which has two hydrazide groups bridging the metal atoms. One aluminum atom binds additionally to two methyl substituents and the other to a methyl group and a terminal hydrazide group.



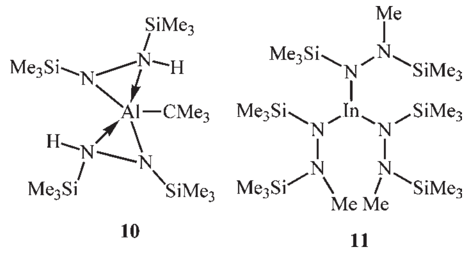
(3)

8 (solid state)

9 (solution)

The formation of mononuclear bis- or trishydrazides was observed very rarely. The compound $Me_3CAl[N(SiMe_3)N(H)SiMe_3]_2$ (**10**; Scheme 2) was obtained by the treatment of $N_2H_2(SiMe_3)_2$ with di-*tert*-butylaluminum hydride.[41] The aluminum atom has a coordination number of 5 with two relatively long Al—N distances [207.2(2) pm] to the β-nitrogen atoms of the hydrazide ligands. Three hydrazide groups bonded to tricoordinate gallium or indium atoms were observed in the

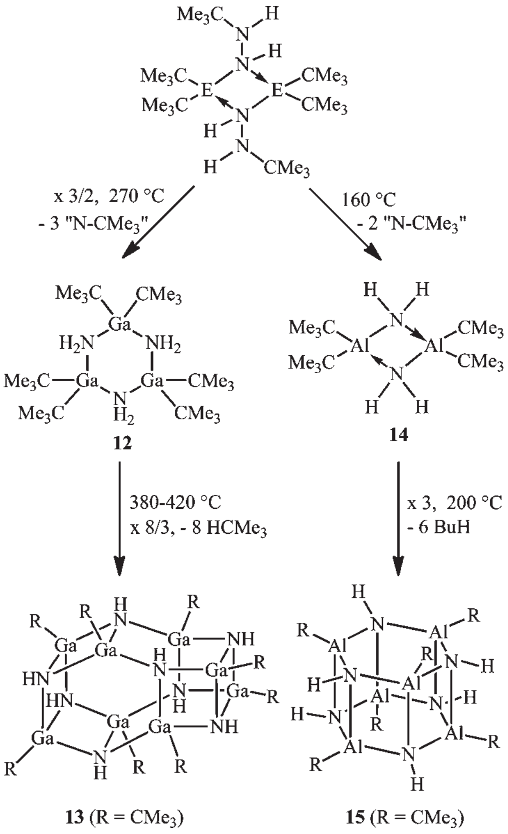
Scheme 2



compounds $E[N(SiMe_3)N(Me)SiMe_3]_3$ (**11**; E = Ga, In; Scheme 2), which were obtained by the reaction of the element halides with the corresponding lithium hydrazide via salt elimination.[42] It is interesting to note that both compounds have sterically shielding 1,2-bis(trimethylsilyl)hydrazide ligands.

■ THERMAL DECOMPOSITION OF HYDRAZIDES WITH THE CLEAVAGE OF N−N BONDS

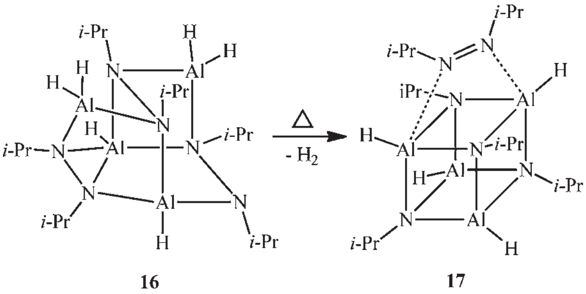
In a first step, thermolysis of the sterically shielded hydrazides $[(Me_3C)_2EN(H)N(H)CMe_3]_2$ (E = Al, Ga) in the absence of a solvent resulted in complete cleavage of the N−N bonds (eq 4). A temperature of 270 °C was required to initiate degradation of the gallium compound.[12] After 3 h and further heating to 300 °C, the trimeric amide $[(Me_3C)_2GaNH_2]_3$ (**12**) was isolated in 70% yield. **12** had been obtained previously by thermolysis of the ammonia adduct $(Me_3C)_3Ga{\leftarrow}NH_3$.[43] Further heating of compound **12** to about 400 °C afforded via elimination of butane the gallium imide $[Me_3CGaNH]_8$ (**13**), which was isolated in a moderate yield of 45%.[12] **13** has an unprecedented decahedral cage structure, which consists of four six-membered Ga_3N_3 heterocycles annulated with six four-membered Ga_2N_2 rings.



(4)

The higher polarity of Al−C bonds compared to Ga−C bonds is likely the reason for the much lower decomposition temperature of the corresponding aluminum hydrazide.[11] Few crystals of the dimeric amide $[(Me_3C)_2AlNH_2]_2$ (**14**, eq 4) were separated from a product mixture obtained at 160 °C. It was characterized by crystal structure determination and NMR spectroscopy. The compound had been obtained previously from thermolysis of the adduct $(Me_3C)_3Al{\leftarrow}NH_3$.[44] Despite the difficulties in isolating **14** in larger quantities, it may justifiably be assumed to be an intermediate in this reaction considering the above-mentioned reaction of the analogous gallium derivative. At 200 °C, the imide $[Me_3CAlNH]_6$ (**15**) was formed by alkane elimination[11] and isolated in 41% yield. **15** has a drumlike structure, with six aluminum and six nitrogen atoms occupying the 12 vertices of the polyhedron. Related structures have been reported previously, but **15** is the first compound of that type that (similar to **13**) has hydrogen atoms attached to the nitrogen atoms of the cage.

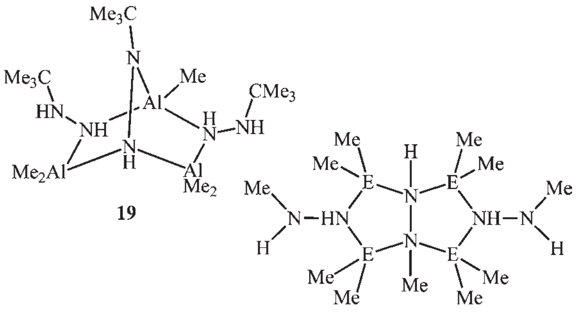
The second step of these reactions comprises elimination of butane and formation of the oligomeric alkylelement imides. Butane has, in fact, been identified by mass spectrometry as a volatile side product in a thermogravimetric experiment.[11] The mechanism of the first step of these thermolysis reactions is, by contrast, not fully understood. Conversion of the starting hydrazides to the dialkylelement amides **12** and **14** requires the formal loss of highly reactive nitrenes. We have not been able to identify any byproducts in the mass spectra of the thermolysis products or in the volatiles from these reactions trapped with liquid nitrogen. In the related thermolysis of the hydrazinediide **16**,[45] we could, however, isolate compound **17** (eq 5), a strong indication that nitrenes may indeed be key species in the thermal decomposition of hydrazines. **16** was obtained by hydroalumination of tetramethyl-2,3-diazabutadiene with $AlH_3{\leftarrow}NMe_2Et$ (see below).[45] It has a complicated cage structure formed by two Al−H, two AlH_2, and three $[^iPrNN^iPr]^{2-}$ groups. Heating this compound in vacuo to 30−70 °C yielded colorless crystals by sublimation. The crystal structure determination showed that cleavage of all N−N bonds had resulted in an aluminum imide with an Al_4N_4 heterocubane skeleton, $(HAlN^iPr)_4$ (**17**). Most fascinating was the presence of a diazene molecule, $^iPrN{=}N^iPr$, which was coordinated weakly with long Al−N distances of 246.5 pm to two aluminum atoms across a face of the cube (eq 5). Diazene is formally a nitrene dimer, and its isolation substantiates the possible formation of nitrenes as key intermediates in the decomposition reactions of hydrazides.



(5)

Thermolysis of the hydrazides $[(Me_3C)_2EN_2H_2Me]_2$ at 160 (E = Al) or 170 °C (E = Ga) afforded two unprecedented compounds (**18**, eq 6), in which two metal atoms are bridged by $[NH_2]^-$ and $[MeNN{=}CH_2]^-$ anions.[12,29] Ammonia was detected by mass spectrometry as the rational byproduct.

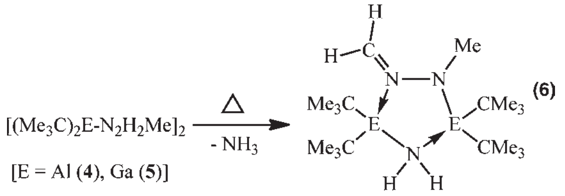
Scheme 3



19

20 (E = Ga, In)

The hydrazonide ligand of **18** features a N−N bond, but surprisingly one nitrogen atom is bonded to a methyl group, while the second is part of a C═N double bond. This is only possible if compounds **18** were formed in a complex rearrangement process. We believe that both N−N bonds of the starting hydrazide are cleaved. Ammonia is eliminated to yield the N═CH_2 group. The second hydrazide is converted into the amido bridge and a nitrene fragment, "N−Me", which inserts into an Al−N bond to the N═CH_2 group. Heating of these compounds to about 400 °C resulted in further decomposition reactions that differed considerably for the two metals. The gallium compound afforded the tetrameric cyanide $[(Me_3C)_2GaC{\equiv}N]_4$, which consists of a planar 12-membered $Ga_4C_4N_4$ heterocycle, in 55% yield.[12] This reaction exemplifies the astonishing thermal stability of the $GaCMe_3$ groups. The aluminum compound, in contrast, was converted to an insoluble, dark-red material of unknown composition.



(6)

18 (E = Al, Ga)

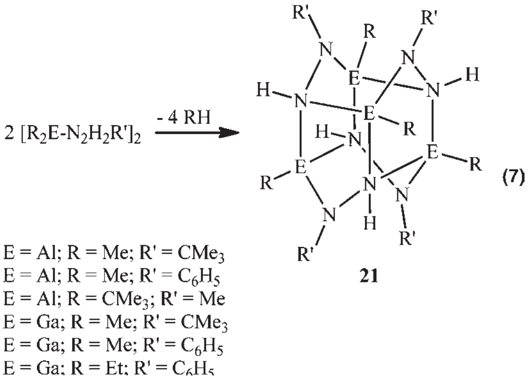
THERMOLYSIS OF HYDRAZIDES WITH PRESERVATION OF THE N−N BONDS (I): FORMATION OF MIXED HYDRAZIDES−1,2-HYDRAZINEDIIDES

Further deprotonation of hydrazides leads formally to dianionic hydrazinediides. Only a few compounds have so far been isolated that have both types of hydrazine groups in a molecule.[10,11,15,22] They may be considered as intermediates in the thermolysis reactions described below, although they could not be isolated or detected by NMR spectroscopy in further reactions. These compounds feature unique bicyclic structures with hydrazinediide ligands as the key building blocks in the central bridging position. $(AlMe_2)_2(MeAl)(HNNCMe_3)[N(H)N(H)CMe_3]_2$ (**19**; Scheme 3) was obtained by the treatment of $AlMe_3$ with $H_2NN(H)CMe_3$ at room temperature.[11] It has an unprecedented heteronuclear norbornane-type structure with a six-membered Al_3N_3 ring in a boat conformation. Two opposite atoms of the heterocycle are bridged by a nitrogen atom of the hydrazinediide group. Its sterically less shielded NH nitrogen atom is coordinated to two aluminum atoms of the $AlMe_2$ groups, while the one bonded to the *tert*-butyl group is tricoordinate and attached to only one aluminum atom. Both nitrogen atoms of the sterically less shielded methylhydrazinediide, $[MeNNH]^{2-}$, are, in contrast, coordinated to two gallium or indium atoms to give two annulated five-membered heterocycles with the hydrazinediide group in the central position (**20**; Scheme 3).[10] The indium derivative was formed spontaneously in 71% yield upon the treatment of $InMe_3$ with $H_2NN(H)Me$ at room temperature. The Ga−C bonds of $GaMe_3$ are less reactive and allow isolation of the relatively persistent adduct $Me_3Ga{\leftarrow}N(H)Me\text{-}NH_2$ (**2**), which is converted into the hydrazinediide in 74% yield only after heating for 2 h in toluene under reflux conditions. A related compound has been obtained from the reaction of $GaMe_3$ with N_2H_4.[22]

THERMOLYSIS OF HYDRAZIDES WITH PRESERVATION OF THE N−N BONDS (II): FORMATION OF 1,2-HYDRAZINEDIIDES

The two negatively charged nitrogen atoms of the hydrazindiide groups, $[HNNR']^{2-}$, are, as shown above, very well suited to bridge up to four metal atoms and to form oligonuclear cage compounds. These ligands are accessible by facile routes via the thermolytic decomposition of simple aluminum or gallium hydrazides in solution or in the solid state. The optimum temperature for the second deprotonation varies from 70 to 180 °C and does not correlate systematically to steric shielding or the polarity of the E−C bonds. These reactions should be conducted with the utmost care and should be preceded by thermogravimetric and calorimetric experiments because, in some cases, violent exothermic decomposition was observed, which on a preparative scale may cause a serious explosion. Details are given in most of the respective references. The yields of the isolated hydrazinediides are between 60 and 80%. Their structures may be derived from Al_4N_4 heterocubanes in which up to four edges are bridged by nitrogen atoms of intact N−N bonds.

The dual deprotonation of hydrazines leads to tetranuclear compounds of the type $[REN(H)N(R')]_4$ (**21**; E = Al, Ga; eq 7; Figure 1), in which two E_2N_4 heterocycles in a boat conformation are connected by four E−N bonds,[11−13,18,25,29] creating four five-membered E_2N_3 heterocycles (cf. early reports on similar structures of boron hydrazinediides[46]). A total of 1 equiv of the corresponding alkane is released per formula unit of the starting hydrazide, and all N−N bonds remain intact. Similar to the situation in the mixed hydrazine−hydrazinediide compounds described in the previous section, the nitrogen atoms of the N−H groups are coordinatively saturated and coordinated to two metal atoms. They occupy half of the vertices of the Al_4N_4 heterocubane skeleton. The tricoordinate NR′ nitrogen atoms are bound to only one metal atom and bridge four of the eight



(7)

21

E = Al; R = Me; R' = CMe_3
E = Al; R = Me; R' = C_6H_5
E = Al; R = CMe_3; R' = Me
E = Ga; R = Me; R' = CMe_3
E = Ga; R = Me; R' = C_6H_5
E = Ga; R = Et; R' = C_6H_5

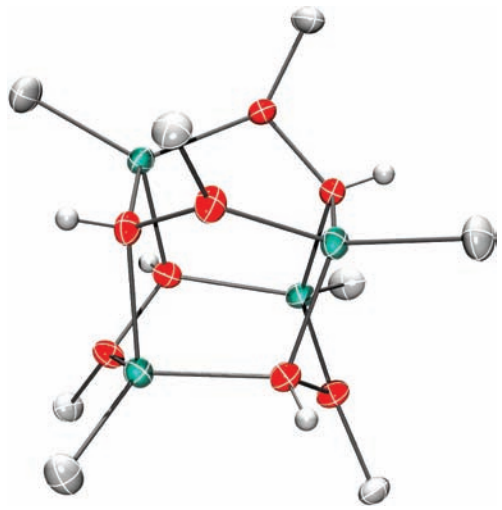


Figure 1. Molecular structure of $(\mathrm{AlMe})_4[\mathrm{N(H)N(CMe_3)}]_4$ (red, nitrogen atoms of hydrazinediides; green, aluminum atoms; the methyl groups of $\mathrm{CMe_3}$ are omitted; NH hydrogen atoms with an artificial radius).

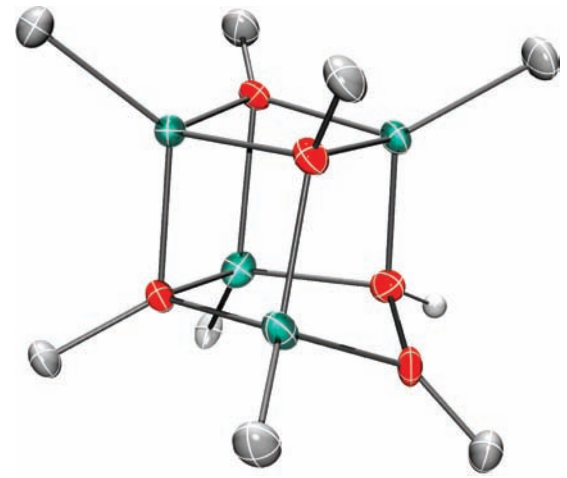
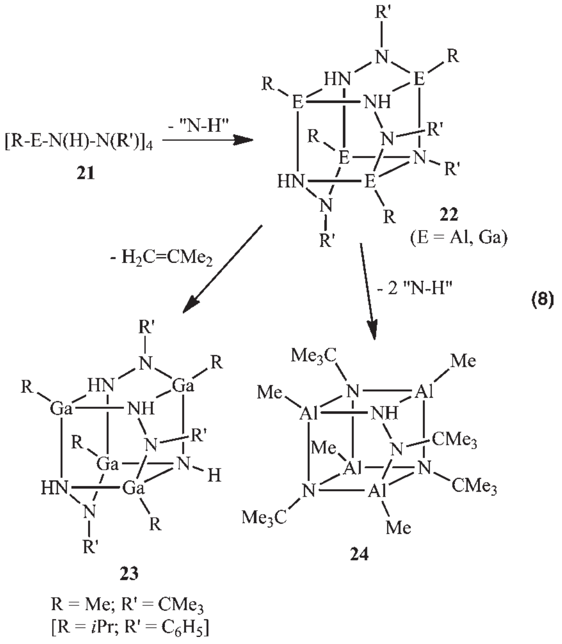


Figure 2. Molecular structure of $(\mathrm{AlMe})_4(\mathrm{NCMe_3})_3[\mathrm{N(H)N(CMe_3)}]$ (**24**; red, nitrogen atoms of hydrazinediide and imide $\mathrm{NCMe_3}$; green, aluminum atoms; the methyl groups of $\mathrm{CMe_3}$ are omitted).

edges of the cube. Their coordination sphere is either trigonal-pyramidal or almost planar.

Insight in the further decomposition processes was gained from the gradual degradation of certain hydrazinediides that allowed isolation and characterization of intermediates (eq 8). In the case of R = Me and R′ = $\mathrm{CMe_3}$, heating of the cages led to cleavage of a single N−N bond and the formation of $(\mathrm{ER})_4[\mathrm{N(H)N(R')}]_3(\mathrm{NR'})$ (**22**; eq 8).[11,12] Formally, a molecule of nitrene, “N−H”, is hereby released per formula unit. The structure of the products may once more be derived from a heterocubane skeleton, but one vertex is now occupied by an imido group, $[\mathrm{NR'}]^{2-}$. Three hydrazido groups remain intact and bridge three vertices of the cube with their tricoordinate nitrogen atoms. These cages have a 3-fold rotation axis and structurally resemble the phosphorus anion “ufosane”, $[\mathrm{P_{11}}]^{3-}$.[47] Further heating of **22** produced different reaction products. The release of isobutene and conversion of *tert*-butylimido into an NH group was observed for E = Ga (**23**).[12] A similar compound was obtained in 69% yield by heating (180 °C) the gallium hydrazide $[(^i\mathrm{Pr_2})\mathrm{Ga_2}[\mathrm{N(H)N(H)C_6H_5}][\mathrm{N(C_6H_5)NH_2}]]$.[12] By contrast, thermolysis of the respective tetraaluminum trishydrazinediide **22** (E = Al) proceeded via the formal release of two further nitrene molecules and yielded compound **24**, which has only a single intact N−N bond but three imido groups, $\mathrm{NCMe_3}$ (Figure 2).[11] **24** showed in solution a remarkable dynamic behavior indicative of a free rotation of the hydrazinediide group across a triangular face of three adjacent aluminum atoms (hydrazine twist). The rotational barrier, as determined by NMR experiments and quantum-chemical calculations (B3LYP/6-311G(d,p) and SCS-MP2), is only 10 kcal/mol. Calculations indicate the rotation to proceed via an intermediate state, which is only 3.4 kcal/mol above the ground-state molecule and is characterized by a change in the coordination number of the nitrogen atoms (NH, 4 → 3; $\mathrm{NCMe_3}$, 3 → 4).[11]



(8)

The remarkable octagallium compound $(\mathrm{GaMe})_8[\mathrm{N(H)N(CMe_3)}]_4\mathrm{O_4}$ (**25**; Figure 3) was formed in a reproducible manner in 23% yield in the presence of stoichiometric quantities of water.[12] Further 1,2-hydrazinediides have been obtained on other routes,[14,48] such as hydroalumination of 2,3-diazabutadienes[45,49] or a diazene,[50] the reaction of hydrazides with element hydrides,[15,32,36,51,52] the treatment of element halides with dilithium bis(trimethylsilyl)hydrazide,[53] or the reaction of a gallium(I) aryl compound with a diaryldiazene.[54] These methods have considerable disadvantages such as the formation of inorganic salts as byproducts, the coordination of lithium cations to the hydrazide groups,[32,49] N−N bond cleavage reactions,[21,49] or limited accessibility of the starting materials. Hydroalumination of tetramethyl-2,3-diazabutadiene has been used for generation of a unique cage and an unprecedented tricyclic compound.[45] The applicability of this method is, however, rather limited because, in most cases, only half of the C═N double bonds are reduced to yield hydrazonides.[49,55]

■ THERMOLYSIS OF HYDRAZIDES WITH PRESERVATION OF THE N−N BONDS (III): FORMATION OF A HYDRAZINETETRAIDE

A unique cage compound (**26**) was obtained from thermolysis of the bicyclic mixed hydrazide−hydrazinediide

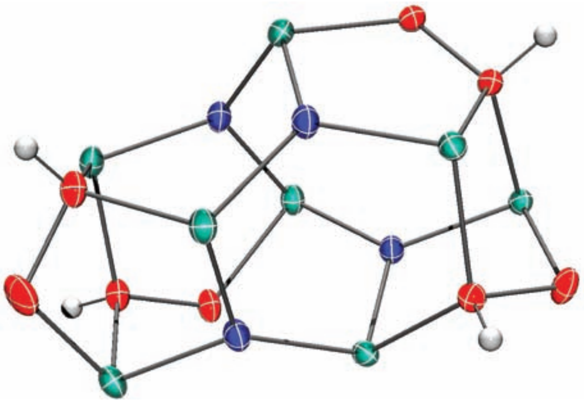
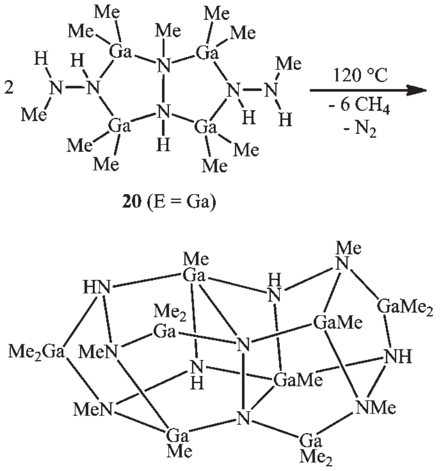


Figure 3. Molecular structure of $(GaMe)_8[N(H)N(CMe_3)]_4O_4$ (**25**; red, nitrogen atoms of hydrazinediide; green, gallium atoms; blue, oxygen atoms; gray, hydrogen atoms of hydrazinediide; the methyl and *tert*-butyl groups are omitted).

$(Me_2Ga)_4[N(H)N(Me)][N(H)N(H)Me]_2$ (**20**; E = Ga) in the absence of a solvent at 120 °C (eq 9).[56] It was isolated in a moderate yield of 42% and features as an extraordinary structural motif a completely deprotonated hydrazine, $[NN]^{4-}$ (hydrazinetetraide or pernitride), fragment, which is stabilized by coordination to six gallium atoms (Figure 4). The metal atoms are in a staggered arrangement. The overall structure comprises eight gallium atoms, the hydrazinetetraide fragment in the center, and four 1,2-hydrazinediide ligands. The cage is composed of 10 five-membered Ga_2N_3 heterocycles in an approximate envelope conformation and one puckered four-membered Ga_2N_2 ring. The N−N bond is with 154.9(6) pm comparatively long. Following the increasing electron density at the nitrogen atoms, a steadily increasing N−N distance is observed, ranging from <145 pm in neutral hydrazines to about 148 pm in monoanionic hydrazides and 155 pm in the tetraide. An emission band in the Raman spectrum at 892 cm^{-1} was identified as the N−N stretching vibration of the hydrazinetetraide moiety.[56] Only a very few transition-metal-stabilized pernitrides have been reported in the literature.[57] They are considered to be important intermediates in nitrogen activation and are investigated for possible applications in materials science.



20 (E = Ga) (9)

26

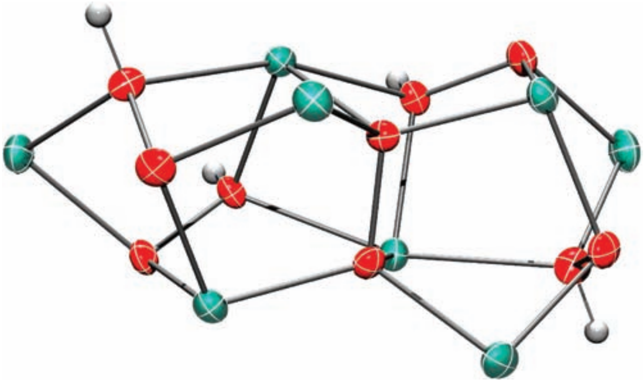
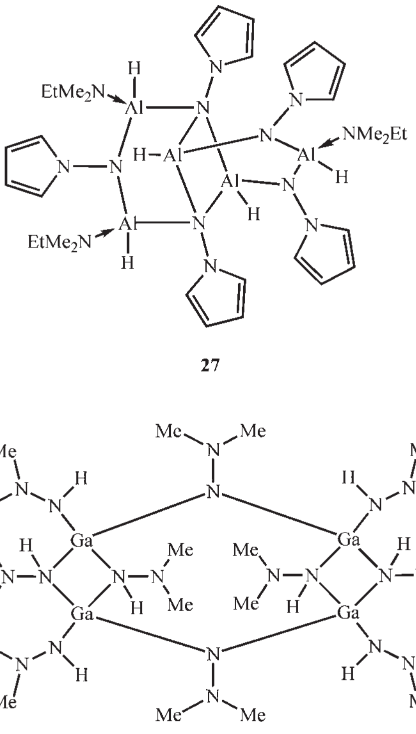


Figure 4. Molecular structure of $(GaMe_2)_4(GaMe)_4(N_2)[N(H)N(Me)]_4$ (**26**; red, nitrogen atoms; green, gallium atoms; gray, hydrogen atoms of hydrazinediide; the methyl groups are omitted).

Scheme 4



27

28

1,1-HYDRAZINEDIIDES

1,2-Deprotonation of hydrazines may be prevented by dialkylation of one of their nitrogen atoms, as exemplified by H_2NNMe_2 or $H_2NNC_4H_4$. Dual deprotonation should yield 1,1-hydrazindiides, R'_2NN^{2-}, which are excellent building blocks for the generation of cages because of the propensity of their terminal nitrogen atoms to coordinate up to three metal atoms simultaneously. Accordingly, the treatment of 1-aminopyrrole with the alane−amine adduct $H_3Al{\leftarrow}NMe_2Et$ yielded compound **27** in a moderate yield of 36% (Scheme 4).[52] Its molecular structure consists of five 1,1-hydrazinediide ligands, three $AlH(NMe_2Et)$ groups, and two AlH groups. The aluminum atoms of the central, significantly puckered Al_2N_2 heterocycle are bridged by an N_2Al unit, while its nitrogen atoms are connected by an Al_2N group. An interesting tricyclic mixed hydrazinide−1,1-hydrazinediide (**28**) was obtained by hydrogen elimination upon heating of the dimeric hydrazide $[H_2GaN(H)NMe_2]_2$ in an excess of dimethylhydrazine to 70 °C (Scheme 4).[37] **28** has two four-membered heterocycles with four monoanionic hydrazides in terminal and bridging positions. They are bridged by two 1,1-hydrazinediide ligands. A similar compound, $[Al\{N(H)NMe_2\}_2]_2[AlN(H)NMe_2]_2(NNMe_2)_4$, was isolated from the reaction of $HAl(NMe_2)_2$ with 1,1-dimethylhydrazine.[58]

CONCLUSIONS

Hydrazides of the heavier group 13 elements have, for some time, been used as single-source precursors for the generation of element nitrides by thermolysis. The mechanisms of the degradation processes and the structures of the intermediates were, however, until recently poorly understood. The most promising route to carrying out these reactions is treatment of the readily available trialkylelement derivatives with hydrazines. Simple adducts were formed that, when heated, gave heterocyclic or cage compounds with monoanionic hydrazide, dianionic hydrazinediide, or even tetraanionic hydrazinetetraide ligands. The special coordination behavior of the bidentate hydrazine ligands has led to a large variety of observable structural motifs. The products of thermolysis depend on the substitution patterns of the starting materials. N−N bond cleavage as the initiating step in the case of the sterically shielded *tert*-butylelement derivatives yielded amide or imide compounds. By contrast, alkane elimination and preservation of the N−N bond was the preferred starting reaction in the case of alkylaluminum or -gallium compounds with smaller substituents such as isopropyl or methyl. Formal elimination of *tert*-butylnitrene, "$NCMe_3$", determined the decomposition reaction of the *tert*-butylelement compounds, while nitrene, "NH", was formally released from the hydrazinediide cages at elevated temperatures. A complete understanding of these reaction pathways is crucial to the development of a rational strategy for the further application of these thermolysis reactions for the deposition of aluminum or gallium nitrides. Systematic investigations into the formation of element nitrides from various hydrazide precursors are currently in progress. Preliminary thermogravimetry experiments have yielded residues whose mass remained constant at temperatures above 300 or 400 °C. The remaining solids are light to dark gray and formed amorphous solids as determined by X-ray diffraction. The weight loss corresponds with an error bar of about ±10% to the formation of nitrides. We therefore conclude that further experiments into the degradation of hydrazides remain a valuable task for future work.

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ACKNOWLEDGMENT

We are grateful to the Deutsche Forschungsgemeinschaft for generous financial support.

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