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From *tert*-Butylhydrazine Adducts of AlR_3 (R = Me, CMe_3) to Oligonuclear AlN Cage Compounds – Evidence for a Hydrazine Twist Across an Al_3 Triangle

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The thermal decomposition of the hydrazine adducts $R_3Al{\leftarrow}NH_2{-}N(H)CMe_3$ (**1a**, R = CMe_3; **1b**, R = Me) was investigated. Compound **1a** afforded the hydrazide $[(Me_3C)_2Al{-}N(H){-}N(H){-}CMe_3]_2$ (**2**) upon heating to 155 °C. Compound **2** is dimeric in the solid state with a four-membered Al_2N_2 heterocycle in its molecular core. Heating of **2** to 190 °C gave the drum-like imidoalane $[Me_3CAlNH]_6$ (**4**) in which the Al and N atoms occupy the vertices of a hexagonal prism. This reaction is believed to proceed via the dimeric amide $[(Me_3C)_2Al{-}NH_2]_2$ (**3**) that was isolated in small quantities from a mixture obtained at a slightly lower temperature. Adduct **1b**, which is sterically less shielded than **1a**, decomposes readily at room temperature to yield an unprecedented Al–N cage compound, $[Me_2Al{-}N(H){-}N(H)CMe_3]_2[MeAl{-}N(CMe_3){-}NH]$ (**5**), with a norbornane-like arrangement of three Al and four N atoms, and a hydrazinediido group in the bridging position. Heating of **5** gave, with the release of methane, the tetraaluminum compound $[MeAlN(H){-}NCMe_3]_4$ (**6**) in which four hydrazinediide moieties are bridged by AlMe groups. Heating of **6** resulted in the gradual degradation of the N–N bonds and the formal release of 1 or 3 equiv. of nitrene, N–H, to give the unique cage compounds $(MeAl)_4[N(H){-}NCMe_3]_3(NCMe_3)$ (**7**) and $(MeAl)_4[N(H){-}NCMe_3](NCMe_3)_3$ (**8**). The structures of compounds **6**–**8** may be derived from Al_4N_4 cubes in which a number of edges (four, three or one) are bridged by nitrogen atoms of hydrazinediido groups.

Introduction

Our longstanding interest in the synthesis and reactivity of hydrazine adducts of the heavy Group 13 elements and their respective hydrazides is due to the fascinating structural diversity[1] of this class of compounds, and their potential applicability as precursors for the generation of element nitrides by MOCVD or related procedures.[2] Several hydrazine adducts of trialkylelement compounds, $R_3E{\leftarrow}NH_2{-}N(H)R'$, have recently been synthesized and characterized by XRD analysis.[3–8] They were found to be monomeric with the sterically low-shielded NH_2 group usually being coordinated to the Group 13 element, despite theoretical calculations indicating this to be the thermodynamically unstable isomer. The thermodynamically favored isomer, in which the more basic N(H)R′ group is coordinated to the metal atom, could only be substantiated in the case of the corresponding Ga derivative with a small methyl substituent (R = R′ = Me).[4] The hydrazine adducts were found to decompose spontaneously at room temperature, or upon slight warming, to yield the corresponding hydrazides featuring monoanionic hydrazide groups.[3,4,6–9] These hydrazides are usually dimeric, with the exception of the sterically crowded monomeric compounds $In[N(SiMe_3){-}NMe_2]_3$[10] and $Me_3C{-}Al[N(SiMe_3){-}N(H)SiMe_3]_2$,[11] and show a variety of structural motifs ranging from four- to six-membered heterocycles,[3,4,6–9,12,13] and zero, one, or two endocyclic N–N bonds (Scheme 1). Transannular repulsion between partially charged metal and nitrogen atoms disfavors the formation of E_2N_2 heterocycles, whereas electrostatic attraction between metal and nitrogen atoms and steric interactions between the substituents favor the creation of small heterocycles. Experimentally, the four-membered ring was found to be the dominant isomer with only few examples of five- and six-membered heterocycles being structurally verified. In the absence of steric influences the five-membered heterocycles were calculated to be thermodynamically favorable.[13] Experiments on the controlled thermolysis of hydrazides have given access to large EN cages such as $[R{-}E{-}N(H){-}NR']_4$ (R = Me, E = Al, R′ = Ph;[7] R = Et, E = Ga, R′ = Ph;[7] R = Me, E = Ga, R′ = CMe_3;[8] R = *i*Pr, E = Ga, R′ = Ph;[8] R = Me, E = Ga, R′ = CMe_3 or Ph[3,14]), $(Me_3CGaNH)_8$[8] and very recently the unprecedented gallium compound $(GaMe)_4$-

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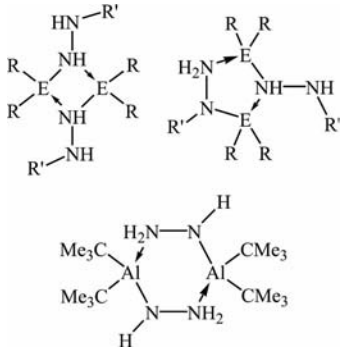
$(GaMe_2)_4[N(H)–NMe]_4(N_2)$[15] that features as a unique structural motif a completely deprotonated tetraanionic N_2^{4-} group stabilized by six gallium atoms. These compounds and larger cages may, under thermolysis conditions, occur as intermediate compounds between the initially formed adducts and the corresponding element nitrides. Their constitution may have considerable influence on the course of the reactions and on the purity of the nitrides finally obtained. A thorough investigation of these intermediates is crucial for the development of a rational strategy for the application of these compounds in materials chemistry. In this paper we present our results on the thermal decomposition of the adducts **1a** and **1b**.

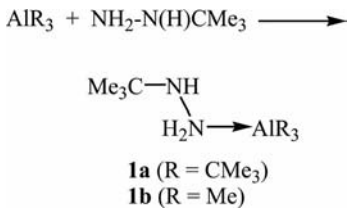


Scheme 1. E = Al, Ga, In.

Results and Discussion

Thermolysis of the Adduct $(Me_3C)_3Al←NH_2–N(H)CMe_3$ (1a)

The hydrazine adducts **1a**[5] and **1b** were synthesized, according to standard procedures, by mixing the corresponding trialkylaluminum compound with *tert*-butylhydrazine in pentane [Equation (1)]. The characterization of the previously unknown adduct **1b** gave no surprising results. NMR spectroscopy and XRD results (Figure 1) for **1b** are consistent with a monomeric species in which the less basic [relative to the N(H) group] but sterically more accessible NH_2 group is coordinated to the aluminum atom. Bond lengths and angles are unexceptional and compare well to reported values of related aluminum–hydrazine adducts [Al1–N1 202.1(4), N1–N2 145.0(6) pm].[5,7] Heating of **1a** to 160 °C resulted in the loss of isobutane (gas evolution at 155 °C) and the formation of the aluminum hydrazide **2** in 72% yield [Equation (2)]. Compound **2** has been obtained previously through salt elimination from the reaction of $(Me_3C)_2AlCl←NH_2–N(H)CMe_3$ with *n*BuLi.[16] The formation of **2** according to Equation (2) with volatile isobutane as the only by-product is a very convenient route to **2**, and is clearly superior to the literature procedure. Our method allows for the synthesis of **2** on a larger scale, which permits its reactivity in further reactions to be studied. Steric reasons are probably responsible for the fact that **2** was found (in the solid state) to consist of a planar four-membered Al_2N_2 heterocycle with the *tert*-butyl groups on the nitrogen atoms being *trans* to each other.[16] The possible formation and stability of five- and six-membered heterocycles and the influence of substituents on their formation, has been discussed in the Introduction.



1a (R = CMe_3)
1b (R = Me) (1)

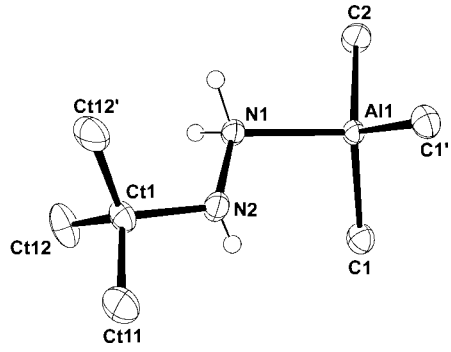
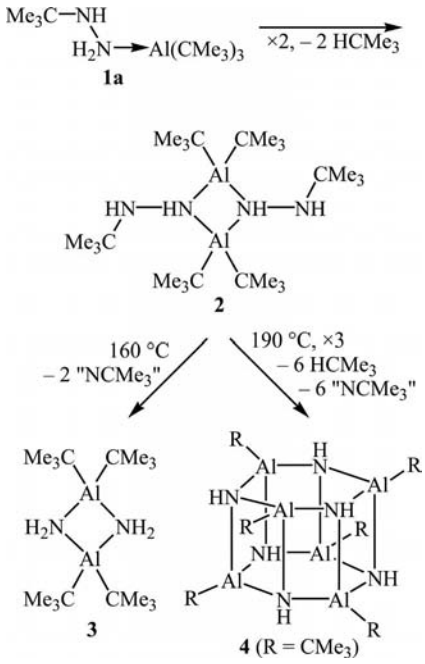


Figure 1. Molecular structure and atomic numbering scheme of **1b**; displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Selected bond lengths [pm]: Al1–N1 202.1(4), N1–N2 145.0(6).



1a ×2, – 2 $HCMe_3$ → **2**; **2** 160 °C, – 2 "$NCMe_3$" → **3**; **2** 190 °C, ×3, – 6 $HCMe_3$, – 6 "$NCMe_3$" → **4** (R = CMe_3) (2)

TGA analysis of **2** revealed a major mass loss (ca. 70%) between 160 and 275 °C. Butane was identified unambiguously in the mass spectrum of the gaseous decomposition products. Further peaks could not be assigned. Heating of the sample to 400 °C gave a grey amorphous powder equiv-

alent to 22% of the original mass, which is close to the calculated value expected for the quantitative formation of AlN (calcd. 18%). Subsequently, we heated a larger quantity of **2** in a Schlenk flask at 160 °C for a period of 2 h. A sticky solid of unknown composition formed at the bottom of the flask, while the glass wall of the flask above the solid was covered with a thin film of a highly viscous liquid. The latter was dissolved in pentane and after recrystallisation from toluene at –45 °C was identified as a mixture of the starting material **2** (which incidentally can be purified by sublimation in vacuo) and a few crystals of **3**. The latter were separated from the starting material by hand under a microscope, and characterized by NMR spectroscopy. The NMR spectroscopic parameters of **3** are identical to data previously reported by Interrante et al.[17] who had obtained this aluminum amide from $Al(CMe_3)_3$ and NH_3 in hot xylene. They generated single crystals by slowly cooling a hot xylene solution of the amide. XRD analysis of these crystals revealed the presence of a trimer with a planar Al_3N_3 heterocycle.[17] Interestingly, a preliminary crystal structure determination of the thermolysis product **3** [Equation (2)] gave a dimeric formula unit with a planar Al_2N_2 heterocycle. We abstain from a detailed discussion of the structural parameters because repeatedly the crystal quality proved to be insufficient to obtain a satisfactory refinement of the structure. Related amides bearing relatively small substituents such as $[Me_2Al–NH_2]_3$,[17,18] *cis*-$[Me_2Al–N(H)Me]_3$[19] and *trans*-$[Me_2Al–N(H)Me]_3$[19] are trimeric with a six-membered Al_3N_3 heterocycle in a chair or skew-boat conformation, whereas the sterically better shielded silyl-substituted amides $[(Me_3Si)_2Al–NH_2]_2$[20] and $[\{(Me_3Si)_2N\}_2Al–NH_2]_2$[21] are dimeric with a planar Al_2N_2 heterocycle. The steric demand of the *tert*-butyl groups of $[(Me_3C)_2Al–NH_2]_n$ may lead to a situation in which the dimeric and trimeric forms become comparable in energy. Ignoring kinetic inhibitions, the trimer $[(Me_3C)_2Al–NH_2]_3$ is likely to be thermodynamically slightly more stable than the dimer $[(Me_3C)_2Al–NH_2]_2$, as the former was obtained at 115 °C, whereas the latter was formed at higher temperature (160 °C). An alternative or additional explanation may be that the formation of the dimer is the result of pre-organization in the dimeric starting material **2**, which with the formal loss of nitrene, $N–CMe_3$, is likely to give the dimeric compound $[(Me_3C)_2Al–NH_2]_2$. The interconversion to give the trimeric formula unit may be hindered by a sufficiently high barrier of activation.

When in a further reaction hydrazide **2** was heated under argon to 190 °C, an aluminum–nitrogen cage compound **4** was obtained after cleavage of all the N–N bonds in **2**. Compound **4** was isolated in a moderate yield of 42% by recrystallization of the reaction residue [Equation (2)]. Other products could not be identified. The NMR spectrum of **4**, which is influenced by its $\bar{3}$ symmetry in solution, is deceptively simple with two singlets for the $AlCMe_3$ and NH protons. The solid-state structure of **4** (Figure 2) shows a hexameric formula unit with a drum-like cage with approximate $\bar{3}$ symmetry. Two independent molecules are found in the unit cell, one of which is located on a centre of symmetry. The hexagonal prisms have two six-membered, almost ideally planar Al_3N_3 heterocycles with a maximum deviation from the least-square plane of ca. 4.4 pm. These six-membered rings are connected by six Al–N bonds. The bond lengths within the six-membered rings (188.4 pm on average) are significantly shorter than those between the rings (196.0 pm). The aluminum and nitrogen atoms all have distorted tetrahedral coordination spheres. The angles within the four-membered rings are very similar and are close to 90°, while the angles in the six-membered rings are smaller for N–Al–N (112.9° on average) than for Al–N–Al (126.7°), and are presumably influenced by the steric demand of the bulky CMe_3 group on Al. The hexagonal prism is a well-known structural motif for oligomeric organoaluminum imides, as is evident from reported structures such as $[HAlNiPr]_6$,[22] $[HAlNnPr]_6$,[23] $[MeAlNPh]_6$,[24] $[HAlN(CH_2)_3NMe_2]_6$[25] etc. Compound **4** is, however, unique in being the first example that features a structural motif with NH rather than NR′ functionalities that may influence the reactivity of the compound, in particular with respect to further degradation.

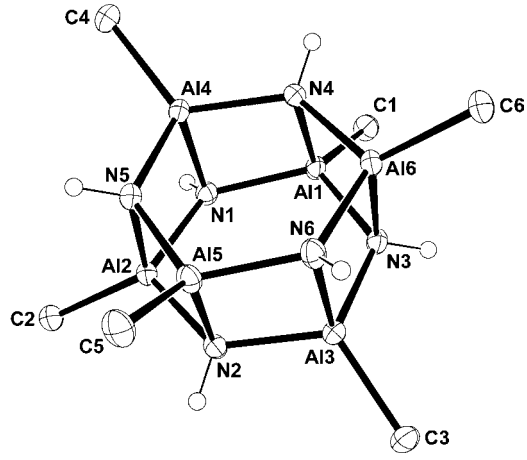


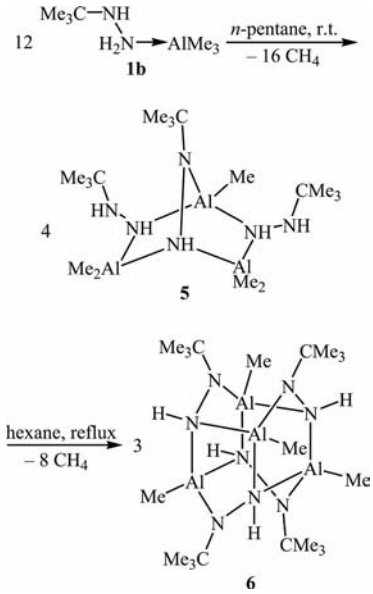
Figure 2. Molecular structure and atomic numbering scheme of **4** (only one molecule is shown); displacement ellipsoids are drawn at the 40% propability level. Methyl groups have been omitted for clarity. Hydrogen atoms of NH groups have been drawn with arbitrary radius. Selected bond lengths (average) [pm] and angles [°] (values for the second molecule of the asymmetric unit are given in square brackets): Al–N (Al_3N_3 ring) 188.4 [188.5], Al–N (Al_2N_2 ring) 196.0 [196.0]; N–Al–N (Al_3N_3 ring) 113.0 [112.8], Al–N–Al (Al_3N_3 ring) 126.8 [126.9], N–Al–N (Al_2N_2 ring) 89.8 [89.9], Al–N–Al (Al_2N_2 ring) 89.8 [89.7].

Reactions of the Adduct $Me_3Al←NH_2–N(H)CMe_3$ (1b)

It was described above that hydrazine adducts may eliminate, in a first step, hydrocarbons at high temperatures to give dimeric hydrazides [cf. Equation (2)]. In the case of the reaction between $AlMe_3$ and NH_2-N(H)Me the hydrazine adduct could not be isolated, and an immediate methane elimination was observed when the two reactants were combined at –30 °C. The isolated product was not the expected hydrazide, but the unusual tetraaluminum sesquihydrazide

$Al[\{\mu\text{-}N(H)\text{–}N(H)Me\}_2AlMe_2]_3$ that in the solid state features an octahedrally coordinated central aluminum atom that is attached to three chelating $[\mu\text{-}N(H)\text{–}N(H)Me]_2\text{-}AlMe_2$ groups.[4] In solution the sesquihydrazide dissociates readily into two dinuclear $Me_2Al[\mu\text{-}N(H)\text{–}N(H)Me]_2Al(Me)[N(H)\text{–}N(H)Me]$ fragments. In contrast, the hydrazine adduct **1b** was easily isolated from the related reaction of $AlMe_3$ with the bulkier $NH_2\text{–}N(H)CMe_3$ at low temperature [Equation (1), see above]. Warming of **1b** to room temperature resulted in spontaneous methane elimination and the formation of the unexpected mixed hydrazide/1,2-hydrazinediide compound **5** in a moderate yield of 45% [Equation (3)]. The composition of **5** was confirmed by its EI mass spectrum that has a 100% peak corresponding to the molecular mass of **5**, and its crystal structure determination, which revealed an unprecedented heteronuclear norbornane-type arrangement of three aluminum and four nitrogen atoms (Figure 3). The ^1H and ^{13}C NMR spectra of **5** are consistent with the compound having the expected approximate mirror-plane through the bridging atoms $N(H)\text{-}N(CMe_3)Al(Me)$ of the norbornane cage. Three signals with an intensity ratio of 2:2:1 are observed for the three different types of methyl groups, and likewise for the NH hydrogen atoms. The single NH resonance stems from the hydrogen atom attached to the bridgehead nitrogen atom and is shifted towards a relatively high field (δ = 1.73 ppm) compared to the other NH resonances (δ = 2.63 and 3.16 ppm). The unique molecular structure of **5** (Figure 3) is reminiscent of a distorted heteronuclear norbornane and may be described either as a six-membered Al_3N_3 heterocycle in a boat conformation with two opposite atoms (Al1 and N11) bridged by a nitrogen atom (N12) of a hydrazinediide group or, alternatively, as two fused five-membered Al_2N_3 heterocycles in an envelope conformation that share atoms N11, N12 and Al1 but have in contrast to norbornane two atoms deviating from the heterocyclic plane (N12 in ring N12, N11, Al2, N21, Al1; N11 in ring N11, N12, Al1, N31, Al3). The overall structure of **5** comprises two $AlMe_2$ groups and an AlMe fragment at the bridgehead position, further two monoanionic hydrazido groups with exocyclic N–N bonds and a twofold deprotonated hydrazinediide in a bridging position. The Al–N bond length [Al1–N12 182.1(1) pm] involving the three-coordinate alkyl-substituted nitrogen atom of the bridging hydrazinediide group is significantly shorter than the Al–N distances involving the four-coordinate nitrogen atoms of the NH groups (195.3 pm on average). Due to the stronger electrostatic repulsion the N–N bond length of the dianionic hydrazinediide moiety [N11–N12 151.2(2) pm] is longer than the N–N distances observed for the monoanionic hydrazide groups (147.8 pm). The latter corresponds well to the standard value detected for many other aluminum or gallium hydrazides (see Introduction).

When **5** was heated in hexane under reflux conditions, methane was eliminated, and the tetraaluminum tetrahydrazinediide $[MeAlN(H)\text{–}NCMe_3]_4$ (**6**) was obtained in good yield (71%) after crystallization from *n*-pentane [Equation (3)].



(3)

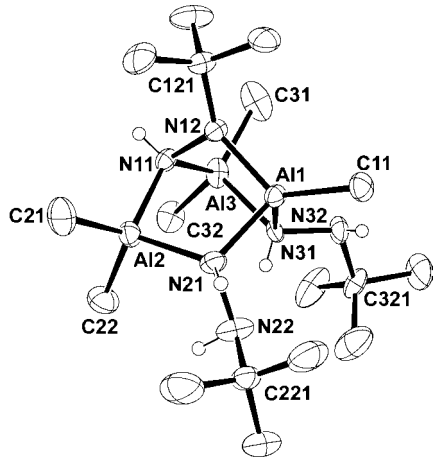
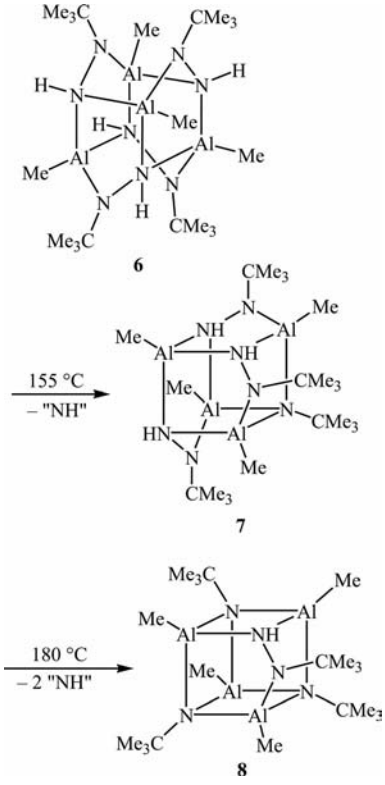


Figure 3. Molecular structure and atomic numbering scheme of **5**; displacement ellipsoids are drawn at the 40% probability level. Methyl groups (CMe_3) have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Selected bond lengths [pm]: Al1–N12 182.1(1), Al1–N21 192.5(2), Al1–N31 193.0(5), Al2–N11 194.4(2), Al2–N21 196.5(2), Al3–N11 195.5(2), Al3–N31 197.0(5), N11–N12 151.2(2), N21–N22 147.5(2), N31–N32 148.0(5).

The related aluminum and gallium derivatives $[MeAlN(H)\text{–}NPh]_4$,[7] $[Me_3CAlN(H)\text{–}NMe]_4$,[6] $[EtGaN(H)\text{–}NPh]_4$[7] and $[MeGaN(H)\text{–}NCMe_3]_4$,[3,14] have recently been synthesized at elevated temperatures directly from the corresponding dimeric hydrazides. Intermediates similar to the above norbornane-like compound **5** may also exist, but have so far never been isolated or identified by spectroscopic methods. Heating of **6** to 155 °C without a solvent yielded, with the formal loss of nitrene (N–H) from a single hydrazindiido ligand, the tetranuclear cage $(MeAl)_4[N(H)\text{–}NCMe_3]_3(NCMe_3)$ (**7**) [Equation (4)]. The corresponding gallium homologue has only recently been synthesized in a similar manner from $[MeGaN(H)\text{–}NCMe_3]_4$.[8] Nitrene in-

termediates that occur in the course of decomposition reactions of aluminum or gallium hydrazides have previously been postulated as being present in the formation of $(Me_3C)_2E(\mu\text{-}NH_2)[\mu\text{-}N(Me)\text{–}N(=CH_2)]E(CMe_3)_2$ (E = Al, Ga, In)[4,8] and a heterocubane Al_4N_4 cage compound.[26] The synthesis of the latter gave a unique adduct of the heterocubane with diazene, R′N=NR′, which may be formed by dimerization of the nitrene intermediate NR′ (R′ = *i*Pr). Further experimental evidence for the actual formation of nitrenes as intermediates in these thermolysis reactions is missing, which may be a result of their exceptionally high reactivity. The NMR spectra of **6** and **7** are very simple and are consistent with the high symmetry of the tetranuclear cages in solution. The chemical shifts in the spectra of **6**, **7** and the related cluster $[Me_3CAlN(H)\text{–}NMe]_4$[6] compare well with those of the reported gallium derivatives,[8] but are shifted – as a consequence of the lower electronegativity of aluminum – to higher field relative to the peaks in the spectra of the gallium compounds. All compounds could also be identified by their molecular ion peaks in their EI mass spectra.



(4)

The molecular structure of **6** (Figure 4) consists of two six-membered Al_2N_4 heterocycles in boat conformation that are linked by four additional Al–N bonds in such a way as to form four Al_2N_3 rings in an envelope conformation. An approximate $\bar{4}$ axis passes through the centers of the two six-membered heterocycles. The Al and N(H) atoms are coordinated in a distorted tetrahedral fashion, whereas the coordination spheres of the three-coordinate N(R′) atoms are almost ideally planar with the sum of all angles being >357°. The Al–N distances involving the three-coordinate nitrogen atoms are, at 182.7 pm (on average), significantly shorter than those involving the four-coordinate nitrogen atoms that are all close to an average value of 194.2 pm. It is interesting to note that the shorter Al–N distances are similar to those in $[Me_3CAlN(H)\text{–}NMe]_4$ (184.9 pm),[6] whereas quite different Al–N distances were observed in **4** for the four-coordinate nitrogen atoms in the six-membered heterocycles (190.8 pm), and 196.4 pm for the bonds connecting them. In contrast, in $[MeAlN(H)\text{–}NPh]_4$ the Al–N distances between the six-membered heterocycles are slightly shorter than those within the cycles.[7] The N–N bond lengths (149.9 pm on average) are within the characteristic range for hydrazinediido ligands (see above). The molecular structure of compound **7** (Figure 5) may be derived from a cube formed by four Al and four N atoms. Three edges of the cube are bridged by N–CMe_3 groups that are part of intact hydrazide groups (N2–N5, N3–N6 and N4–N7). The cube is completed by a *tert*-butylimide group (N1). The molecular structure approaches that of a regular polyhedron in which a threefold rotation axis passes through opposite vertices occupied by an AlMe group (Al1–C1) and the single imide ligand N–CMe_3 (N1–C10). The Al–N distances involving the nitrogen atoms of the hydrazinediido ligands correlate with the atomic coordination numbers and are shortest for the three-coordinate nitrogen atoms (184.7 vs. 193.1 pm on average). The Al–N distances involving the imide nitrogen atom are 193.8 pm. The N–N bond lengths (149.7 pm) are similar to those of **5** and **6**. The gallium analogue of **7**, $(MeGa)_4[N(H)\text{-}NCMe_3]_3(NCMe_3)$ **[7(Ga)]**, has only recently been synthesized.[8] This analogue shows disorder similar to that of the aluminum derivative **7**. The molecular structure of **7(Ga)** could be solved and refined only now in conjunction with that of **7** (Figure 6). An important point is that both compounds crystallize in the orthorhombic crystal system, but are not isostructural. Particularly interesting is that the length of

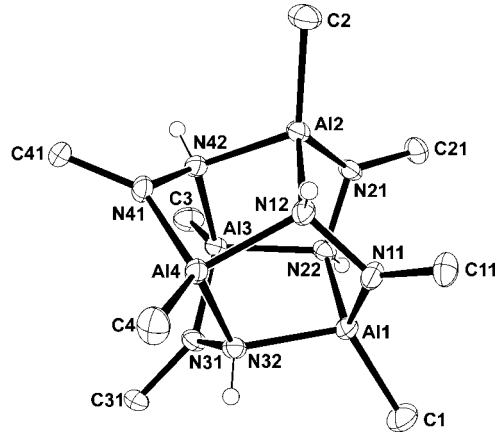


Figure 4. Molecular structure and atomic numbering scheme of **6**; displacement ellipsoids are drawn at the 40% propability level. Methyl groups (CMe_3) have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Selected bond lengths (average) [pm]: Al–N(CMe_3) 182.6, Al–N(H) 194.2, N–N 149.9.

the unit-cell *c*-axis of the gallium compound **7(Ga)** is half the length of that of **7**. The crystal structures differ in the crystal packing of their molecules. The packing of the gallium cages approaches that of a hexagonal close packed arrangement (ABAB sequence), whereas the aluminum cages pack in an ABCDABCD arrangement with a helical dislocation of the layers (Figure 7). Due to the higher electronegativity of gallium compared to aluminum, and the lower charge separation between Ga and N, the electrostatic contributions to the metal–nitrogen bonds are smaller in **7(Ga)** than in the Al derivative. The Ga–N bonds are longer than the corresponding Al–N bonds in **7** [Ga–N(CMe_3) of hydrazinediide (193.4 pm); Ga–N(H) of hydrazinediide (197.9 pm); Ga–N1 (imide) (198.9 pm)], whereas the average N–N bond length (146.4 pm) in **7(Ga)** is shorter than in **7**.

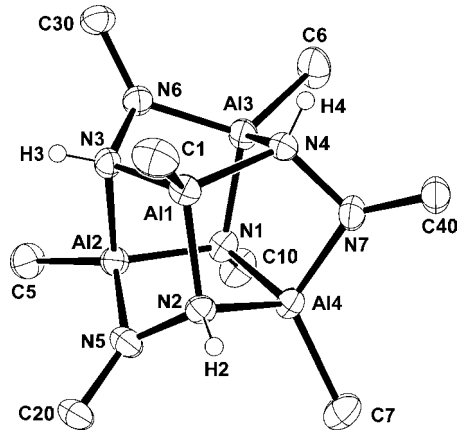


Figure 5. Molecular structure and atomic numbering scheme of **7**; displacement ellipsoids are drawn at the 40% probability level. Methyl groups (CMe_3) have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Selected bond lengths (average) [pm]: Al–N (hydrazinediide, CN = 3) 184.9, Al–NH (hydrazinediide, CN = 4) 193.1, Al–N1 (imide, CN = 4) 193.8, N–N 149.5.

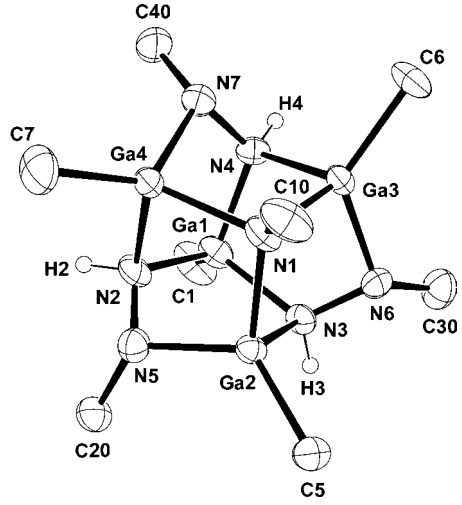


Figure 6. Molecular structure and atomic numbering scheme of **7(Ga)**; displacement ellipsoids are drawn at the 40% probability level. Methyl groups (CMe_3) have been omitted for clarity. Hydrogen atoms (NH only) have been drawn with arbitrary radius. Selected bond lengths (average) [pm]: Ga–N (hydrazinediide, CN = 3) 193.4, Ga–NH (hydrazinediide, CN = 4) 197.9, Ga–N1 (imide, CN = 4) 198.9, N–N 146.4.

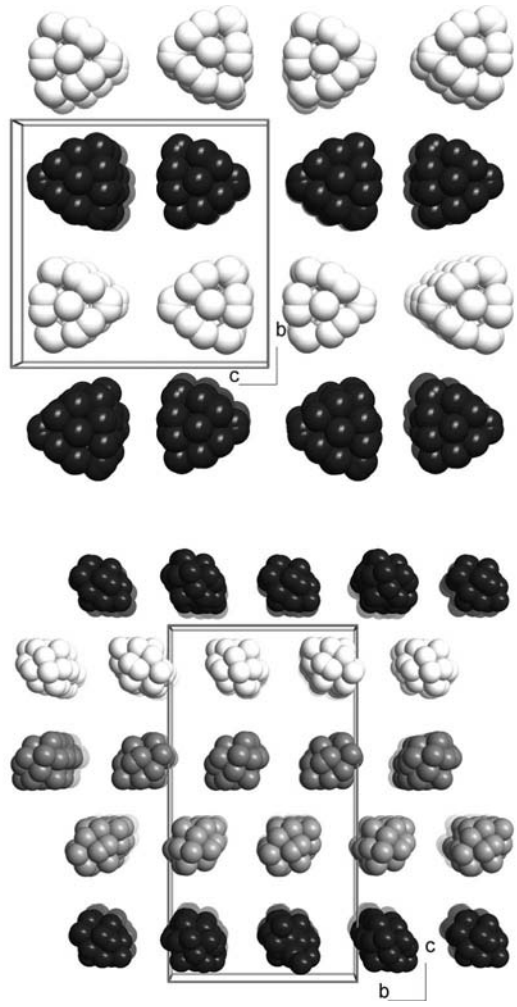
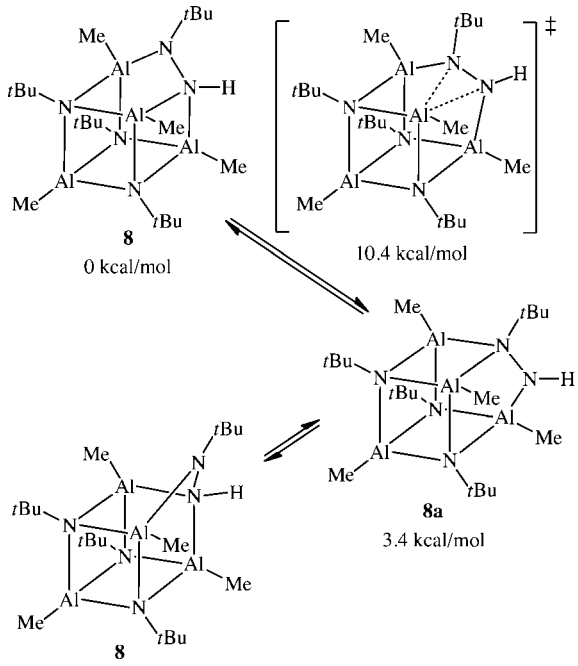


Figure 7. Packing of the molecules in the solid-state structures of **7(Ga)** (top) and the analogous aluminum compound **7** (bottom).

When neat compound **7** was heated to 180 °C, there was a formal loss of 2 equiv. of "NH" to yield the cage compound **8** that was isolated in a moderate yield of 57% [Equation (4)]. In contrast, the related thermolytic decomposition of the gallium analogue of **7**, **7(Ga)**, in refluxing toluene resulted in the loss of one molecule of isobutene from the *tert*-butylimide ligand and the formation of the compound $(MeGa)_4[N(H)–NCMe_3]_3(NH)$.[8] Compound **8** may be described as an AlN heterocubane in which one vertex is occupied by a hydrazinediido unit (Figure 8). The ^1H and ^{13}C NMR spectra of **8** are surprisingly simple showing, apart from the unique NH proton (^1H) signal, only two sets of resonances with an intensity ratio of 1:3 corresponding to the Me and CMe_3 groups, respectively. While this result contrasts with the molecule's lack of symmetry in the solid state, it may readily be explained by considering a low activation energy for the rotation of the hydrazinediido ligand that allows for essentially free rotation of the ligand across one face of the Al_4 tetrahedron formed with three

adjacent Al atoms (Al1′, Al2, Al3 in Figure 8). The rotation is very fast, and only at –90 °C could splitting of the AlMe resonances in the ^{1}H NMR spectrum into two broad signals (δ = –0.01 and –0.10 ppm, intensity ratio 1:2; [D$_8$]toluene) be observed. The rotational barrier was estimated with the Eyring equation to be 9.3 kcal/mol. Quantum chemical calculations have been performed to investigate this dynamic process. The two possible isomers **8** and **8a** [Equation (5)] differ in energy by only 3.4 kcal/mol. Isomer **8** represents the global minimum. The N–H nitrogen atom in **8** has a coordination number of four (Al–N 196.3 and 197.1 pm), whereas the N–CMe$_3$ nitrogen atom has an environment that is in accordance with previous results and the crystal structure of **8** (see below) and is tricoordinate (Al–N 187.4 pm). Isomer **8a** represents the inverse situation with the N–H group coordinated to only one aluminum atom (Al–N 186.3 pm), while the nitrogen atom attached to the *tert*-butyl group is coordinatively saturated (Al–N 201.2 and 202.4 pm). A transition state that has a structure with a rotated hydrazinediide subunit and with the N–N bond being side-on coordinated to an aluminum atom was located on the energy hypersurface. The calculated relative energy of only 10.4 kcal/mol is in excellent agreement with the experimental value. The transition state is close to the structure of the less stable isomer **8a**, since the Al–N(H) and Al–N(CMe$_3$) distances involving the side-one coordinated aluminum atom (223.9 and 203.2 pm) more closely resemble the distances observed in the isomer that has a higher relative energy with respect to **8**. The N–N bond lengths of all forms (**8**, **8a** and transition state) are almost unaffected with values between 149.0 and 149.1 pm.



(5)

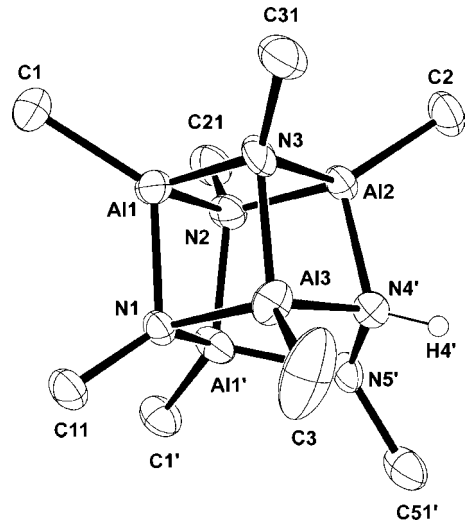


Figure 8. Molecular structure and atomic numbering scheme of **8**; displacement ellipsoids are drawn at the 40% propability level. Methyl groups (CMe$_3$) have been omitted for clarity. The hydrogen atom (NH) has been drawn with an arbitrary radius. Selected bond lengths (average) [pm]: Al1–N5 199(1), Al3–N4′ 193.4(6), Al2–N4′ 193.0(5), Al–N (imido, CN = 4) 194.8, N4–N5 146(1).

In the XRD-determined structure of **8** the molecule (Figure 8) is disordered over a crystallographic mirror plane. This disorder leads to an overlap of the hydrazinediide group with a *tert*-butylimide group (N4–N5–C51 and N3–C31 or N4′–N5′–C51′ and N3′-C31′, respectively) and results in relatively large standard deviations for the associated bond lengths and angles. Therefore, we abstain from a detailed discussion of the structural parameters. Nevertheless, the overall molecular structure of **8** has been established unequivocally. The unprecedented structural motif of a single hydrazinediide unit at a vertex of a distorted heterocubane may be derived from related regular Al_4N_4 parent compounds such as (HAlN*i*Pr)$_4$, (MeAlN*i*Pr)$_4$, (*i*PrCH$_2$-AlNSiPh$_3$)$_4$, (PhAlNPh)$_4$, (HAlNCMe$_3$)$_4$, etc.[25f,26,27] As in the compounds described above the imide nitrogen atoms are coordinated to three aluminum atoms. The NH group of the hydrazinediido ligand bonds to two metal atoms, while its second nitrogen atom bearing the *tert*-butyl group is three-coordinate and has contact to only one aluminum atom. Cages derived from heterocubanes similar to the aluminum hydrazindiides have been reported with zinc.[28] Partial protolysis gave ZnON derivatives in which OH or OR groups replace the imido groups (N–CMe$_3$) of the aluminum compounds **7** or **8**. No rotation of the single hydrazine ligand was reported for the zinc analogue of **8**.

Conclusion

The thermolysis of trialkylaluminum–hydrazine adducts opens facile access to the formation of heterocyclic or cage-like compounds having monoanionic hydrazido or dianionic hydrazinediido ligands. A broad variety of structural motifs is observed for the products due to the particular coordination behavior of the bidentate hydrazine ligand that is similar to that of aluminum or gallium hydroxylamides or peroxides.[29] A different reaction behavior was

observed depending on the substitution patterns of the starting materials. N–N bond cleavage was the first step with sterically shielded tris(*tert*-butyl)aluminum, whereas methane elimination with the retention of the N–N bond was the preferred starting reaction with trimethylaluminum–hydrazine. Formal elimination of *tert*-butylnitrene, N–CMe_3, determines the decomposition reaction of the bis(*tert*-butyl)aluminum compound, while nitrene, N–H, is released at elevated temperatures from the hydrazide groups of the sterically less shielded dimethylaluminum derivatives. A complete understanding of these reaction pathways is crucial for the development of a rational strategy for the role of these thermolysis reactions in the deposition of aluminum or gallium nitrides.

Experimental Section

General: All manipulations were carried out under argon with standard Schlenk techniques. Solvents were distilled from drying agents and degassed. NMR spectra were recorded in [D_6]benzene at ambient probe temperature with the following Bruker instruments: Avance I (^{1}H, 400.13 MHz; ^{13}C, 100.6 MHz), Avance III (^{1}H, 400.03 MHz; ^{13}C, 100.59 MHz) or AC 200 (^{1}H, 200.13 MHz, ^{13}C, 50.32 MHz) and referenced internally to residual solvent resonances (chemical shift data δ in ppm). ^{13}C NMR spectra were all proton-decoupled. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster. IR spectra were recorded as Nujol mulls between KBr, CsBr or CsI plates with a Shimadzu Prestige 21 spectrometer, EI mass spectra with a Varian mass spectrometer. Pure $AlMe_3$ was obtained by fractionated distillation of a commercially available 1 M solution in *n*-hexane (Aldrich); treatment of the adduct H_2N–N(H)CMe_3·HCl (Aldrich) with freshly prepared NaOMe in methanol and repeated distillation gave the hydrazine H_2N–N(H)CMe_3.

Me_3Al←NH_2–N(H)CMe_3 (1b): H_2N-N(H)CMe_3 (0.97 g, 1.18 mL, 11.0 mmol) was added at –30 °C to a solution of $AlMe_3$ (0.79 g, 11.0 mmol) in *n*-pentane (40 mL) to give the hydrazine adduct **1b** in quantitative yield. The reaction mixture was stirred for 15 min at this temperature and then concentrated in vacuo. Storage at – 80 °C yielded X-ray quality crystals of **1b**. M.p. –20 °C. ^{1}H NMR (C_6D_6, 200 MHz, 300 K): δ = 3.09 (br. s, 2 H, NH_2), 2.66 (br. s, 1 H, N*H*), 0.51 (s, 9 H, NCMe_3), –0.37 (s, 9 H, AlMe_3) ppm. ^{13}C NMR (C_6D_6, 50 MHz, 300 K): δ = 55.8 (N*C*), 28.0 (NCMe_3), –5.1 (AlMe_3) ppm. EI-MS (70 eV, 373 K): *m*/*z* (%) = 144 (16) [M – CH_4]$^+$, 88 (75) [H_2N-N(H)CMe_3]$^+$. IR (nujol, CsI): $\tilde{\nu}$ = 3316 (w), 3217 (w) (υNH); 2959 (vs), 2922 (vs), 2868 (vs) (nujol); 1599 (m) (δNH); 1462 (s), 1389 (m), 1368 (s) (nujol); 1192 (vs) (δCH_3, δNH); 1109 (w), 1047 (m), 1026 (w), 943 (m), 914 (w), 880 (w) (υ$_{as}CC_3$, υCN, υ$_s$NN); 822 (m), 799 (m) (υ$_s CC_3$); 606 (m), 524 (w), 455 (w) (υAlC, υAlN, δCC_3).

[(Me_3C)$_2$Al–N(H)–N(H)CMe_3]$_2$ (2): Compound **2** has already been reported in the literature and was obtained by salt elimination.[16] A considerably improved procedure is described here: Neat (Me_3C)$_3$-Al←NH_2-N(H)CMe_3 (**1a**)[5] (0.88 g, 3.1 mmol) was heated to 155 °C. At this temperature a visible gas evolution occurred, and the reaction mixture started to slowly solidify. The mixture was kept at this temperature for 2 h to give a colorless solid that was heated at 160 °C for another 30 min. The reaction mixture was then allowed to cool to room temperature and recrystallized from *n*-pentane (8 mL) at –45 °C to give **2** as colorless crystals (0.57 g, 72% yield). Characterization: See ref.[16]

[(Me_3C)$_2$Al–NH_2]$_2$ (3): Compound **2** (0.18 g, 0.40 mmol, based on the dimeric formula unit) was heated at 160 °C under argon over a period of 3 h whereby its colour changed from colorless to pale yellow. The solid was heated at 165 °C for an additional 1.5 h and then cooled to room temperature to give a pale yellow and sticky solid at the bottom of the reaction vessel. The solid of unknown composition was dissolved in *n*-pentane and then removed. The remaining oil covering the walls of the flask was dissolved in *n*-pentane and transferred into a Schlenk flask. The solvent was removed in vacuo, and the obtained residue was dissolved in toluene. Storing of the solution at –30 °C for several days yielded small quantities of a crystalline mixture of **2** (cubes) and **3** (platelets). The structure of **3** was confirmed by XRD and its characteristic NMR spectroscopic data that are in accordance with those of the trimer reported in the literature.[17]

[Me_3CAlNH]$_6$ (4): Solid **2** (0.60 g, 1.32 mmol) was heated at 175 °C. A pale yellow, highly viscous melt formed slowly. Afterwards, the substance was heated to 190 °C in a silicon oil bath for 6 h. ***Caution:*** Explosive decomposition was observed upon very fast heating above these temperatures. Recrystallization of the reaction product from toluene (5 mL) at –45 °C yielded colorless crystals of compound **4** (0.11 g, 42%). M.p. >350 °C (argon, sealed capillary). ^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ = 1.05 (s, 9 H, CMe_3), 0.58 (br. s, 1 H, N*H*) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 300 K): δ = 29.6 (CMe_3) 26.1 (*C*Me_3) ppm. MS-EI (70 eV, 393 K): *m*/*z* (%) = 594 (14) [M]$^+$, 579 (3) [M – Me]$^+$, 537 [M – CMe_3]$^+$, 480 (3) [M – 2 CMe_3]$^+$. IR (nujol, CsI): $\tilde{\nu}$ = 3358 (m), 3254 (w), 3204 (w) (υNH); 2957 (vs), 2924 (vs), 2855 (vs) (nujol); 1466 (s), 1398 (m), 1371 (s) (nujol); 1303 (vw), 1202 (vs) (δCH_3, δNH); 1138 (vw), 1024 (m), 1001 (w), 947 (m), 912 (w), 870 (m) (υ$_{as}CC_3$, υCN); 820 (w), 773 (m) (υ$_s CC_3$); 687 (vs), 575 (w), 536 (w), 457 (m) (υAlC, υAlN, δCC_3). $C_{24}H_{60}Al_6N_6$ (594.7): calcd. C 48.5, H 10.2, N 14.1; found C 48.9, H 10.1, N 13.5.

[Me_2Al–N(H)–N(H)CMe_3]$_2$[MeAl–N(CMe_3)–NH] (5): Neat H_2N–N(H)CMe_3 (1.24 g, 1.50 mL, 14.1 mmol) was added at room temperature to a solution of $AlMe_3$ (1.01 g, 14.1 mmol) in *n*-pentane (50 mL). The intermediate formation of the hydrazine adduct **1b** was evident from a slight turbidity of the reaction mixture and an initial gas evolution that ceased after several minutes. The reaction mixture was stirred for 30 min to give a colorless solution that was concentrated in vacuo and stored at –30 °C to give colorless crystals of compound **5** (0.89 g, 45%). Compound **5** was difficult to isolate in pure form. The NMR spectra showed, in most cases, small quantities of impurities. Compound **5** is thermally relatively unstable, and marked decomposition was observed in benzene and toluene solutions at room temperature after ca. 1 h. M.p. 72 °C (dec.) (argon, sealed capillary). ^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ = 3.16 (br. s, 2 H, NH-N*H*CMe_3), 2.63 (br. s, 2 H, N*H*-NHCMe_3), 1.73 (br. s, 1 H, Al_2N*H*, bridgehead), 1.06 (s, 9 H, NCMe_3 of hydrazinediide), 0.89 (s, 18 H, NH-NHCMe_3), –0.34 (s, 3 H, Al*Me*), –0.37 and –0.39 (each s, 6 H, AlMe_2) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 300 K): δ = 54.4 and 53.7 (NH*C*Me_3) 49.1 (N*C*Me_3), 28.3 (NCMe_3), 27.4 (NHNCMe_3), –3.8 (br., Al*Me*), –8.3 and –9.6 (each br, AlMe_2) ppm. MS-EI (70 eV, 353 K): *m*/*z* (%) = 416 (100) [M]$^+$, 401 (9) [M – Me]$^+$, 344 (29) [M – $NHCMe_3$]$^+$, 299 (98) [M – $NHCMe_3$ – 3 Me]$^+$. IR (nujol, CsBr): $\tilde{\nu}$ = 3358 (m), 3254 (m), 3204 (w) (υNH); 2957 (vs), 2924 (vs), 2855 (vs) (nujol); 1466 (s), 1389 (m), 1371 (m) (nujol); 1202 (vs) (δCH_3, δNH); 1138 (w), 1024 (m), 1001 (w), 947 (m), 912 (m), 868 (s) (υ$_{as}CC_3$, υCN, υ$_s$NN); 820 (w), 773 (w) (υ$_s CC_3$); 687 (s), 575 (w), 536 (vw), 457 (w) (υAlC, υAlN, δCC_3).

[MeAlN(H)–$NCMe_3$]$_4$ (6): A solution of compound **5** (1.10 g, 2.64 mmol) in *n*-hexane (25 mL) was heated under reflux condi-

tions for 2 h. During this period a significant amount of gas was released. The reaction mixture was then cooled to room temperature, and the solvent was removed in vacuo to give a colorless solid. Recrystallization from *n*-pentane (10 mL) at –15 °C yielded colorless crystals of **6** (0.72 g, 71%). M.p. 152 °C (dec.) (argon, sealed capillary). ^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ = 1.73 (s, 1 H, N*H*CMe$_3$), 1.12 (s, 9 H, NC*Me*$_3$), –0.45 (s, 3 H, Al*Me*) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 300 K): δ = 53.9 (N*C*Me$_3$), 29.8 (NC*Me*$_3$), –11.3 (br., Al*Me*) ppm. MS-EI (10 eV, 373 K): *m*/*z* (%) = 512 (20) [M]$^+$, 384 (5) [(MeAlNH–NCMe$_3$)$_3$]$^+$, 326 (55) [(MeAlNH–NCMe$_3$)$_3$ – HCMe$_3$]$^+$. IR (nujol, KBr): $\tilde{\nu}$ = 3325 (w), 3283 (m), 3163 (vw) (υNH); 2920(vs), 2851 (vs) (nujol); 1604 (w) (δNH); 1462 (vs), 1377 (s) (nujol); 1300 (m) (δCH$_3$); 1197 (s), 1038 (m), 999 (w), 937 (w) 914 (vw) (υ$_{as}$CC$_3$, υCN, υ$_s$NN); 794 (vw), 772 (vw) (υ$_s$CC$_3$); 725 (vw) (nujol); 687 (vw), 659 (vw), 582 (vw), 532 (w), 505 (vw), 478 (w), 417 (w) (υAlC, υAlN, δCC$_3$). $C_{20}H_{52}Al_4N_8$ (512.6): calcd. C 46.9, H 10.2, N 21.9; found C 47.3, H 10.2, N 21.0.

(MeAl)$_4$[N(H)–NCMe$_3$]$_3$(NCMe$_3$) (7): Compound **6** (0.65 g, 1.27 mmol) was heated without solvent to 155 °C. Decomposition of compound **6** started below its "melting" point. The substance was kept at 155 °C for 2 h. After cooling to room temperature, the product was recrystallized from *n*-hexane (5 mL) at 2 °C to give colorless crystals of compound **7** (0.40 g, 63%). ***Caution:*** Heating of the solid compound **6** above 155 °C may lead to violent and explosive decomposition. M.p. 183 °C (argon, sealed capillary). ^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ = 1.77 (s, 3 H, N*H*CMe$_3$), 1.52 (s, 9 H, NC*Me*$_3$), 1.05 (s, 27 H, NH–NC*Me*$_3$), –0.21 (s, 9 H, Al*Me*), –0.36 [s, 3 H, (HN)$_3$Al*Me*] ppm. ^{13}C NMR (C_6D_6, 100 MHz, 300 K): δ = 53.7 (NHN*C*Me$_3$), 52.8 (N*C*Me$_3$), 34.6 (NC*Me*$_3$), 29.8 (NHNC*Me*$_3$), –6.4 (br., AlMe) ppm. MS-EI (10 eV, 373 K): *m*/*z* (%) = 497 (7) [M]$^+$, 411 (6) [M – Me – NCMe$_3$]$^+$, 396 (100) [M – 2 Me – NCMe$_3$]$^+$. IR (nujol, KBr): $\tilde{\nu}$ = 3302 (m) (υNH); 2920 (vs), 2851 (vs) (nujol); 1601 (w) (δNH); 1462 (vs), 1366 (s) (nujol); 1285 (m) (δCH$_3$); 1227 (m), 1184 (vw), 1123 (vw), 1076 (vw), 1034 (m), 995 (w), 945 (vw), 926 (vw), 899 (w), 860 (w), 783 (m) (υ$_{as}$CC$_3$, υCN, υ$_s$NN); 714 (m) (nujol); 652 (vw), 629 (vw), 597 (vw), 567 (w), 536 (m), 463 (w) (υAlC, υAlN, δCC$_3$). $C_{20}H_{51}Al_4N_7$ (497.6): calcd. C 48.3, H 10.3, N 19.7; found C 48.1, H 10.4, N 19.4.

(MeAl)$_4$[N(H)–NCMe$_3$](NCMe$_3$)$_3$ (8): Compound **7** (0.75 g, 1.51 mmol) was heated (by means of an oil bath filled with silicon oil) in a Schlenk flask at 180 °C for 5 h. The initially colorless solid starting material was converted into a pale brown and viscous mixture, which by the end of the reaction had turned into a glassy porous solid. Small amounts of a colorless solid had sublimed during the reaction to the upper parts of the Schlenk flask. The residue at the bottom of the flask was then dissolved in *n*-pentane (5 mL) and the solution kept at –28 °C to give **8** (0.40 g, 57%). M.p. 212 °C (argon sealed capillary). ^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ = 1.86 (s, 1 H, NH), 1.29 (s, 27 H, NC*Me*$_3$), 1.09 (s, 9 H, NHNC*Me*$_3$), –0.02 (s, 3 H, Al*Me*), –0.17 [s, 9 H, (Al*Me*)] ppm. ^{13}C NMR (C_6D_6, 100 MHz, 300 K): δ = 53.9 (NHN*C*Me$_3$), 52.3, (N*C*Me$_3$), 35.6 (NHNC*Me*$_3$), 29.8 (NC*Me*$_3$), –6.3 (br., Al*Me*$_3$) ppm. MS-EI (10 eV, 313 K): *m*/*z* (%) = 467 (23) [M]$^+$, 452 (100) [M – Me]$^+$, 382 (18) [M – NNCMe$_3$]$^+$. IR (nujol, KBr): $\tilde{\nu}$ = 3294 (w) (υNH); 2920 (vs), 2851 (vs) (nujol); 1458 (s), 1373 (s) (nujol); 1300 (w) (δCH$_3$); 1227 (w), 1192 (m), 1030 (m), 937 (w), 891 (vw), 818 (vw) 779 (w) (υ$_{as}$CC$_3$, υCN, υ$_s$NN); 717 (w) (nujol); 594 (vw), 517 (vw), 463 (w), 413 (w) (υAlC, υAlN, δCC$_3$). $C_{20}H_{49}Al_4N_5$ (467.6): calcd. C 51.4, H 10.6, N 15.0; found C 49.8, H 10.5, N 15.2.

X-ray Crystallography: Crystals suitable for X-ray crystallography were obtained by recrystallization from *n*-pentane (**1b**, **5**, **6**), cyclopentane (**4**), *n*-hexane (**7**) and toluene (**8**). Intensity data were collected with a Bruker APEX II and a Stoe IPDS diffractometer with monochromated Mo-K_α (**4**, **5**, **7**, **8**) and Cu-K_α (**1b**, **6**) radiation. Compound **1b** melts below room temperature; a crystal was selected and mounted on the diffractometer into a cooled stream of nitrogen. The collection method involved ω-scans. Data reduction was carried out with the program SAINT+.[30] The crystal structures were solved by direct methods with SHELXTL.[31] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculations based on F^2 with SHELXTL. Hydrogen atoms (except NH of compounds **1b**, **3**, **5**–**7**) were positioned geometrically and allowed to ride on their respective parent atoms. The molecules of **1b** are located on a crystallographic mirror plane; NH and Me groups are disordered.

Table 1. Crystal data and structure refinement details for compounds **1b** and **3**–**8**.

Compound	**1b**	**4**	**5**	**6**	**7**	**7(Ga)**	**8**
Empirical formula	$C_7H_{21}AlN_2$	$C_{24}H_{60}Al_6N_6$	$C_{17}H_{47}Al_3N_6$	$C_{20}H_{52}Al_4N_8$	$C_{20}H_{51}Al_4N_7$	$C_{20}H_{51}Ga_4N_7$	$C_{20}H_{49}Al_4N_5$
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$Pmn2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Pbca$	$P2_12_12_1$	$Pnma$
a [pm]	923.28(3)	1219.2(3)	1635.8(4)	1210.63(2)	1186.90(4)	1130.20(5)	1132.82(7)
b [pm]	904.61(2)	1483.5(2)	942.3(2)	1552.89(2)	1639.30(6)	1601.68(8)	1595.8(1)
c [pm]	654.09(2)	1602.5(2)	1701.3(4)	1673.88(2)	3085.0(1)	1662.55(7)	1576.5(1)
α [°]	90	72.64(2)	90	90	90	90	90
β [°]	90	82.44(2)	92.99(4)	105.617(1)	90	90	90
γ [°]	90	76.19(2)	90	90	90	90	90
V [nm^3]	0.54630(3)	2.6806(9)	2.619(1)	3.03068(7)	6.0024(4)	3.0096(2)	2.8499(3)
Z	2	3	4	4	8	4	4
T [K]	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
Density (calcd.) [Mg/m^3]	0.974	1.105	1.056	1.123	1.101	1.476	1.090
Absorption coefficient [mm^{-1}]	1.175 (Cu-K_α)	0.202 (Mo-K_α)	0.157 (Mo-K_α)	1.596 (Cu-K_α)	0.175 (Mo-K_α)	3.562 (Mo-K_α)	0.179 (Mo-K_α)
θ range [°]	4.89–72.19	4.79–28.17	1.25–31.46	3.95–72.41	2.17–27.91	1.77–29.23	1.82–27.83
Independent reflections	989	11939	8061	5728	7173	8023	3502
R_{int}	0.0557	0.0885	0.0451	0.0316	0.0569	0.0628	0.0555
Parameters	66	514	319	321	433	378	217
R_1[a] [$I > 2\sigma(I)$]	0.0605 [894]	0.0573 [7384]	0.0547 [5296]	0.0371 [5090]	0.0484 [5106]	0.0472 [5363]	0.0777 [2418]
wR_2 (all data)[b]	0.1665	0.1417	0.1638	0.1063	0.1290	0.0965	0.2220
Largest difference peak/hole [e nm^{-3}]	576/–407	448/–399	538/–250	343/–324	452/–183	640/–480	897/–334

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma|F_o|^2\}^{1/2}$.

Compound **4** has 1.5 molecules in the asymmetric unit; one molecule is located on a crystallographic center of symmetry. One hydrazine group (N31) of **5** showed disorder; the atoms were refined in split positions (with an occupancy ratio of 0.44:0.56). The complete molecules of **7** and **7(Ga)** are disordered across pseudo-mirror planes; the atoms were refined in split positions (with occupancy ratios of 0.75:0.25 and 0.62:0.38, respectively). The molecules of **8** showed disorder over a crystallographic mirror plane, which led to the overlap of the hydrazide and a *tert*-butylimide ligands. Further crystallographic data are summarized in Table 1. CCDC-804087 (**1b**), -804088 (**4**), -804089 (**5**), -804090 (**6**), -804091 (**7**), -804093 [**7(Ga)**] and -804093 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Database Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum-Chemical Calculations: All computations were performed with the Gaussian 09 suite of programs.[32] The Becke three-parameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP)[33] with the 6-311G(d,p) basis set were used to compute the geometries and the normal-mode vibration frequencies of the structures. For single-point energy calculations on DFT-optimized geometries the SCS-MP2 method[34] was used. The transition structure was localized with the option: opt = (qst2, noeigentest, calcfc). In order to verify the character of the stationary points, they were subjected to frequency analyses. The vibration related to the imaginary frequency corresponds to the nuclear motion along the reaction coordinate under study. An intrinsic reaction coordinate (IRC) calculation was performed in order to unambiguously connect the transition structure with the structures of **8** and **8a**.

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[1] W. Uhl, in *Structure and Bonding*, Springer Verlag, Berlin, Heidelberg, **2003**, p. 41–66.
[2] a) S. J. Pearton, F. Ren, *Adv. Mater.* **2000**, *12*, 1571–1580; b) D. K. Gaskill, N. Bottka, M. C. Lin, *Cryst. Growth* **1986**, *77*, 418–423; c) H. Okumura, S. Misaura, S. Yoshida, *Appl. Phys. Lett.* **1991**, *59*, 1058–1060; d) S. Miyoshi, K. Onabe, N. Ohkouchi, H. Yaguchi, R. Ito, S. Fukatsu, Y. Shiraki, *J. Cryst. Growth* **1992**, *124*, 439–442; e) R. T. Lee, G. B. Stringfellow, *J. Electron Mater.* **1999**, *28*, 963–969; f) M. Mizuta, S. Fujieda, Y. Matsumoto, T. Kawamura, *Jpn. J. Appl. Phys.* **1986**, *25*, L945–L948; g) S. Fujieda, M. Mizuta, Y. Matsumoto, *Jpn. J. Appl. Phys.* **1987**, *26*, 2067–2071; h) H. Okumura, S. Yoshida, S. Misawa, E. Sakuma, *J. Cryst. Growth* **1992**, *120*, 114–118; i) V. Lakhotia, D. A. Neumayer, A. H. Cowley, R. A. Jones, J. G. Ekerdt, *Chem. Mater.* **1995**, *7*, 546–552; j) A. Devi, R. Schmid, J. Müller, R. A. Fischer, *Top. Organomet. Chem.* **2005**, *9*, 49–80.
[3] D. W. Peters, E. D. Bourret, M. P. Power, *J. Organomet. Chem.* **1999**, *582*, 108–115.
[4] W. Uhl, T. Abel, A. Hepp, S. Grimme, M. Steinmetz, *Eur. J. Inorg. Chem.* **2008**, 543–551.
[5] W. Uhl, T. Abel, J. Kösters, F. Rogel, *Z. Naturforsch., Teil B* **2008**, *63*, 117–123.
[6] W. Uhl, T. Abel, A. Hepp, T. Nilges, F. Rogel, E.-U. Würthwein, N. Ghavtadze, *Inorg. Chem.* **2009**, *48*, 752–759.
[7] W. Uhl, T. Abel, J. Kösters, B. Rezaeirad, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1014–1022.
[8] W. Uhl, T. Abel, E. Hagemeier, A. Hepp, M. Layh, B. Rezaeirad, H. Luftmann, *Inorg. Chem.* **2011**, *50*, 325.
[9] W. Uhl, C. H. Emden, W. Massa, *J. Organomet. Chem.* **2006**, *691*, 1382–1388.
[10] B. Luo, C. J. Cramer, W. L. Gladfelter, *Inorg. Chem.* **2003**, *42*, 3431–3437.
[11] W. Uhl, J. Molter, B. Neumüller, *Organometallics* **2000**, *19*, 4422–4224.
[12] a) H. Nöth, T. Seifert, *Eur. J. Inorg. Chem.* **2002**, 602–612; b) H. Nöth, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1931–1938; c) W. Uhl, J. Molter, B. Neumüller, *Inorg. Chem.* **2001**, *40*, 2011–2014.
[13] W. Uhl, J. Molter, R. Koch, *Eur. J. Inorg. Chem.* **2000**, 2255–2262.
[14] D. W. Peters, M. P. Power, E. D. Bourret, J. Arnold, *Chem. Commun.* **1998**, 753–754.
[15] W. Uhl, B. Rezaeirad, M. Layh, E. Hagemeier, E.-U. Würthwein, N. Ghavtadze, I. Kuzu, *Chem. Eur. J.* **2010**, *16*, 12195–12198.
[16] W. Uhl, J. Molter, B. Neumüller, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2284–2292.
[17] L. V. Interrante, G. A. Sigel, M. Garbauskas, C. Heyna, G. A. Slack, *Inorg. Chem.* **1989**, *28*, 252–257.
[18] R. Dinnebier, J. Müller, *Inorg. Chem.* **2003**, *42*, 1204–1210.
[19] G. M. McLaughlin, G. A. Sim, J. D. Smith, *J. Chem. Soc., Dalton Trans.* **1972**, 2197–2203.
[20] J. F. Janik, E. N. Duesler, R. T. Paine, *Inorg. Chem.* **1987**, *26*, 4341–4345.
[21] K. J. L. Paciorek, J. H. Nakahara, L. A. Hoferkamp, C. George, J. L. Flippen-Anderson, R. Gilardi, W. R. Schmidt, *Chem. Mater.* **1991**, *3*, 82–87.
[22] M. Cesari, G. Perego, G. Del Piero, S. Cucinella, E. Cernia, *J. Organomet. Chem.* **1974**, *78*, 203–213.
[23] G. Del Piero, M. Cesari, G. Perego, S. Cucinella, E. Cernia, *J. Organomet. Chem.* **1977**, *129*, 289–298.
[24] A.-A. I. Al-Wassil, P. B. Hitchcock, S. Sarisaban, J. D. Smith, C. L. Wilson, *J. Chem. Soc., Dalton Trans.* **1985**, 1929–1934.
[25] a) G. Perego, G. Dozzi, *J. Organomet. Chem.* **1981**, *205*, 21–30; further hexameric alanes: b) G. Del Piero, S. Cucinella, M. Cesari, *J. Organomet. Chem.* **1979**, *173*, 263–268; c) G. Del Piero, G. Perego, S. Cucinella, M. Cesari, A. Mazzei, *J. Organomet. Chem.* **1977**, *136*, 13–18; d) A. Stasch, S. S. Kumar, V. Jancik, H. W. Roesky, J. Magull, M. Noltemeyer, *Eur. J. Inorg. Chem.* **2004**, 4056–4060; e) N. D. Reddy, S. S. Kumar, H. W. Roesky, D. Vidovic, J. Magull, M. Noltemeyer, H.-G. Schmidt, *Eur. J. Inorg. Chem.* **2003**, 442–448; f) C. Schnitter, S. D. Waezsada, H. W. Roesky, M. Teichert, I. Usón, E. Parisini, *Organometallics* **1997**, *16*, 1197–1202; g) J. E. Park, B.-J. Bae, Y. Kim, J. T. Park, I.-H. Suh, *Organometallics* **1999**, *18*, 1059–1067; h) F. Cheng, S. Clark, S. J. Archibald, S. M. Kelly, J. S. Bradley, *J. Organomet. Chem.* **2005**, *690*, 1205–1208.
[26] W. Uhl, J. Molter, B. Neumüller, *Chem. Eur. J.* **2001**, *7*, 1510–1515.
[27] a) G. Del Piero, M. Cesari, G. Dozzi, A. Mazzei, *J. Organomet. Chem.* **1977**, *129*, 281–288; b) D. M. Choquette, M. J. Timm, J. L. Hobbs, T. M. Nicholson, M. M. Olmstead, R. P. Planalp, *Inorg. Chem.* **1993**, *32*, 2600–2603; c) T. R. R. McDonald, W. S. McDonald, *Acta Crystallogr., Sect. B* **1972**, *28*, 1619–1622; d) C. J. Harlan, S. G. Bott, A. R. Barron, *J. Chem. Soc., Dalton Trans.* **1997**, 637–641; e) K. M. Waggoner, P. P. Power, *J. Am. Chem. Soc.* **1991**, *113*, 3385–3393; f) T. Belgardt, S. D. Waezsada, H. W. Roesky, H. Gornitzka, L. Häming, D. Stalke, *Inorg. Chem.* **1994**, *33*, 6247–6251.
[28] a) S. Jana, R. Fröhlich, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2006**, 3936–3942; b) S. Jana, R. Fröhlich, N. W. Mitzel, *Chem. Eur. J.* **2006**, *12*, 592–599; c) S. Jana, R. Fröhlich, N. W. Mitzel, *Z. Naturforsch., Teil B* **2006**, *61*, 838–845; d) S. Jana, R. Föhlich, N. W. Mitzel, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1477–1484.
[29] Hydroxylamides: a) N. W. Mitzel, C. Lustig, *Angew. Chem.* **2001**, *113*, 4521–4524; *Angew. Chem. Int. Ed.* **2001**, *40*, 4390–4392; b) N. W. Mitzel, C. Lustig, M. Woski, *Dalton Trans.* **2004**, 397–401; c) P. Bösing, A. Willner, T. Pape, A. Hepp,

N. W. Mitzel, *Dalton Trans.* **2008**, 2549–2556; peroxides: d) W. Uhl, M. R. Halvagar, *Angew. Chem.* **2008**, *120*, 1981–1983; *Angew. Chem. Int. Ed.* **2008**, *47*, 1955–1957; e) W. Uhl, M. R. Halvagar, M. Layh, *Chem. Commun.* **2009**, 4269–4271; f) W. Uhl, M. R. Halvagar, M. Claesener, *Chem. Eur. J.* **2009**, *15*, 11298–11306; g) W. Uhl, B. Jana, *Chem. Eur. J.* **2008**, *14*, 3067–3071; h) W. Uhl, M. R. Halvagar, H. R. Bock, B. Jasper-Peter, M. Layh, *Z. Naturforsch., Teil B* **2009**, *64*, 1369–1374.

[30] a) *SAINT+*, version 6.02 (includes XPREP and SADABS), Bruker AXS Inc., Madison, Wisconsin, USA, **1999**; b) G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, **1996**.

[31] a) *SHELXTL-Plus*, release 4.1, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1990**; b) G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Structures*, University of Göttingen, Germany, **1997**.

[32] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, revision A.02, Gaussian, Inc., Wallingford, CT, **2009**.

[33] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[34] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095–9102.

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