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The Unique Decomposition Behavior of the Dimeric Dialkylaluminum Hydrazide $[(Me_3C)_2Al-N(H)-N(H)-Me]_2$−Butane versus Ammonia Elimination

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The hydrazine adducts $(Me_3C)_3E\leftarrow NH_2-N(H)-Me$ [E = Al (**1**), Ga(**2**)] afforded the corresponding dimeric hydrazides $[(Me_3C)_2E-N(H)-N(H)-Me]_2$ (**3** and **4**) upon heating to 95 and 300 °C, respectively, by the release of isobutane. The molecular structure of **3** in the solid state comprises a five-membered Al_2N_3 heterocycle (**3b**), while **4** possesses a four-membered Ga_2N_2 ring with two exocyclic hydrazine groups (**4a**). Quantum-chemical calculations revealed only small energetic differences between both isomers. The structures determined in the solid state correspond to the thermodynamically favored ones. In solution, equilibrium mixtures between both forms were detected. Further thermolysis of the aluminum compound **3** gave different products depending on the reaction conditions. Below its melting point, isobutane was released. A cage compound (**5**) was formed, which has four $Al-CMe_3$ groups and four hydrazindiido ligands $[N(H)-N(Me)]^{2-}$ with all N−N bonds enclosed in the cage. Fast heating of **3** above the melting point (149 °C) yielded a singular product (**6**) by a remarkable rearrangement process and formal release of ammonia. The hydrazonido ligand $[N(Me)-N(=CH_2)]^-$ resulted, which has a reformed N−N bond and an N=C double bond and is in a bridging position between two aluminum atoms. An amido group (NH_2) completes the five-membered Al_2N_3 heterocycle of **6**.

Introduction

Investigations into the syntheses, structures, and properties of organoelement hydrazides with the elements aluminum, gallium, and indium found interest in recent research, because these compounds are suitable to form the corresponding nitrides under relatively mild conditions.[1] Besides these aspects of a potential application, these hydrazido compounds exhibit a fascinating coordination behavior which is caused by the two lone pairs of electrons on neighboring nitrogen atoms and leads to the formation of a broad variety of heterocyclic or cagelike compounds.[2] The synthesis of these compounds succeeds through several efficient routes: (i) The reaction of lithium hydrazides with chloroelement derivatives or the treatment of hydrazine adducts of dialkylelement

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chlorides with butyllithium affords hydrazides by salt elimination.[3−10] (ii) Release of alkanes or elemental hydrogen occurs when hydrazines possessing at least one N−H function are treated with trialkylelement derivatives or dialkylelement hydrides.[3,4,11−21] (iii) The addition of Al−H bonds to 2,3-diazabutadienes or diazenes (hydroalumination) opened access to some unusual heterocyclic or cagelike hydrazides.[22,23] (iv) The exchange of amido versus hydrazido ligands combined with hydrogen release was applied in a single reaction.[18] The second method (ii) involves the formation of hydrazine adducts as the initiating step. In several cases, such adducts were isolated and characterized by crystal structure determinations.[6,8−10,15,19−21,24,25] Steric interactions influence their structures, and in most cases, the less-shielded NH_2 groups are attached to the coordinatively unsaturated metal atoms. Only one compound was reported, $Me_3Ga{\leftarrow}N(Me)(H){-}NH_2$, in which the more basic nitrogen atom bearing a methyl group is involved in the metal−nitrogen bond.[21] Recently, we published a series of adducts of the tri(*tert*-butyl)element compounds $E(CMe_3)_3$ (E = Al, Ga, In) with methyl-, phenyl-, and *tert*-butylhydrazine,[25] which are excellent starting compounds for the generation of hydrazides by the heating and release of alkanes. We preferred this method in current investigations because it yields the hydrazides in a very pure form without the necessity of removing any byproduct by filtration or recrystallization. We report here on the thermolysis of two methylhydrazine adducts, which gave unprecedented products and reaction courses.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (cyclopentane and *n*-pentane over $LiAlH_4$). The adducts $(Me_3C)_3Al{\leftarrow}NH_2{-}N(H){-}Me$ (**1**) and $(Me_3C)_3Ga{\leftarrow}NH_2{-}N(H){-}Me$ (**2**) were obtained according to literature procedures.[25] The assignment of the NMR spectra is based on heteronuclear multiple-bond correlation, heteronuclear single quantum coherence, rotating-frame Overhauser enhancement spectroscopy, distortionless enhancement by polarization transfer (DEPT135), and insensitive nuclei enhanced by polarization transfer data.

Synthesis of Bis[di(*tert*-butyl)aluminum-methylhydrazide], 3. The adduct **1** (5.37 g, 22.0 mmol) was slowly heated to 95 °C in an oil bath without a solvent. It was stored at this temperature until gas evolution stopped. The gaseous byproduct was collected in a trap cooled by liquid nitrogen and was identified as isobutane by NMR and MS. After cooling to room temperature, the solid product was evacuated (10^{-2} Torr) to completely remove isobutane. The colorless product **3** was directly formed at very high purity. Yield: 3.70 g (90%). Cyclopentane is suitable for recrystallization. Mp (argon; sealed capillary): 149 °C. MS (EI, 20 eV, 370K, *m/z*): 343 (13%) $M^+ - NMe$; 315 (100) $M^+ -$ *t*-BuH. ^1H ([D_8]toluene, 400 MHz, 300 K), isomer **3a** possessing a four-membered Al_2N_2 heterocycle: δ 3.73 (2 H, q, $^3J_{H-H} = 6.4$ Hz, MeN*H*), 2.19 (6 H, d, $^3J_{H-H} = 6.4$ Hz, HN*Me*), 2.07 (2 H, d, $^3J_{H-H} = 3.6$ Hz, AlN*H*), 1.10 (36 H, s, *t*-Bu). ^1H ([D_8]toluene, 400 MHz, 300 K), isomer **3b** possessing a five-membered Al_2N_3 heterocycle: δ 3.29 (2 H, s, br., NH_2), 2.89 (1 H, q, $^3J_{H-H} = 6.4$ Hz, *H*NMe), 2.56 (3 H, s, AlN*Me*), 2.50 (1 H, d, $^3J_{H-H} = 1.2$ Hz, AlN*H*), 2.31 (3 H, d, $^3J_{H-H} = 6.4$ Hz, HN*Me*), 1.09 (36 H, s, *t*-Bu). ^1H ([D_8]toluene, 400 MHz, 260 K), isomer **3a**: δ 3.67 (2 H, q, $^3J_{H-H} = 6.4$ Hz, MeN*H*), 2.08 (6 H, d, $^3J_{H-H} = 6.4$ Hz, HN*Me*), 2.04 (2 H, d, $^3J_{H-H} = 3.6$ Hz, AlN*H*), 1.13 (36 H, s, *t*-Bu). ^1H ([D_8]toluene, 400 MHz, 260 K), isomer **3b**: δ 3.18 (2 H, s, br., NH_2), 2.85 (1 H, q, $^3J_{H-H} = 6.4$ Hz, *H*NMe), 2.51 (3 H, s, AlN*Me*), 2.47 (1 H, d, $^3J_{H-H} = 1.2$ Hz, AlN*H*), 2.23 (3 H, d, $^3J_{H-H} = 6.4$ Hz, HN*Me*), 1.18 and 1.07 (each 18 H, s, *t*-Bu). The resonances became broader upon further cooling. ^{13}C NMR ([D_8]toluene, 100 MHz, 300 K), isomer **3a**: δ 42.8 ($N{-}CH_3$), 32.2 (C*Me*$_3$), 15.6 (AlC). ^{13}C NMR ([D_8]toluene, 100 MHz, 300 K), isomer **3b**: δ 44.6 (AlN*Me*), 43.9 (NN*Me*), 31.9 (C*Me*$_3$), 15.3 (AlC). ^{15}N NMR (C_6D_6, 40.5 MHz, 300 K), isomer **3a**: δ 84.4 (Al_2N), 55.2 (Me−N−H). ^{15}N NMR (C_6D_6, 40.5 MHz, 300 K), isomer **3b**: 73.6 ($AlNH_2$), 72.9 (Al_2N), 61.0 (Me−N−H), −179.9 (?, Al−N−Me). IR (paraffin, CsBr plates, cm^{-1}): 3316 w, 3296 w, 3212 m, 3175 m, 3126 m ν(NH); 2925 vs, 2697 s (paraffin); 1590 s δ(NH); 1453 vs, 1378 vs (paraffin); 1282 m $\delta(CH_3)$; 1223 s, 1181 s, 1145 s, 1079 m, 1036 m, 1001 m, 934 s $\nu_{as}(CC_3)$, ν(CN), ν(NN); 811 s $\nu_s(CC_3)$; 722 w (paraffin); 690 s, 603 s, 498 s, 405 s ν(AlC), ν(AlN), $\delta(CC_3)$. Anal. calcd for $C_{18}H_{46}N_4Al_2$ (372.5): C, 58.0; H, 12.4; N, 15.0; Al, 14.5. Found: C, 58.3; H, 12.5; N, 15.0; Al, 14.3.

Synthesis of Bis[di(*tert*-butyl)gallium-methylhydrazide], 4. The adduct **2** (1.018 g, 3.55 mmol) was heated without a solvent to about 300 °C for 30 min. Gas evolution occurred. After cooling to room temperature, the solid product was evacuated (10^{-2} Torr) to completely remove isobutane. The solid residue was recrystallized from *n*-pentane (20/−30 °C) to yield colorless crystals of **3**. Yield: 0.52 g (64%). Mp (argon; sealed capillary): 128 °C. MS (EI, 20 eV, 305 K, *m/z*; only the three most intensive peaks of every fragment, complete isotopic patterns, are in accordance with calculated spectra): 456 (1%), 458 (1%), 460 (0.4%) M^+; 411 (24%), 413 (31%), 415 12(%) $M^+ - 3Me$; 399 (64%), 401 (75%), 403 24%) $M^+ -$ *t*-Bu. ^1H ([D_8]toluene, 400 MHz, 300 K), isomer **4a** possessing a four-membered Ga_2N_2 heterocycle: δ 2.28 (6 H, d, $^3J_{H-H} = 6.0$ Hz, HN*Me*), 1.23 (36 H, s, br., *t*-Bu). The signals of the N−H hydrogen atoms coincide and cannot be assigned unambiguously. ^1H ([D_8]toluene, 400 MHz, 300 K), isomer **4b** possessing a five-membered Ga_2N_3 heterocycle: δ 2.95 (1 H, s, br., GaNH), 2.84 (1 H, q, $^3J_{H-H} = 6.8$ Hz, *H*NMe), 2.74 (3 H, s, GaN*Me*), 2.33 (3 H, d, $^3J_{H-H} = 6.8$ Hz, HN*Me*), 1.23 (36 H, s, *t*-Bu). The resonance of the NH_2 group could not be assigned unambiguously. ^{13}C NMR ([D_8]toluene, 100 MHz, 300 K), isomer **4a**: δ 44.2 ($N{-}CH_3$), 32.4 (C*Me*$_3$), 23.5 (GaC). ^{13}C NMR ([D_8]toluene, 100 MHz, 300 K), isomer **4b**: δ 47.9 (GaN*Me*), 44.3

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(NN*Me*). The *tert*-butyl resonances coincide with those of **4a**. ^{15}N NMR (C_6D_6, 40.5 MHz, 300 K): δ 76.1, 73.3, 66.4, 61.0. IR (paraffin, CsBr plates, cm^{-1}): 3352 m, 3308 m, 3213 w, 3157 m, 3113 w ν(NH); 2922 vs, 2827 vs (paraffin); 1597 s δ(NH); 1466 vs (paraffin); 1412 w $\delta(CH_3)$; 1381 s (paraffin); 1360 s, 1250 sh $\delta(CH_3)$; 1229 m, 1180 m, 1112 s, 1070 m, 1039 w, 1009 s, 978 w, 937 s, 887 m $\nu_{as}(CC_3)$, ν(CN), ν(NN); 810 vs $\nu_s(CC_3)$; 667 w, 588 w, 557 w, 530 s, 457 m ν(GaC), ν(GaN), $\delta(CC_3)$. Anal. calcd for $C_{18}H_{46}N_4Ga_2$ (458.0): C, 47.2; H, 10.1; N, 12.2; Ga, 30.4. Found: C, 47.8; H, 10.3; N, 11.8; Ga, 30.6.

Synthesis of the Cage Compound 5. Neat di(*tert*-butyl)aluminum methylhydrazide **3** (0.82 g, 2.20 mmol based on the monomeric formula unit) was heated to 135 °C in an oil bath under normal pressure. The solid did not melt under these conditions. The product and the starting compound sublimed partially to the colder part of the Schlenck vessel. After 20 h, compound **3** was almost completely consumed. Isobutane was detected as described before (synthesis of **3**). The product was treated with a few milliliters of *n*-pentane to remove soluble impurities. Product **5** remained in a pure form. Further purification and the generation of crystals were achieved by sublimation in a vacuum (10^{-2} Torr, 140 °C). Yield: 0.32 g (57%). Mp (sealed capillary): 189 °C. MS (EI, 70 eV, 350K, *m*/*z*): 512 (2%) M$^+$, 256 (1%) 1/2M$^+$, 43 (100%) NNMe$^+$. ^{1}H (C_6D_6, 400 MHz): δ 2.81 (12 H, s, NMe), 1.95 (4 H, s, NH), 1.11 (36 H, s, CMe_3). ^{13}C NMR (C_6D_6, 100 MHz): δ 45.1 (NMe), 29.8 (C*Me*$_3$), 25.1 (*C*Me$_3$). IR (paraffin, CsBr plates, cm^{-1}): 3428 m, br., 3348 m, 3229 m ν(NH); 2922 vs, 2853 vs (paraffin); 1647 m, 1612 m δ(NH); 1460 vs, 1379 s (paraffin); 1315 m $\delta(CH_3)$; 1163 s, 1119 w, 1088 s, 1001 m, 970 w, 935 w, 914 m $\nu_{as}(CC_3)$, ν(CN), ν(NN), $\nu_s(CC_3)$; 812 m $\delta(CC_3)$; 723 m (paraffin); 648 w, 613 w, 584 w, 517 w ν(AlC), ν(AlN), $\delta(CC_3)$. Anal. calcd for $C_{20}H_{52}N_8Al_4$ (512.6): C, 46.9; H, 10.2; N, 21.9; Al, 21.1. Found: C, 47.4; H, 10.4; N, 21.4; Al, 21.2.

Synthesis of the Heterocyclic Hydrazonide 6. Neat di(*tert*-butyl)aluminum methylhydrazide, **3** (0.53 g, 2.85 mmol based on the monomeric formula unit), was rapidly heated in a prewarmed oil bath to 160 °C. Melting of the solid was accompanied by gas evolution, which was finished within a few minutes. The color changed from colorless to brownish. Solid material remained after cooling to room temperature, which contained compound **6** in high purity; sublimation in a vacuum (10^{-2} Torr, 160 °C) or recrystallization from *n*-pentane afforded colorless crystals of **6**. Yield: 0.23 g (45%). Mp (argon, sealed capillary): 156 °C. MS (EI, 70 eV, 300K, *m*/*z*): 355 (1%) M$^+$, 340 (3%) M$^+$ − Me, 313 (100%) M$^+$ − NN=CH$_2$, 298 (94%) M$^+$ − CMe$_3$. ^{1}H (C_6D_6, 400 MHz): δ 5.48 (1 H, d, $^2J_{H-H} = 7.6$ Hz, *N* = CH *cis* to Al), 5.35 (1 H, d, $^2J_{H-H} = 7.6$ Hz, N=CH *cis* to N), 2.36 (3 H, s, NMe), 1.09 (18 H, s, CMe_3 at Al−NMe), 1.04 (18 H, s, CMe_3 at Al−N=CH$_2$), 0.27 (2 H, s, br., NH$_2$); isomers in low concentration at δ 1.05 and 1.00 (I) and δ 1.13, 1.10, 1.06, and 1.03 (II, each s, CMe_3). ^{13}C NMR (C_6D_6, 100 MHz): δ 118.0 (N=C), 35.6 (N−Me), 31.8 (C*Me*$_3$ at Al−NMe), 31.1 (C*Me*$_3$ at Al−N=C), 15.6 (Al−C at Al−NMe), 14.3 (Al−C at Al−N=C). IR (paraffin, CsBr plates, cm^{-1}): 3410 m, 3246 s, 3213 s, 3142 m ν(NH); 2920 vs, 2853 s, 1454 vs, 1375 vs (paraffin); 1186 s, 1134 m, 1080 s, 1016 m, 976 w, 941 m, 895 w $\delta(CH_3)$, $\nu_{as}(CC_3)$, ν(CN), ν(NN); 816 m $\nu_s(CC_3)$; 723 w (paraffin); 660 m, 519 m, 500 m, 415 s, 380 s, 339 m ν(AlC), ν(AlN), $\delta(CC_3)$. Anal. calcd for $C_{18}H_{43}N_3Al_2$ (355.5): C, 60.8; H, 12.2; N, 11.8; Al, 15.2. Found: C, 60.6; H, 12.4; N, 12.0; Al, 15.5.

Crystal Structure Determinations. Single crystals were obtained by cooling the solutions in cyclopentane (**3b**, −30 °C) and *n*-pentane (**4a** and **6**, −30 °C) or by sublimation in a vacuum (**5**, 10^{-2} Torr, 140 °C). The crystallographic data were collected with Bruker APEX and Bruker Smart 6000 diffractometers [graphite-monochromated Mo Kα (**3b**, **4a**, **5**) and Cu Kα (**6**) radiation]. The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Table 1. All structures were solved by direct methods using the program system SHELXTL PLUS[26] and refined with the SHELXL-97[26] program via full-matrix least-squares calculations based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}(C)$. The central five-membered heterocycle of compound **3b** is disordered over a crystallographic center of symmetry. The four nitrogen atoms were refined with site occupancy factors of 0.5. Furthermore, one *tert*-butyl (CT2) group showed disorder; the carbon atoms were refined on split positions with occupancy factors of 0.61 and 0.39. The molecules of **4a** are located on crystallographic centers of symmetry. Two independent molecular halves are in the asymmetric unit. Compound **5** crystallized as systematically twinned crystals. Refinement was performed in space group $P4_2/n$ with the twin matrix [−1, 0, 0; 0, 1, 0; 0, 0, −1]. The aristotype may be $P4_2/nbc$, $P4_2/ncm$, $P4_2/nmc$, or $P4_2/nnm$. The twin ratio is 0.51:0.49.

Table 1. Crystallographic Data for **3b**, **4a**, **5**, and **6**

	3b	**4a**	**5**	6
empirical formula	$C_{18}H_{46}N_4Al_2$	$C_{18}H_{46}N_4Ga_2$	$C_{20}H_{52}N_8Al_4$	$C_{18}H_{43}N_3Al_2$
cryst syst	monoclinic	monoclinic	tetragonal	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P4_2/n$	$P2_1/c$
a (pm)	889.3(1)	1131.0(2)	1263.25(3)	1196.67(3)
b (pm)	1253.6(2)	1242.0(3)	1263.25(3)	1377.21(3)
c (pm)	1167.6(2)	1726.0(4)	955.75(3)	1416.67(4)
β (deg)	111.08(1)	103.00(3)	90	101.289(1)
V (nm^3)	1.2146(3)	2.3624(8)	1.52519(7)	2.2896(1)
Z	2	4	2	4
temp (K)	150(2)	150(2)	150(2)	110(2)
D_{calcd} (g cm^{-3})	1.019	1.288	1.116	1.031
independent data	2359	6906	1501	4290
observed data	1686	4963	1348	3387
params	175	239	83	222
μ(mm^{-1})	0.127	2.288	0.175	1.154
R1[a]	0.0474	0.0400	0.0448	0.0603
wR2 (all data)[b]	0.1337	0.1031	0.1214	0.1830
residual density (e nm^{-3})	+229/−218	+1312/−730	+586/−243	+687/−408

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Quantum-Chemical Calculations. All computations have been performed using the Gaussian 03 suite of programs.[27] The Becke

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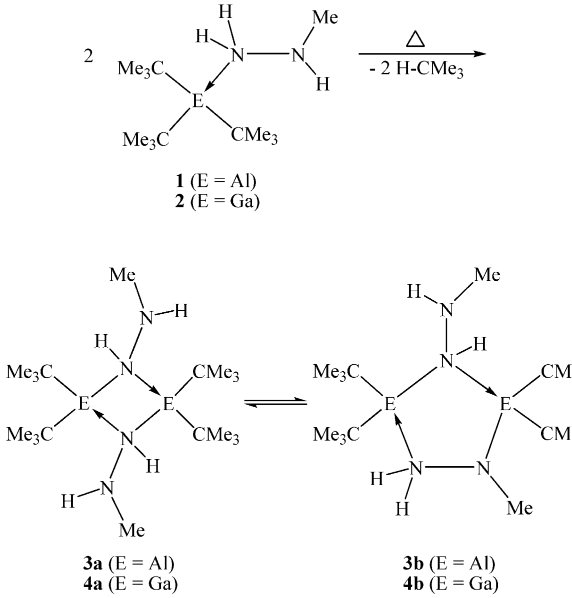
(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004. Details of the quantum chemical calculations (Gaussian archive entries) may be obtained from E.-U.W. upon request.

three-parameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP) with the 6-311+G(d,p) basis set were used to compute the geometries and the normal mode vibrations. For single-point energy calculations on DFT-optimized geometries, the SCS-MP2 method[28] was applied. Atomic charges were calculated with the natural bond orbital (NBO) method at the B3LYP/6-311+G(d,p) level as implemented in the Gaussian 03 program.

Results and Discussion

Synthesis of the Dimeric Hydrazides 3 and 4. The hydrazine adducts $(Me_3C)_3E \leftarrow NH_2-N(H)-Me$ [E = Al (**1**), Ga (**2**)] were obtained in almost quantitative yields by treatment of the corresponding trialkylelement compounds with methylhydrazine.[25] They have relatively low melting points of 52 and 42 °C, respectively. In both cases, the hydrazine ligands are coordinated via the nitrogen atoms of the NH_2 groups. When the aluminum compound was heated above its melting point, gas evolution started at about 95 °C (eq 1). The melt was stored at this temperature until gas evolution was complete. The gas was collected in a trap cooled by liquid nitrogen and was identified as isobutane by NMR spectroscopy and mass spectrometry. A colorless solid remained after cooling to room temperature and evaporation of all volatiles. Owing to the NMR spectroscopic characterization, compound **3** was directly formed at very high purity and an almost quantitative yield. Dissolution of the residue in cyclopentane and cooling of the solution to −30 °C yielded colorless crystals of **3**. The gallium adduct **2** is thermally much more stable. Heating up to 300 °C was required to initiate gas evolution, which was complete after about 0.5 h at this temperature. Cooling of the product and recrystallization from *n*-pentane gave the gallium hydrazide **4** in 64% yield. These strongly differing thermal stabilities of both adducts clearly depend on the different polarities of the E−C bonds. Due to the low electronegativity of aluminum compared to that of gallium, the Al−C bonds are relatively polar with marked carbanionic character at the respective carbon atoms and, hence, a stronger basicity of the alkyl groups. The corresponding tri(*tert*-butyl)indium methylhydrazine[25] adduct did not decompose on a specific route, but elemental indium precipitated and a mixture of unknown products was formed.



1 (E = Al)
2 (E = Ga)

(1)

3a (E = Al)
4a (E = Ga)

3b (E = Al)
4b (E = Ga)

Mass spectrometric characterization verified the expected dimeric formula units for both products. However, the ^1H spectra of the purified products are complicated and indicate the occurrence of at least two isomers in solution. Schematic representations of their probable molecular structures are given in eq 1. The centro-symmetric isomers containing four-membered heterocycles in their molecular centers (**3a** and **4a**) show simple sets of resonances of only one kind of hydrazido ligand. The Al−N−H hydrogen atoms of **3a** give a doublet by coupling to the N−H protons at the β-nitrogen atoms. A quartet resulted for the β-hydrogen atoms by a coupling to the N-methyl groups (the coupling to the α-N−H group was not resolved), and a doublet was observed for the N-methyl hydrogen atoms. The second isomer **3b** gave a relatively complicated spectrum with signals of two chemically different hydrazido ligands. One set of resonances closely resembles that of **3a** with a doublet and a quartet of N−H and a doublet of the N-methyl hydrogen atoms. They verify the occurrence of a $-N(H)-N(H)-Me$ group. The second hydrazido ligand showed sharp singlets of NH_2 and CH_3 hydrogen atoms, which are in accordance with a $-N(CH_3)-NH_2$ ligand. The *tert*-butyl groups gave a singlet for **3a** which remained unchanged upon cooling. A splitting of the corresponding resonance of **3b** into two broad singlets occurred at 260 K. They became considerably broader upon further cooling (200 K). Warming up to 340 K did not result in any significant change compared with the room temperature spectra. In particular, the integration ratio between the different species remained unchanged. In accordance with the occurrence of both isomers, the ^{15}N NMR spectrum of **3** gave five resonances of N−H groups ($\delta = 55.2-84.4$) which could clearly be assigned due to their coupling with the corresponding hydrogen atoms. The sixth resonance is at a relatively high field ($\delta = -197.9$) and may belong to the singular N−Me group of the five-membered ring which is not bonded to a hydrogen atom. However, its assignment could not be clarified unambiguously. These observations give nice evidence for the occurrence of the five-membered heterocycle containing two chemically different AlR_2 moieties, although actually the occurrence of four distinct *tert*-butyl resonances[7,10] is required by the molecular symmetry. The spectra of the gallium compound **4** showed broader and partially overlapping resonances, but the four- and a five-membered heterocycles could clearly be identified. A third isomer may occur; however, its resonances are more or less completely covered. The heterocycles were detected in different ratios. While the five-membered ring represents the main component for the aluminum compound **3**, the four-membered heterocycle is slightly favored for the gallium compound **4**. The ratios are about 5:3 at room temperature. The dynamic behavior of dimeric dialkylgallium or dialkylindium hydrazides has been established previously.[10,12,13,15,20] But this is the first time that it was observed

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[28] Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.

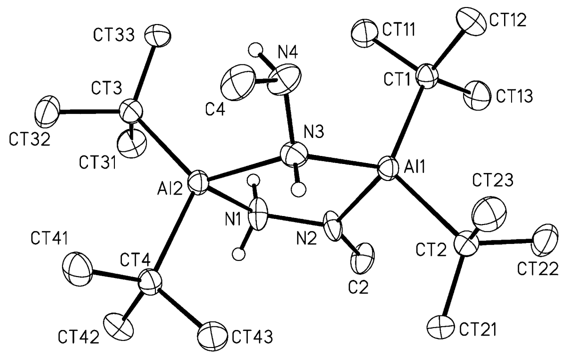


Figure 1. Molecular structure and numbering scheme of **3b**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms, with the exception of those attached to nitrogen, are omitted for clarity. Important bond lengths [pm] and angles [deg]: Al1−N1 199.8(2), Al1−N2 191.8(4), Al1−N3 195.1(4), Al1′−N3 195.4(5), N1−N2′ 141.5(5), N3−N4 136.3(6), N2−Al1−N3 90.6(2), Al1−N3−Al1′ 117.1(2), Al1−N2−N1′ 118.8(4), Al1−N1−N2′ 115.2(4); Al1′, N1′, and N2′ generated by $-x + 2$, $-y$, $-z + 1$.

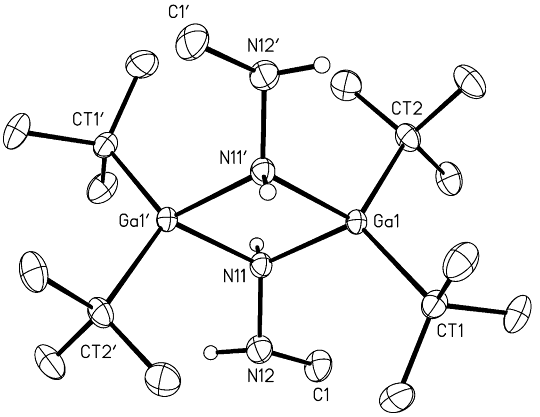


Figure 2. Molecular structure and numbering scheme of **4a**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of those attached to nitrogen are omitted for clarity. Only one of the independent dimeric molecules is shown; distances and angles of the second molecule are given in square brackets. Important bond lengths [pm] and angles [deg]: Ga1−N11 203.0(2) [207.1(3)], Ga1−N11′ 203.9(2) [204.1(3)], N11−N12 145.2(3) [143.4(4)], N11−Ga1−N11′ 83.61(9) [79.7(1)], Ga1−N11−Ga1′ 96.39(9) [100.3(1)]; Ga1′ and N11′ generated by $-x + 1$, $-y + 1$, $-z$.

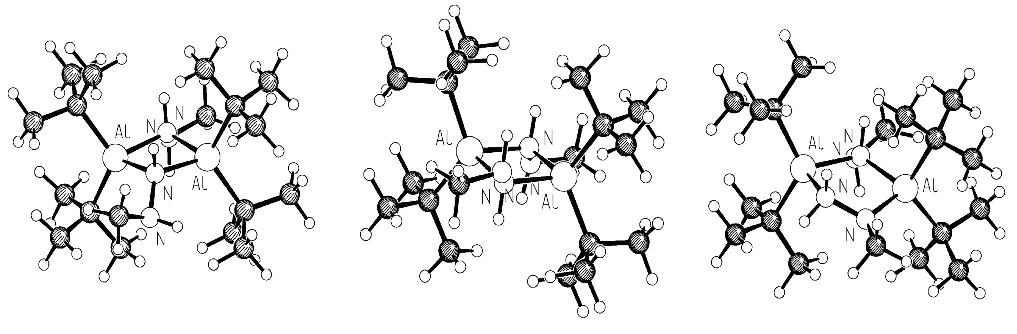
for dimeric dialkylaluminum hydrazides. It was often interpreted in terms of cis/trans isomerization. However, we believe that the reversible formation of different ring sizes in solution may offer a reasonable alternative for the description of these exchange processes.

Interestingly, compounds **3** and **4** possess different molecular structures in the solid state, and the constitutions of the main components in solution are preserved in the crystals. Thus, compound **3** adopts the five-membered Al_2N_3 heterocycle with one exocyclic and one endocyclic N−N bond (**3b**, Figure 1), while compound **4** has a four-membered Ga_2N_2 ring in its molecular center with two exocyclic N−N bonds (**4a**, Figure 2). Compound **4a** has Ga−N distances in a narrow range between 203 and 207 pm, while more pronounced differences occur in **3b**. The shortest Al−N bond (Al1−N2 191.8 pm) includes the negatively charged nitrogen atom of the −N(Me)−NH_2 ligand, of which each nitrogen atom is coordinated to only one aluminum atom. The longest Al−N distance (Al1−N1 199.8 pm) was observed for the dative bond involving the NH_2 group. Intermediate values (195.3 pm on average) were detected for the Al−N distances to the negatively charged nitrogen atom N3 which bridges two aluminum atoms. Both independent molecules of **4a** are located on crystallographic centers of symmetry. Hence, the Ga_2N_2 ring is planar. The Al_2N_3 heterocycle adopts an envelope conformation with the N2 atom 40 pm above the plane spanned by the atoms Al1, N3, Al1′, and N1′. The structural motif of a five-membered Al_2N_3 ring was observed in relatively few cases.[7,10] The same holds for six-membered E_2N_4 rings.[3,7,16] By far, most structures contain four-membered E_2N_2 heterocycles.

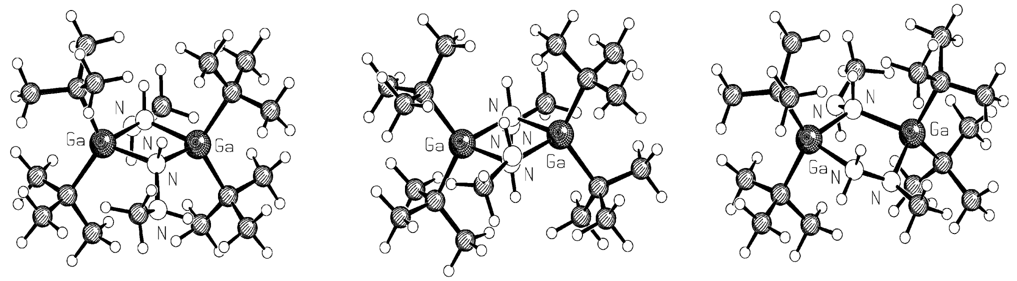
In order to compare the relative energies of the four- (trans and cis isomers) and five-membered ring structures **3a**, **3b**, **4a**, and **4b**, gas-phase quantum chemical calculations have been carried out at the SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level. The results are presented in Figure 3. As the calculations indicate, the five-membered heterocycle **3b** has been found to be lowest in energy for the Al heterocycles, followed by *cis*-**3a**. *trans*-**3a** has the highest calculated energy, but in all cases, the differences in energy are small. These results are in accordance with preliminary calculations reported for another aluminum hydrazide in an earlier publication.[7] In contrast, the four-membered ring (*cis*-**4a**) is the most favorable structure for the gallium hydrazides, and the five-memberend ring has an intermediate energy. The differences are considerably smaller than those for the isomers of **3**.

The main reason for the lower stability of the four-membered Al_2N_2 ring of **3** is in our opinion the relatively strong transannular electrostatic repulsion between both positively charged Al atoms (+2.02 calculated NBO charge) on the one side and both negatively charged nitrogen atoms (−1.13 calculated NBO charge) on the other. The calculated NBO charges on the gallium and nitrogen atoms of compound **4** are lower (+1.73 and −1.01, respectively), indicating a weaker repulsive interaction. Furthermore, the calculated distances between the metal (Al···Al or Ga···Ga) and N atoms (N···N) are shorter for the Al_2N_2 rings compared to the Ga_2N_2 heterocycles. The NBO charges and the E−E and N−N distances are given in Table 2. The balance between steric and electrostatic repulsion may determine the respective molecular structure adopted by these dimeric aluminum or gallium hydrazides. Electrostatic repulsion favors the formation of larger heterocycles, while an optimum attraction between positively charged aluminum or gallium atoms and negatively charged nitrogen atoms may favor the four-membered rings. Furthermore, the latter may exhibit a lower steric repulsion between the substituents attached to aluminum or gallium and those of the hydrazido ligands which for the E_2N_2 systems are usually bonded to the exo nitrogen atoms.

Thermolysis of Compound 3. In only a few cases, the thermolysis of aluminum or gallium hydrazides or the spontaneous release of alkanes or hydrogen was applied for the generation of oligocyclic or cagelike compounds containing intact N−N bonds.[14,15,18,21,25] The aluminum hydrazide **3** was a promising starting material for such experiments. It



a) *cis*-**3a** [3.17] *trans*-**3a** [4.24] **3b** [0.00]



b) *cis*-**4a** [0.00] *trans*-**4a** [1.75] **4b** [0.69]

Figure 3. Optimized structures and relative energies [kcal/mol] of compounds (a) *cis*-**3a**, *trans*-**3a**, and **3b** and (b) *cis*-**4a**, *trans*-**4a**, and **4b**, calculated at the SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level including zero-point correction.

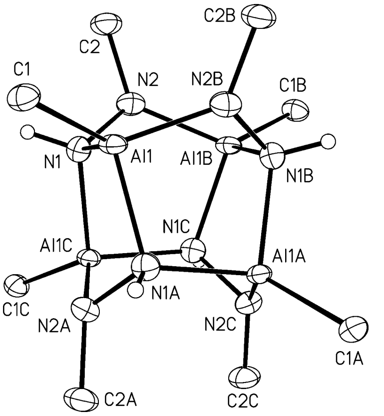


Figure 4. Molecular structure and numbering scheme of **5**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms, with the exception of those attached to nitrogen, are omitted for clarity. Important bond lengths [pm] and angles [deg]: Al1−N1 190.8(2), Al1−N1A 196.4(2), Al1−N2B 184.9(2), N1−N2 149.3(3), Al1−N1−N2 112.7(1), N1−Al1−N1A 97.00(9), N1−Al1−N2B 107.93(9), N1A−Al1−N2B 94.63(9), N1−N2−Al1B 109.7(1), Al1−N1−Al1C 107.5(1), N2−N1−Al1C 105.8(1). N1A generated by $-y + 1/2$, x, $-z + 3/2$; Al1B and N2B by $-x + 1/2$, $-y + 1/2$, z; Al1C by y, $-x + 1/2$, $-z + 3/2$.

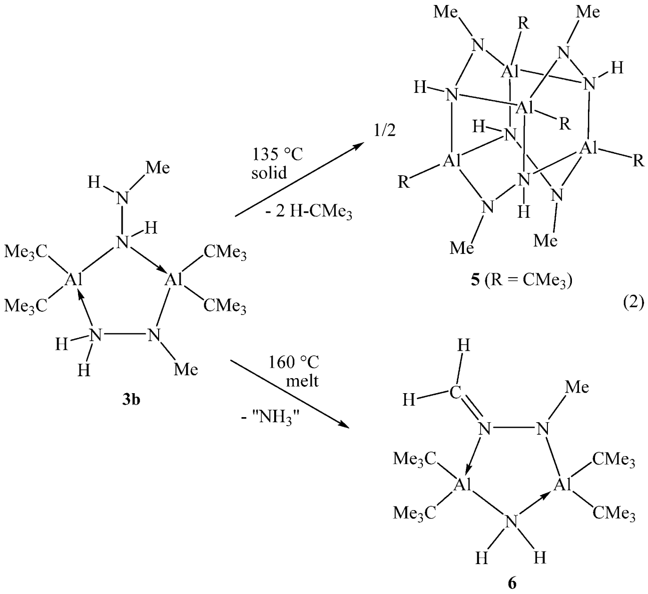
has polar Al−C bonds, and hence, the alkyl groups may react as strong bases and good leaving groups by the deprotonation of the hydrazido ligands. Accordingly, the particular reactivity of the Al−C bonds allowed the formation of **3** under relatively mild conditions compared to the synthesis of the gallium hydrazide **4** (see above). Temperature influenced the course of these thermolysis reactions with the selective formation of two completely different products.

Table 2. Calculated Transannular E···E and N···N Distances and NBO Charges in the Four-Membered Heterocycles of **3a** and **4a** (B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p))

compound	E−E distance (pm)	N−N distance (pm)	charge on E atoms	charge on N atoms
cis-**3a**	301.6	268.3	+2.02	−1.13
trans-**3a**	303.0	267.8	+2.03	−1.13
cis-**4a**	313.4	276.0	+1.74	−1.01
trans-**4a**	316.8	273.0	+1.72	−1.01

Isobutane was formed when solid **3** was heated to 135 °C, which is slightly below the melting point of 149 °C. The alkane was collected in a trap cooled by liquid nitrogen and was identified by NMR spectroscopy and mass spectrometry. An amorphous solid remained (**5**, eq 2), which had a low solubility in hydrocarbons and could be purified by washing with *n*-pentane. Compound **5** was obtained directly at high purity. Sublimation in a vacuum afforded colorless crystals. Crystal structure determination (Figure 4) revealed a tetranuclear cage compound, [Me$_3$C−Al−N(H)−N(Me)]$_4$, in which four Al−R groups are bridged by four hydrazindiido ligands having intact N−N bonds. The structure of the cage may be described by two six-membered Al$_2$N$_4$ rings in a boat conformation, which are linked by four Al−N bonds to give four additional five-membered Al$_2$N$_3$ heterocycles. Alternatively, the structure may be derived from an Al$_4$N$_4$ heterocubane, of which four edges are bridged by N−Me groups. All aluminum atoms have a coordination number of four and are coordinated by three nitrogen atoms and the terminal *tert*-butyl group. The coordination modes of the nitrogen atoms are different and depend on their substituents.

The N−H groups bridge two aluminum atoms. Their nitrogen atoms have a distorted tetrahedral surrounding. The N−Me groups are attached to only one aluminum atom. Their nitrogen atoms are bonded to three different atoms (H, N, and Al), and the sum of the angles (348.9°) indicates a pyramidal coordination sphere. The N−N distances (149.3 pm) are longer than usually observed for monoanionic hydrazido groups (about 145 pm). That lengthening may be caused by the electrostatic repulsion between both negatively charged nitrogen atoms. Three distinct Al−N distances occur: 184.9 pm to the tricoordinated nitrogen atoms, 190.8 pm for the remaining Al−N bonds of the six-membered heterocycles, and 196.4 pm between these rings. This highly symmetric structure gave a simple ^{1}H spectrum with singlets for the N−H, N−Me, and *tert*-butyl groups in the expected integration ratio.



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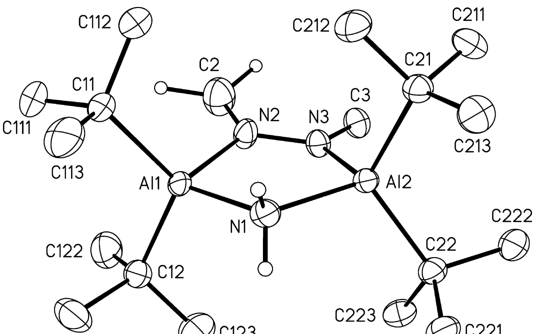

Figure 5. Molecular structure and numbering scheme of **6**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms of methyl groups are omitted for clarity. Important bond lengths [pm] and angles [deg]: Al1−N1 194.7(2), Al1−N2 193.6(2), Al2−N1 194.7(2), Al2−N3 193.8(2), N2−N3 134.1(3), N2−C2 133.3(4), N3−C3 136.7(3), N1−Al1−N2 93.75(9), Al1−N1−Al2 112.5(1), Al1−N2−N3 119.2(2), Al2−N3−N2 117.7(2), N1−Al2−N3 94.33(9), C2−N2−N3 119.0(2), Al1−N2−C2 121.6(2), N2−N3−C3 119.4(2), Al2−N3−C3 122.6(2).

Another product was obtained when the thermolysis of **3** was not conducted in the solid state, but in the melt at 160 °C (eq 2). Gas evolution occurred, which was finished after a few minutes. An amorphous colorless solid formed upon cooling to room temperature, which consists of the pure product **6**. Crystalline material was obtained by recrystallization from *n*-pentane or by sublimation in a vacuum. Crystal structure determination revealed an absolutely unexpected molecular structure (Figure 5). It comprises a five-membered Al_2N_3 heterocycle in which both aluminum atoms are bridged by a NH_2 group and a N_2 moiety. One nitrogen atom of the N_2 group is bonded to a methyl group; the other one is part of a $N{=}CH_2$ double bond. Thus, a hydrazonido ligand, $-N(Me)-N{=}CH_2$, formed. Bond lengths ($N{=}CH_2$, 133.3 pm; $N-CH_3$, 136.7 pm; N−N, 134.1 pm) correspond to a delocalized π-bonding in its backbone. The values differ from those observed for related aluminum or gallium hydrazonides, in which the distances verify a more localized bonding situation.[29] However, the relatively short N−N bond length corresponds in particular to data obtained for organic hydrazone derivatives.[29] In contrast to other aluminum or gallium hydrazonides,[29] the Al−N distances are in a narrow range between 193.6 and 194.7 pm and do not allow for a differentiation between "dative" or "covalent" interactions. Once more, this observation is in accordance with a delocalized bonding situation. The central heterocycle is almost planar, with the nitrogen atoms N2 and N3 only about 11 pm above and below the average plane. The results of the NMR spectroscopic characterization are in accordance with the molecular structure obtained by crystal structure determination. In the ^{1}H spectrum, two signals were observed for the chemically different *tert*-butyl groups. The methyl group at the N3 nitrogen atom gives a singlet ($\delta = 2.36$), and the hydrogen atoms at the sp^2 carbon atom ($N{=}CH_2$) exhibit resonances characteristic of an AB spin system with a geminal coupling constant of 7.6 Hz ($\delta = 5.48$ and 5.35). The formation of **6** may involve the cleavage and partial reformation of N−N bonds. Formally, ammonia was eliminated to afford the N=C double bond. However, it could be identified only in a mass spectrum obtained in a thermogravimetry experiment. A thermally unstable and reactive nitrene, N−Me, may be released as an intermediate by forming the bridging NH_2 group. It may insert into an Al−N bond to give the hydrazonido ligand. The release of nitrene was recognized and discussed once before, when we found its secondary product, a dialkyldiazene, weakly coordinated to an Al_4N_4 heterocubane-type molecule.[23] The ^{1}H spectrum of the crystalline solid of **6** shows the resonances of two further components with relatively low intensities. One has four ($\delta = 1.13$, 1.10, 1.06, and 1.03), and the other one two singlets ($\delta = 1.05$ and 1.00) of equal intensity in the *tert*-butyl range of the spectrum. The ratio of the three species changed with the temperature, and the resonances became broader upon warming. We suppose that isomers exist in

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(29) (a) Uhl, W; Molter, J.; Neumüller, B.; Schmock, F. *Z. Anorg. Allg. Chem.* **2001**, *627*, 909. (b) Uhl, W.; Molter, J.; Neumüller, B. *J. Organomet. Chem.* **2001**, *634*, 193. (c) Kim, S.-J.; Yang, N.; Kim, D.-H.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 4036. (d) Tosi, G.; Cardellini, L.; Bocelli, G. *Acta Crystallogr., Sect. B* **1988**, *44*, 55. (e) Menczel, G.; Samay, G.; Simon, K. *Acta Chim. Acad. Sci. Hung.* **1972**, *72*, 441. (f) Okumura, C.; Osano, Y. T.; Murayama, T.; Matsuzaki, T. *Anal. Sci.* **1990**, *6*, 485. (g) Porter, L. C.; Ming, L.; Cervantes-Lee, F.; Murray, H. H. *Monatsh. Chem.* **1993**, *124*, 775.

solution having, for instance, a four-membered heterocycle in their molecular core. Thermolysis of compound **3** in solution (mesitylene at 155 °C or undecane at 200 °C) gave inseparable mixtures of many unknown products.

Depending on the conditions, the thermolysis of the aluminum hydrazide **3** afforded very selectively two different products. An aluminum hydrazindiide cage (**5**) was produced upon the heating of **3** in the solid state by the expected release of isobutane, while in the melt, a rearrangement occurred with the formation of a five-membered heterocycle containing a bridging hydrazonido ligand (**6**). These observations are of particular importance in view of the potential application of such organoaluminum or -gallium hydrazides for the deposition of the corresponding nitrides. The development of a reasonable strategy for such experiments must consider the results reported here because the different decomposition pathways of hydrazides will influence the optimum reaction temperature and the purity of the products.

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

Supporting Information Available: X-ray crystallographic files in CIF format for the compounds $[Al(CMe_3)_2]_2[N(Me)-NH_2]$-$[N(H)-N(H)-Me]$ (**3**), $[Ga(CMe_3)_2]_2[N(H)-N(H)-Me]_2$ (**4**), $[Al(CMe_3)-N(H)-N(Me)]_4$ (**5**), and $[Al(CMe_3)_2]_2(NH_2)[N(=CH_2)-N(Me)]$ (**6**). This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determinations are also available from the Cambridge Crystallographic Data Center upon quoting the depository numbers CCDC-699245 (**3b**), -699246 (**4a**), -699247 (**5**), and -699248 (**6**).

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