Synthesis of Aluminum Hydrazides by Hydroalumination of 2,3-Diazabutadienes—Formation of an $Al_4(N_2)_3$ Cage Compound and an $Al_3(N_2)_3$ Macrocyclic Ligand

Werner Uhl,* Jens Molter, and Bernhard Neumüller[a]

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Abstract: Treatment of 1,1,4,4-tetramethyl-2,3-diazabutadiene with the alane adduct $[AlH_3(NMe_2Et)]$ yielded the hydrazine derivative $(AlH_2)_2(AlH)_2(N_2iPr_2)_3$ (**1**) by the hydroalumination of both C–N double bonds. Compound **1** has a complicated cage structure formed by three hydrazido groups and four aluminium atoms. As a particularly interesting structural motif it contains a N–N group side-on-coordinated to one aluminium atom through its lone pairs of electrons. Sublimation of **1** gave a heterocubane-type compound $(HAlNiPr)_4$ (**2**) by the complete cleavage of all N–N bonds, one face of which is bridged by weakly coordinated diisopropyldiazene with a N=N double bond. Repeated sublimation gave the pure, unsupported heterocubane molecule **3**. Heating of the rough product of the reaction of alane and diazabutadiene to 90 °C in a closed vessel yielded another product $Al(AlH_2)_3(N_2iPr_2)_3$ (**4**), which contains a cyclic chelating ligand formed by three hydrazido groups and three aluminium atoms. This heterocycle coordinates a fourth aluminum atom in the molecular center by close contacts to all six nitrogen atoms. A strongly flattened, distorted octahedral coordination sphere results for the inner metal atom.

Keywords: aluminum · cage compounds · heterocycles · hydrazides · N ligands · rearrangement

Introduction

Aluminum and gallium hydrazides have attracted considerable interest because they are potentially useful as starting materials for the formation of the corresponding nitrides by chemical vapor deposition or by thermolysis of macroscopic samples. Several methods for the synthesis of these compounds have been published, such as the treatment of hydrazines with trialkylelement compounds by the release of alkane,[1–3] the formation of hydrogen in a similar reaction by employing dialkylaluminum hydride[4, 5] or $LiAlH_4$,[6] the reaction of lithium hydrazides with dialkylelement chlorides,[6–8] the hydroalumination of azobenzene,[9] and the treatment of adducts of trimethylsilylhydrazine and dialkylaluminum chlorides[10] with *n*-butyllithium.[11] At present, we are very interested in hydroalumination reactions of polyenes or polyynes which open a facile method for the syntheses of polyaluminum compounds. These studies have led to the formation of carbaalanes containing novel clusters of aluminum and carbon atoms[12] or compounds with two or more coordinatively unsaturated aluminum atoms,[13] the latter are very effective chelating Lewis acids and have already been employed for the coordination of nitrate[14] and azide anions.[15] In continuation of this work we treated 2,3-diazabutadiene derivatives with aluminum hydrides to hydroaluminate the C–N double bonds and to open a new and facile route for the synthesis of aluminum hydrazido derivatives which may also be suitable as chelating ligands. We report here on reactions starting with the alane adduct $[AlH_3(NMe_2Et)]$.

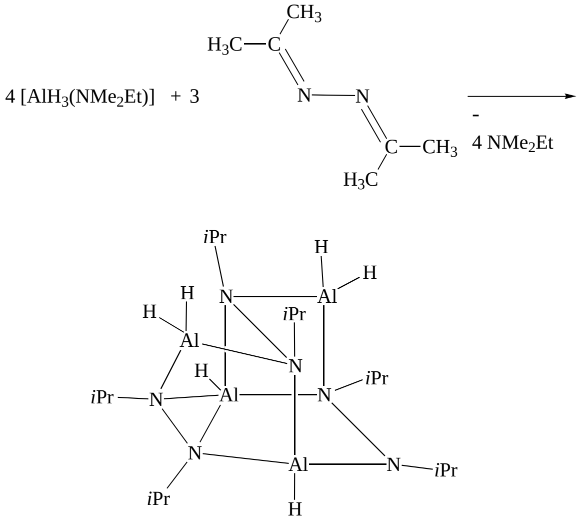
Results and Discussion

$[AlH_3(NMe_2Et)]$ is only sparingly soluble in nonpolar solvents such as *n*-pentane, and in our initial investigations we employed toluene as a solvent in the reaction of 1,1,4,4-tetramethyl-2,3-diazabutadiene with the alane adduct at low temperature. But in all cases, only oily residues were obtained which contained mixtures of several unknown products, none of which could be isolated by recrystallization or distillation. Therefore, we dissolved the organic component in *n*-pentane, cooled that solution to −50 °C and added two molar equivalents of the alane adduct dissolved in a small quantity of toluene [Eq. (1)]. After warming to room temperature and

---

[a] Prof. Dr. W. Uhl, J. Molter, Prof. Dr. B. Neumüller
Fachbereich Chemie der Philipps Universität
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421-2825653
E-mail: uhl@chemie.uni-marburg.de

0947-6539/01/0707-1510 $ 17.50+.50/0



(1)

1

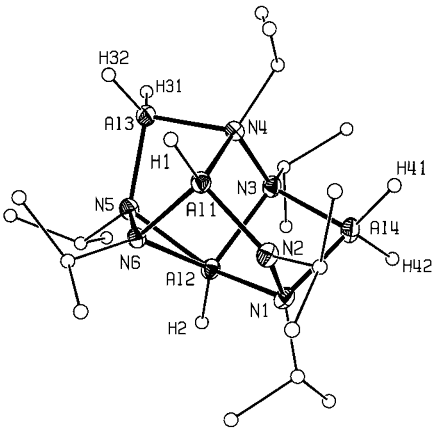
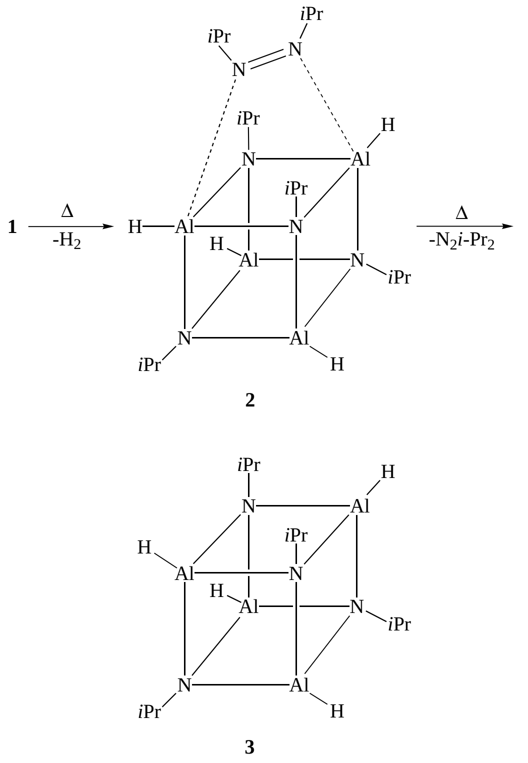


Figure 1. Molecular structure of **1**; the thermal ellipsoids are drawn at the 40% probability level; carbon and hydrogen atoms with arbitrary radius; methyl hydrogen atoms omitted. Selected bond lengths [pm]: Al1–N2 183.5(2), Al1–N6 195.1(2), Al1–N4 200.1(2), Al2–N1 200.9(2), Al2–N3 204.3(2), Al2–N5 203.8(2), Al2–N6 191.9(2), Al3–N4 198.7(2), Al3–N5 188.1(2), Al4–N1 191.5(2), Al4–N3 196.5(2), N1–N2 151.5(2), N3–N4 153.2(2), N5–N6 154.4(2).

evaporation of the solvent an amorphous residue remained which rapidly decomposed in pure toluene by gas evolution. Because of its insolubility in pure *n*-pentane it was dissolved in a warm (50 °C) mixture of *n*-pentane and toluene. The solution was rapidly cooled to – 40 °C, but nevertheless partial decomposition occurred. Colorless crystals of the product **1** were isolated in a small, but reproducible yield of 14%. Decomposition occurred in benzene or other polar solvents so that the NMR spectroscopic characterization failed. Five sharp symmetric and asymmetric Al–H stretching vibrations were detected in the IR spectrum between 1775 and 1917 cm^{-1} which clearly exclude the occurrence of hydrido bridges and verify a complicated molecular structure. The decomposition of the crystals of **1** was observed at low temperature (45 °C); an amorphous powder of **1** decomposed slowly even at room temperature to give a mixture of several unknown products.

The molecular structure of compound **1** (Figure 1) was clarified by an X-ray crystal structure determination. It contains a complicated, asymmetric cage which is schematically shown in Equation (1) and comprises three hydrazido groups and four aluminum atoms. The hydrazido groups are attached to two isopropyl groups and two aluminum atoms in 1,2-position; they may formally be considered as dianionic and were formed by the complete hydroalumination of all C=N double bonds of the starting diazabutadiene derivative. The aluminum atoms Al1 and Al2 are bonded to only one hydrogen atom, while Al3 and Al4 are attached to two hydrogen atoms. Al2 has a coordination number of five and N2 a coordination number of three, all remaining Al and N atoms of the cage are tetracoordinate. The N–N bonds (av 153.0 pm) are longer than usually detected in monoaluminum and monolithium hydrazides;[2–4, 6, 8, 10, 11, 16] this may be caused by the electrostatic repulsion between both negatively charged nitrogen atoms and was similarly observed before in a dilithium hydrazide[17] or the tricyclic compound $[(Me_3C)_2Al]_4[N_2H_2]_2$, which also contained dianionic hydrazido groups.[5] One of the hydrazido groups (N5,N6) is side-on-coordinated to an aluminum atom (Al2) through the the lone pairs of electrons on its nitrogen atoms. This is a quite unusual structural motif which to the best of our knowledge was observed before only in the aluminum dihydrazide $Me_3CAl[N(SiMe_3)N(H)(SiMe_3)]_2$[18] and the tricyclic compound $[(Me_3C)_2Al]_4[N_2H_2]_2$.[5] The Al–N distances differ markedly by 20.8 pm between 183.5 and 204.3 pm, but all are in the normal range of polar covalent and dative Al–N interactions.[19] The shortest distance is observed between Al1 and the three-coordinate nitrogen atom N2, the longest one is between the five-coordinate Al2 and N3 atoms. The side-on-coordinated N_2 group is asymmetrically attached to Al2 with Al–N distances of 191.9 and 203.8 pm.

Product **1** has the aluminum and hydrazido components in a four to three molar ratio; however, carrying out the reaction of the starting compounds in the corresponding molar ratio did not lead to a higher yield of **1**. To further investigate the decomposition reaction we heated **1** in vacuo between 30 and 70 °C [Eq. (2)]. Colorless crystals of **2** sublimed which were embedded in a colorless highly viscous liquid. An X-ray crystal structure determination of the solid **2** revealed a remarkable adduct of the heterocubane-type molecule $(HAlN\textit{i}Pr)_4$ with an azopropane (1,2-diisopropyldiazene) molecule *i*PrN=N*i*Pr (Figure 2). The diazene molecule adopts a *Z* configuration, and its N=N bond length (123.6 pm) is similar to that of other diazenes.[20] It is located above the diagonal of one face of the Al_4N_4 heterocubane, and each nitrogen atom of the diazene coordinates to one aluminum atom of the cage. However, the resulting Al–N distances are very long (Al1–N6 246.6 pm, Al2–N5 246.4 pm) indicating only a weak bonding interaction. Owing to that weak coordination the heterocubane is only slightly distorted, and two bonds at the bridged face (Al1–N3 and Al2–N4) are lengthened to 199.6 pm compared to the average value of the remaining Al–N bonds (191.5 pm). The isolation of compound **2** gives some insight



(2)

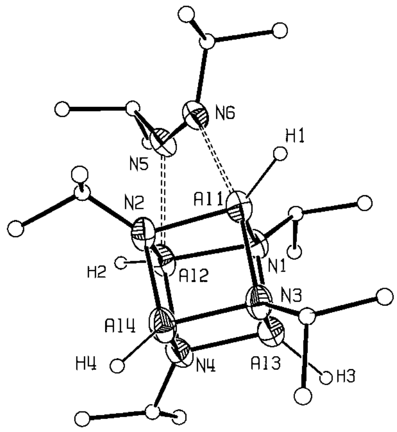


Figure 2. Molecular structure of compound **2;** the thermal ellipsoids are drawn at the 40% probability level; carbon and hydrogen atoms with arbitrary radius; methyl hydrogen atoms omitted. Selected bond lengths [pm] and angles [°]: Al1–N1 194.5(3), Al1–N2 193.9(3), Al1–N3 199.6(3), Al2–N1 194.0(2), Al2–N2 193.3(3), Al2–N4 199.6(3), Al3–N1 191.1(3), Al3–N3 190.4(3), Al3–N4 189.0(3), Al4–N2 189.9(3), Al4–N3 189.5(3), Al4–N4 189.0(3), N5–N6 123.6(3), Al1–N6 246.6(3), Al2–N5 246.4(3); N5-N6-C6 124.1(3), N6-N5-C5 124.6(3).

into the decomposition mechanism of **1**. Evidently, the N–N bonds are partially cleaved by the insertion of Al atoms into N–N bonds. One hydrazido group is transformed to the corresponding diazene which was trapped here as an adduct with a heterocubane molecule. The proposed mechanism would further require the release of one equivalent of elemental hydrogen, and indeed gas evolution was observed in the course of the sublimation.

Repeated sublimation of the product finally gave the pure heterocubane compound $(HAlN\mathit{i}Pr)_4$ (**3**) [Eq. (2)] which has been reported.[21] We found a different crystal system and space group (orthorhombic, *Pccn* in reference [21]), thus details of the crystal structure determination are included in Table 1. Compound **3** (Figure 3) has an almost regular

Table 1. Crystal data, data collection parameters and structure refinement of compounds **1**, **2**, **3** and **4**.[a]

	1	**2**	**3**	**4**
formula	$C_{18}H_{48}Al_4N_6$	$C_{18}H_{46}Al_4N_6$	$C_{12}H_{32}Al_4N_4$	$C_{18}H_{48}Al_4N_6$
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group[24]	$P2_1/n$ (no. 14)	$I2/a$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
Z	4	8	8	2
temperature [K]	212(2)	212(2)	212(2)	212(2)
ρ_{calcd} [g cm^{-3}]	1.146	1.065	1.076	1.096
a [pm]	1547.6(1)	1851.73(15)	3254.8(4)	981.3(1)
b [pm]	986.3(1)	945.90(6)	1023.7(1)	1011.8(1)
c [pm]	1882.3(1)	3264.5(2)	1309.3(2)	1467.7(1)
α [°]	90	90	90	90.64(1)
β [°]	112.90(1)	97.337(9)	105.56(1)	91.20(1)
γ [°]	90	90	90	108.18(1)
V [nm^3]	2.6467(3)	5.6710(7)	4.2026(9)	1.3840(2)
μ [mm^{-1}]	0.192	0.179	0.219	0.184
crystal size [mm]	0.5 × 0.5 × 0.25	0.55 × 0.55 × 0.45	0.44 × 0.40 × 0.32	0.44 × 0.40 × 0.32
diffractometer	CAD4	STOE IPDS	CAD4	CAD4
radiation	$Mo_{K\alpha}$; graphite monchromator			
2Θ range [°]	$4.3 \leq 2\Theta \leq 50.3$	$4.4 \leq 2\Theta \leq 52.0$	$5.0 \leq 2\Theta \leq 50.0$	5.0 £ 2Θ £ 50.1
index ranges	$0 \leq h \leq 18$	$-22 \leq h \leq 22$	$-38 \leq h \leq 0$	$-11 \leq h \leq 11$
	$0 \leq k \leq 11$	$-11 \leq k \leq 11$	$-12 \leq k \leq 0$	$-12 \leq k \leq 12$
	$-22 \leq l \leq 20$	$-39 \leq l \leq 39$	$-15 \leq l \leq 15$	$0 \leq l \leq 17$
independent reflections	4611 [R(int) = 0.0315]	5528 [R(int) = 0.1960]	3746 [R(int) = 0.0375]	4869 [R(int) = 0.0247]
reflections $I > 2\sigma(I)$	3802	2814	2580	3480
parameters	289	345	205	289
R[b]	0.0367	0.0544	0.0645	0.0461
$wR2$[c]	0.0998	0.1477	0.1801	0.1409
max./ min. residual [10^{30} e m^{-3}]	0.293/ – 0.264	0.285/ – 0.345	0.793/ – 0.422	0.309/ – 0.282

[a] Program: SHELXTL-Plus, SHELXL-97;[25]solutions by direct methods; full matrix refinement with all independent structure factors. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $(I > 2\sigma(I))$. [c] $wR^2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$ (all data).

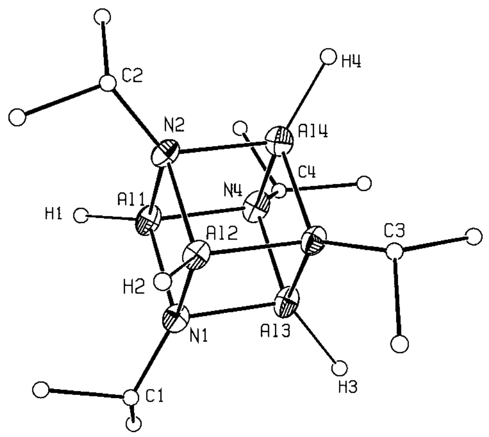
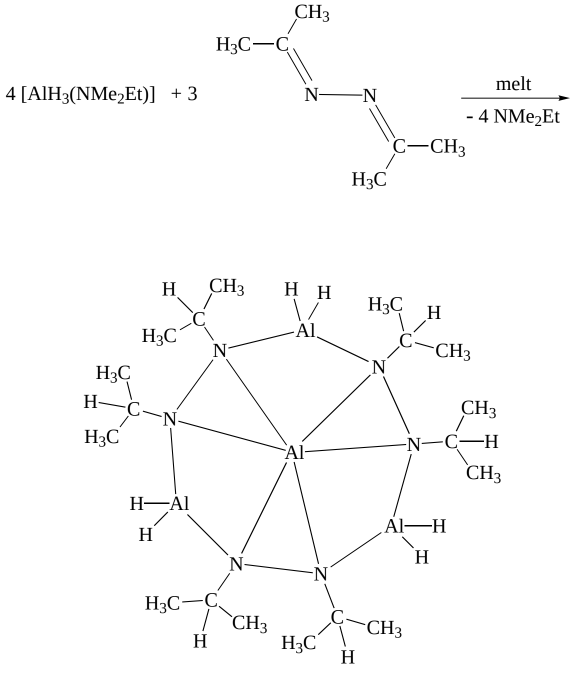


Figure 3. Molecular structure of compound **3;** the thermal ellipsoids are drawn at the 40 % probability level; methyl hydrogen atoms are omitted; carbon and hydrogen atoms with arbitrary radius. Selected bond lengths [pm]: Al1–N1 192.0(3), Al1–N2 193.0(3), Al1–N4 192.3(3), Al2–N1 192.7(3), Al2–N2 192.2(3), Al2–N3 191.9(3), Al3–N1 191.6(3), Al3–N3 192.4(2), Al3–N4 191.8(3), Al4–N2 191.6(3), Al4–N3 192.3(3), Al4–N4 193.1(3); Al-N-Al (av) 89.4, N-Al-N (av) 90.6°.

heterocubane structure with Al–N distances between 191.6 and 193.1 pm, and Al-N-Al and N-Al-N angles of 89.4 and 90.6°, respectively. It melts at 63 °C, and decomposition was observed only above 150 °C.

Another main product (**4**) was formed upon heating of the crude product of the reaction of diazabutadiene with the alane adduct in a closed vessel so that gas evolution was prevented [Eq. (3)]. Compound **3** was detected by NMR spectroscopy



(3)

4

only as a minor component of the reaction mixture. The product **4** was isolated in a pure form by recrystallization from *n*-hexane in 62 % yield. It is thermally stable in solution, and the crystals melt at 95 °C. As was shown by NMR spectroscopy all isopropyl groups and all Al-H hydrogen atoms are chemically equivalent. But interestingly the ^{27}Al NMR spectrum showed two resonance signals at $\delta = -9$ and $+113$ in the characteristic ranges of aluminum atoms with coordination numbers of six and four, respectively.[22]

The result of the X-ray crystal structure determination of **4** is depicted in Figure 4. A remarkable, highly symmetric new molecule was formed in which a central six-coordinate aluminum atom Al1 is surrounded by a nine-membered cyclic chelating ligand formed by three hydrazido groups and three aluminum atoms. All nitrogen atoms of the hydrazido groups are attached to the inner aluminum atom, thus, once again three-membered AlN$_2$ heterocycles are formed. The N–N distances are 152.3 pm on average, which as shown above is quite normal for dianionic hydrazido groups with electrostatic repulsion between both negatively charged nitrogen atoms. The relatively small distance between the coordinating atoms leads to a distorted octahedral coordination sphere of Al1, which may be described best as a strongly flattened trigonal antiprism or as a trigonal-planar coordination of aluminum by three hydrazido ligands. The aluminum atoms are exactly within the molecular plane, but the nitrogen atoms are located alternately only 55 pm (av) above or below that plane. Very acute angles of 46.7° at the central atoms result in AlN$_2$ triangles that include the N–N bonds, while between these triangles values of 92.0° are observed. The Al–N distances differ only slightly: within the Al$_3$N$_9$ ring a value of 195.0 pm (av) was determined, while the distances to the inner aluminum atom Al1 are little shorter (192.1 pm). The three aluminum atoms of the chelate ring are attached to two hydrogen and two nitrogen atoms to give a distorted tetrahedral coordination sphere. The diisopropylhydrazido groups adopt a characteristic *gauche* conformation with torsion angles of 83° (av). Owing to the molecular symmetry the nitrogen atoms have a chiral environment. This constitu-

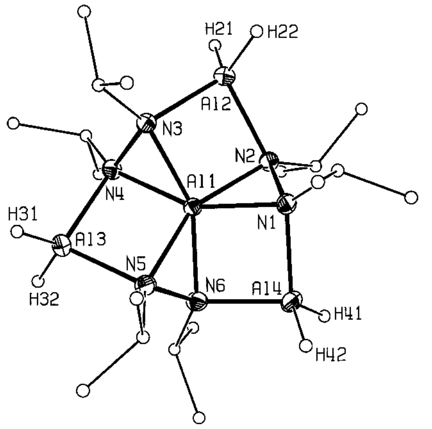


Figure 4. Molecular structure of compound **4;** the thermal ellipsoids are drawn at the 40 % probability level; methyl hydrogen atoms omitted; carbon and hydrogen atoms with arbitrary radius. Selected bond lengths [pm]: Al1–N1 191.9(2), Al1–N2 191.6(2), Al1–N3 192.0(2), Al1–N4 192.4(2), Al1–N5 192.6(2), Al1–N6 191.9(2), Al2–N2 194.8(2), Al2–N3 195.5(2), Al3–N4 195.0(2), Al3–N5 194.1(2), Al4–N1 195.1(2), Al4–N6 195.7(2), N1–N2 152.7(3), N3–N4 151.6(3), N5–N6 152.5(3).

tion remained unchanged in solution, and we observed diastereotopic methyl groups in the ^{1}H and ^{13}C NMR spectra. Compound **4** is an isomer of the cage compound **1** and may be generated formally by the migration of one hydrogen atom of one AlH group to the second AlH group of the cage. However, pure **1** could not be transformed into **4** on heating. Evidently, a component of the crude product of the reaction, for instance excess $[AlH_3(NMe_2Et)]$, is needed to facilitate the rearrangement. A structure similar to that of **4** was observed for the ethylene diamido compound $[Al(HNCH_2CH_2NH)_3(AlMe_2)_3]$,[23] in which, however, the coordinating nitrogen atoms are separated by ethylene groups and in which a more regular octahedral coordinating sphere of the inner atom results.

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene over Na/benzophenone; *n*-hexane and *n*-pentane over $LiAlH_4$). The starting compounds are commercially available and were used without further purification: alane adduct $[AlH_3(NMe_2Et)]$ (MOCHEM, Marburg) and 1,1,4,4-tetramethyl-2,3-diazabutadiene (Aldrich).

Synthesis of 1: A solution of $[AlH_3(NMe_2Et)]$ (5.62 g, 54.6 mmol) in toluene (5 mL) was added dropwise to a cooled (−50 °C) solution of 1,1,4,4-tetramethyl-2,3-diazabutadiene (3.6 mL, 3.03 g, 27.1 mmol) in *n*-pentane (20 mL). The solution was warmed to 5 °C over a period of 8 h. At this temperature, all volatile components of the mixture were distilled off in vacuo. The residue was rapidly dissolved in a warm (50 °C) mixture of toluene and *n*-hexane, and the solution was cooled to −40 °C. Colorless crystals of **1** were obtained after about 1 h. Yield: 0.59 g (14 %, based on diazabutadiene); m.p. (argon, sealed capillary) 45 °C (decomp); IR (CsBr, paraffin): $\tilde{\nu} = 1917$ m, 1888 m, 1829 m, 1812 s, 1775 m νAlH; 1461 vs, 1378 vs paraffin; 1349 w, 1303 w δCH_3; 1167 w, 1142 m, 1125 m, 1112 m νCC; 1041 vw, 999 w, 976 w, 944 w, 924 w, 888 vw, 833 m νCN, νNN; 811 vw, 780 s, 751 s, 739 m, 720 s, 669 m, 650 m δAlH; 575 w, 516 vw, 486 vw, 456 w cm^{-1} νAlN; 346 vw δCC; MS (EI); *m/z* (%): 455.2 (2) $[M^+ - H]$, 341.8 (1) $[M^+ - N_2iPr_2H_2]$.

Synthesis of 2 and 3: A cooled (−50 °C) solution of 1,1,4,4-tetramethyl-2,3-diazabutadiene (1.31 g, 11.7 mmol) in *n*-pentane (20 mL) was treated with the alane amine adduct (2.44 g, 23.7 mmol) in toluene (5 mL). The mixture was warmed to room temperature (4 h). All volatile components were removed in vacuo, the residue was evacuated (0.5 Torr) and heated to 70 °C over a period of 4 h. Colorless crystals of compound **2** embedded in a colorless oil sublimed at a constant pressure to a water-cooled glass wall. The end of sublimation was indicated by a spontaneous decrease of the pressure to 0.1 Torr. Repeated sublimation of the product at 0.01 Torr and 70 °C gave the pure product **3**. Yield: 0.34 g (26 % of **3**, based on diazabutadiene). Compound **2** was not obtained in a pure form free of the highly viscous liquid and was therefore not characterized further. Characterization of **3**:[21] M. p. argon, sealed capillary) 63 °C; ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 1.29$ (d, $^3J_{H,H} = 6.3$ Hz, 6 H; Me), 3.27 (septet, $^3J_{H,H} = 6.3$ Hz, 1 H; NCH); ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 29.3$ (Me), 46.2 (NC); IR (CsBr, paraffin): $\tilde{\nu} =$ 1861 vs, 1462 vs, 1380 vs paraffin; 1365 vs, 1336 vs, 1283 w δCH_3; 1164 vs, 1135 vs, 1087 w, 1012 vs, 846 vs νCN, νCC; 687 vs, 640 sh, 606 sh δAlH; 558 vw, 524 m, 481 w, 462 w, 446 w, 431 w νAlN; 381 vw, 343 vw cm^{-1} δCC; MS (EI); *m/z* (%): 339.1 (33) $[1/2M^+ - H]$, 326 (100) $[1/2M^+ - Me]$.

Synthesis of 4: A solution of the alane amine adduct (2.45 g, 23.8 mmol) in toluene (5 mL) was added to a cooled (−50 °C) solution of 1,1,4,4-tetramethyl-2,3-diazabutadiene (1.6 mL, 1.35 g, 12.1 mmol) in *n*-pentane (20 mL). The mixture was warmed to +5 °C over a period of 10 h. At this temperature all volatile components were distilled off in vacuo. The residue was warmed to 90 °C in a closed glass vessel in 30 min. After cooling to room temperature the solid crude product was recrystallized from *n*-hexane (20/−40 °C). Yield: 1.14 g (62 %, based on diazabutadiene), m. p. (argon, sealed capillary) 95 °C; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 1.35$ and 1.33 (each 3 H, d, $^3J_{H,H} = 7$ Hz, diastereotopic methyl groups), 3.99 (1 H, septet, $^3J_{H,H} = 7$ Hz; NCH), 4.72 (1 H, br.; AlH); ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 25.1$ and 25.5 (diastereotopic methyl groups), 57.1 (NC); ^{27}Al NMR (C_6D_6, 104.3 MHz): $\delta = 113$ (four-coordinate Al atoms), −9 (six-coordinate Al atom); IR (CsBr, paraffin): $\tilde{\nu} = 1860$ vs, 1834 vs, 1820 vs νAlH; 1461 vs, 1378 vs paraffin; 1344 m, 1319 w δCH_3; 1169 s, 1144 s, 1119 s, 1010 s, 971 s, 932 m, 835 m νCN, νCC; 783 s, 723 vs, 631 s, 613 s δAlH; 579 s, 553 s, 505 s, 465 s νAlN; 398 m cm^{-1} δCC; MS (EI); *m/z* (%): 342.2 (55) $[M^+ - N_2iPr_2]$; molar mass (cryoscopically in benzene) calcd 456.5; found 440 g mol^{-1}.

Crystal structure determinations: Single crystals were obtained by recrystallization from hot *n*-hexane/toluene on rapid cooling to −40 °C (**1**), from *n*-hexane (**4**) or by sublimation in vacuo (**2** and **3**). Crystal data and structure refinement parameters are given in Table 1.[26] One isopropyl group of compound **2** (C4) showed a disorder; the methyl group C42 was refined on split positions with occupancy factors of 0.66 to 0.34.

Acknowledgement

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

---

[1] D. W. Peters, E. D. Bourret, M. P. Power, J. Arnold, *J. Organomet. Chem.* **1999**, *582*, 108; D. W. Peters, M. P. Power, E. D. Bourret, J. Arnold, *Chem. Commun.* **1998**, 753.

[2] V. C. Gibson, C. Redshaw, A. J. P. White, D. J. Williams, *Angew. Chem.* **1999**, *111*, 1014; *Angew. Chem. Int. Ed.* **1999**, *38*, 961.

[3] Y. Kim, J. H. Kim, J. E. Park, H. Song, J. T. Park, *J. Organomet. Chem.* **1997**, *545–546*, 99; D. Cho, J. E. Park, B.-J. Bae, K. Lee, B. Kim, J. T. Park, *J.* Organomet. Chem. **1999**, *592*, 162.

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

[5] W. Uhl, J. Molter, B. Neumüller, *Inorg. Chem.*, submitted.

[6] H. Nöth, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1931.

[7] D. A. Neumayer, A. H. Cowley, A. Decken, R. A. Jones, V. Lakhotia, J. G. Ekerdt, *Inorg. Chem.* **1995**, *34*, 4698.

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

[9] K. Niedenzu, P. Fritz, W. Weber, *Z. Naturforsch. B* **1967**, *22*, 225.

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

[11] W. Uhl, J. Molter, R. Koch, *Eur. J. Inorg. Chem.* **2000**, 2255; W. Uhl, J. Molter, B. Neumüller, *Z. Anorg. Allg. Chem.* in press.

[12] W. Uhl, F. Breher, *Eur. J. Inorg. Chem.* **2000**, 1.

[13] W. Uhl, F. Breher, *J. Organomet. Chem.* **2000**, *608*, 54.

[14] W. Uhl, F. Hannemann, W. Saak, R. Wartchow, *Eur. J. Inorg. Chem.* **1998**, 921.

[15] W. Uhl, F. Hannemann, *J. Organomet. Chem.* **1999**, *579*, 18.

[16] K. Bode, U. Klingebiel, *Adv. Organomet. Chem.* **1996**, *40*, 1; S. Dielkus, C. Drost, R. Herbst-Irmer, U. Klingebiel, *Angew. Chem.* **1993**, *105*, 1689; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1625.

[17] C. Drost, C. Jäger, S. Freitag, U. Klingebiel, M. Noltemeyer, G. M. Sheldrick, *Chem. Ber.* **1994**, *127*, 845; K. Bode, C. Drost, C. Jäger, U. Klingebiel, M. Noltemeyer, Z. Zak, *J. Organomet. Chem.* **1994**, *482*, 285; E. Gellermann, U. Klingebiel, M. Schäfer, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1131.

[18] W. Uhl, J. Molter, B. Neumüller, *Organometallics*, **2000**, *19*, 4422.

[19] A. Haaland, in *Coordination Chemistry of Aluminum* (Ed.: G. H. Robinson), VCH, Weinheim, **1993**. Further recent examples for dative versus covalent ionic Al–N interactions: K. Kincaid, C. P. Gerlach, G. R. Giesbrecht, J. R. Hagadorn, G. D. Whitener, A. Shafir, J. Arnold, *Organometallics* **1999**, *18*, 5360; N. Emig, F. P. Gabbaï, H. Krautscheid, R. Réau, G. Bertrand, *Angew. Chem.* **1998**, *110*, 1037; *Angew. Chem. Int. Ed.* **1998**, *37*, 989; N. Emig, H. Nguyen, H. Krautscheid, R. Réau, J.-B. Cazaux, G. Bertrand, *Organometallics* **1998**, *17*, 3599; D. A. Atwood, J. A. Jegier, M. P. Remington, D. Rutherford, *Austr. J. Chem.* **1996**, *49*, 1333; I. Krossing, H. Nöth, H. Schwenk-Kircher, *Eur. J. Inorg. Chem.* **1998**, 927.

[20] P. S. Engel, *Chem. Rev.* **1980**, *80*, 99; M. Schmittel, A. Schulz, C. Rüchardt, E. Hädicke, *Chem. Ber.* **1981**, *114*, 3533.

0947-6539/01/0707-1514 $ 17.50+.50/0

[21] G. Del Piero, M. Cesari, G. Dozzi, A. Mazzei, *J. Organomet. Chem*. **1977**, *129*, 281.

[22] R. Benn, A. Rufiñska, H. Lehmkuhl, E. Janssen, C. Krüger, *Angew. Chem*. **1983**, *95*, 808; *Angew. Chem. Int. Ed. Engl*. **1983**, 22, 779; R. Benn, A. Rufiñska, *Angew. Chem*. **1986**, *98*, 851; *Angew. Chem. Int. Ed. Engl*. **1986**, *25*, 861.

[23] Z. Jiang, L. V. Interrante, D. Kwon, F. S. Tham. R. Kullnig, *Inorg. Chem*. **1992**, *31*, 4815.

[24] *International Tables for Crystallography, Space Group Symmetry, vol. A* (Ed.: T. Hahn), Kluwer Academic Publishers, Dordrecht, **1989**.

[25] SHELXTL-Plus, Release 4.2 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-Ray Instruments Inc., Madison, USA, **1990**; G. M. Sheldrick, SHELXL-97, Program for the Refinement of Structures, Universität Göttingen, **1997**.

[26] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151593 (**1**), CCDC-151594 (**2**), CCDC-151595 (**3**), and CCDC-151596 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: October 31, 2000 [F2838]