Synthesis and Structures of Some Aluminum Pseudohalides

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Dedicated to Professor Michael Veith on the occasion of his 60th birthday

The reactions of bis(2,2,6,6-tetramethylpiperidino)aluminum bromide (tmp2AlBr) with Me3SiN3 or Me3SiCN lead to trimeric tmp2AlN3 and tmp2AlCN, respectively, while the reaction with Me3SiOCN produces the bicyclic compound \([\text{tmpCON(SiMe}_3]_2\)\]. Similarly, di(tert-butyl)aluminum bromide reacts with Me3SiCN to give tetrameric \((\text{Me3C})_2\text{AlCN}\), 4. The compounds \((\text{Me3C})_2\text{AlN}_3\) and \((\text{Me3C})_2\text{AlOCN}\), obtained as oily products, have tetracoordinated Al atoms as shown by NMR spectroscopy, but the degree of oligomerization has not been determined.

Key words: Trimeric Bis(tetramethylpiperidino)aluminum Azide, Trimeric Bis(tetramethyl-piperidino)aluminum Cyanide, Tetrameric (Di-tert-butyl)aluminum Cyanide, X-Ray Structures

Introduction

Amongst the aluminum pseudohalides the aluminum azides received most attention in recent years. One reason for this is that they are, like gallium azides and indium azides, precursors for AlN [1], GaN [2, 3], and InN [4] which are useful materials for application in microelectronics and optoelectronics. Al(N3)3 [5 – 7] was the first example of an aluminum azide, and its THF solution was used for the syntheses of triazoles [8]. Later, in 1967 and 1972, N. Wiberg et al. described aluminum halide azides [9, 10]. The first dialkylaluminum azides were reported by K. Dehnicke et al. [11] and J. Atwood et al. [12]. These proved to be trimeric with azide groups bridging two Al atoms by the \(\alpha\)-N-atoms (see formula A). Although Et2AlN3 is also trimeric, it possesses \(\alpha,\gamma\)-bridging azide groups [13] as depicted by B. On the other hand, the association of the aluminum azides can be prevented by donor molecules, e.g. pyridine, to give compounds of type C [14]. Another variation is realized for bis(dimethylaminopropyl)aluminum azide D with a pentacoordinated Al atom [15], a structural motif also found in bis(dimethylaminobenzyl)aluminum azide [15]. Related to the present work is the dimeric bis(piperidino)aluminum azide E [16]. Azido bridges of type B were found for NaAl(N3)4 · 4 THF [17]. Both cations are hexacoordinated by two THF molecules and four azido groups building a two dimensional network.

Results and Discussion

Synthesis

We have shown that bis(2,2,6,6-tetramethylpiperidino)aluminum alkoxides, alkylthiolates and alkylselenides are monomeric compounds with tricoordinated Al atoms [18] due to the steric requirement of the tmp group. In contrast, the fluoride tmp2AlF is dimeric with bridging fluoride atoms [19], while the other three bis(tetramethylpiperidino)aluminum halides are monomeric [20]. Thus is was of interest to prepare and determine the structures of bis(tetramethylpiperidino)aluminum pseudohalides to see whether these are monomeric or associated.
NaN₃ was reacted with tmp₂AlBr [20] in an attempt to synthesize tmp₂AlN₃. In toluene a reaction occurred as the solution was free of an Al compound after a few hours. Obviously, a reaction according to eq. (1) did not occur, assuming that tmp₂AlN₃ is soluble in toluene. From the solid, which was isolated, no tmp₂AlN₃ could be extracted by a number of non-polar and polar solvents. In case of Et₂O or THF as the solvent the product in solution proved to be a small amount of tmpH by ¹H NMR spectroscopy. So, most likely, an insoluble aluminate Na[AlN₃Br(tmp)₂] (eq. 2) or a mixture of aluminates are formed.

\[
\text{tmp}_2\text{AlBr} + \text{NaN}_3 \rightarrow \text{tmp}_2\text{AlN}_3 + \text{NaBr} \quad (1)
\]

\[
\text{tmp}_2\text{AlBr} + \text{Me}_3\text{SiN}_3 \rightarrow \text{tmp}_2\text{AlN}_3 + \text{Me}_3\text{SiBr} \quad (3)
\]

However, the reaction according to eq. (3) proceeded quantitatively within a day in toluene solution. This type of reaction was successful in the synthesis of several other aluminium azides [9, 10]. I precipitated from the solution. Though I is only sparingly soluble, the filtrate yielded single crystals of I at −4 °C in low yield within a few days.

The cyanide tmp₂AlCN, 2, was obtained in analogy to I as shown in eq. (4). It is also sparingly soluble in hydrocarbon solvents, ethers and chloromethanes. Nevertheless, some single crystals of 2 could be separated from the toluene filtrate after storing the solution at −4 °C.

Compounds 1 and 2 are trimeric. They do not add bases such as pyridine or PMe₃ in order to form more soluble complexes. 2 also did not dissolve in Et₂O, THF or tert-butyl(methyl) ether, even under reflux conditions. Only small amounts of tmpH could be detected in these solutions. Thus the Al atoms of the two compounds interact strongly with the pseudohalide groups. On the other hand, when tmp₂AlBr was first reacted with a Lewis base, e.g. forming the adduct tmp₂AlBr·py, no reaction occurred after subsequent addition of Me₃SiCN.

When Me₃SiOCN was treated with tmp₂AlBr in toluene solution no reaction according to eq. (5) was observed as the stoichiometry was not 1:1 but 2:1. The reaction proceeded as shown in eq. (6) to produce a bicyclic compound with a pentacoordinated Al atom.

\[
\text{tmp}_2\text{AlBr} + \text{Me}_3\text{SiNCO} \rightarrow \text{tmp}_2\text{AlOCN} + \text{Me}_3\text{SiBr} \quad (5)
\]

\[
\text{tmp}_2\text{AlBr} + 2\text{Me}_3\text{SiNCO} \rightarrow \text{Me}_3\text{AlOCN} + 2\text{Me}_3\text{SiBr} \quad (6)
\]

On a first glance this is surprising. However, because Me₃Si-N=C=O is a CO₂ analogue, which can insert into the AlN bonds, this Al-N insertion reaction wins the competition over the substitution reaction at the AlBr bond. Reaction (6) is independent of stoichiometry and temperature (−78 °C to 100 °C). In contrast, Me₃Si-NCS did not react with tmp₂AlBr.

The tmp group mimics in its steric demand the tBu₂N group. In spite of the bulkiness of tmp it does not prevent the oligomerization of 1 and 2, the most likely reason being that the linear N₃ and CN groups require less space than either a Cl or Br atom, and, therefore, the pseudohalide anions are comparable to the fluoride ligand in dimeric tmp₂AlF with fluoride bridges [19].

Sterically more demanding than two tmp groups are two tBu groups attached to an Al atom. Therefore, we also studied the reactions of tBu₂AlBr with Me₃Si-pseudohalides. The result of the reaction of tBu₂AlBr with Me₃SiCN in toluene is shown in eq. (7). The reaction proceeds slowly, 12 h were necessary for completion. Compound 4 was isolated as a solid in 86% yield by cooling the solution to −4 °C. In contrast, the azide tBu₂AlN₃, 5, which was prepared similarly from Me₃SiN₃ and tBu₂AlBr, was obtained only as an oil. From the reaction of tBu₂AlBr with Me₃SiNCO a waxy material resulted, probably impure tBu₂AlOCN, which could also not be crystallised. Therefore, the latter two compounds could not be characterized structurally by X-ray methods. Their ²⁷Al NMR spectra proved the presence of tetra-coordinated Al atoms showing a single signal, but the ¹H NMR spectra displayed many more signals than expected for the pure compounds.

\[
t\text{Bu}_2\text{AlBr} + \text{Me}_3\text{SiCN} \rightarrow t\text{Bu}_2\text{AlOCN} + \text{Me}_3\text{SiBr} \quad (7)
\]
NMR spectra

The low solubility of 1 and 2 in deuterated solvents made it difficult to obtain $^{27}$Al and even $^1$H NMR spectra. However, when the suspensions that formed during the reactions (3) and (4) were used for recording of the NMR spectra then some of the data could be obtained. Even under these conditions we found $\delta^{27}$Al only for 1 at 99.4 ppm but not for 2. $^1$H NMR signal for the tmp group could be observed for both compounds: They are, as expected, rather similar, showing only single signals for all CMe$_2$ groups, indicating free rotation about the respective Al-N bonds. On the other hand, no problems arose in recording the $^1$H, $^{13}$C, $^{27}$Al and $^{29}$Si NMR spectra of the spirocyclic compound 3. The protons H6/7 and H3/4 were both observed as broad signals, a somewhat unusual feature because the CMe$_2$ protons of tmp$_2$Al compounds are, in general, well resolved. On the other hand, four $^1$H NMR signals were found for the CMe$_2$ groups of compound 3 which points to hindered rotation about the respective Al-N bond in accord with a “tetragonal” pyramidal structure of the molecule. Its Me$_3$Si groups are represented by a single and sharp $^1$H NMR signal at 1.0 ppm. The $^{13}$C NMR spectrum of 3 showed the carbamide C atom at 178.8 ppm, and its $^{27}$Al NMR signal was observed at 56.0 ppm. This lies in the range typical for pentacoordinated aluminum atoms [21]. Moreover, the $^{29}$Si NMR signal was observed at 1.3 ppm in accord with other silyl substituted aminates.

While compound tBu$_2$AlCN, 4, exhibits a single $^1$H resonance at 1.24 ppm for the tert-butyl group and two $^{13}$C NMR signals, the $^{13}$C atom of the CN group could not be detected. This is a well known phenomenon for C atoms bound to a nucleus with a high quadrupol moment [22]. $\delta^{27}$Al at 131.0 ppm ($h_{1/2} = 5600$ Hz) for 4 points to the presence of a tetra-coordinated Al atom. $^{27}$Al resonances for (tBu$_2$AlX)$_n$ compounds (X = OR, NR$_2$) range from 146 to 172 ppm [21, 22]. For tBu$_2$AlN$_1$, the $^{27}$Al chemical shift of 145.8 ppm ascertains the presence of tetra-coordinated Al centers which are also observed for (tBu$_2$AlNCO)$_n$ ($\delta^{27}$Al = 141 ppm; $h_{1/2} = 4400$ Hz).

Molecular structures

NMR and IR data allowed no conclusion as to the degree of association of compounds 1, 2, 4 and 5. However, for the first two of these they indicated a high degree of symmetry. X-ray structure determinations showed that 1 and 2 are trimers, while 4 is a tetramer. The aluminum azide 1 crystallizes in the triclinic space group P1 with two independent trimeric units. Fig. 1 shows the structure of one of these molecules whose structural parameters are almost identical. The azide groups form $\alpha$, $\gamma$-bridges between two Al atoms. This results in a twelve-membered nonplanar Al$_3$N$_9$ ring structure. The endocyclic N-Al-N bond angles range from 146.8 to 161.4 degrees, and the exocyclic N-Al-N bond angles range from 119.6 to 129.9 degrees. The Al-N bond lengths range from 1.842(4) to 1.894(4) Å, and the N-Al-N bond angles range from 105.5(1) to 114.0(1) degrees.

Fig. 1. The molecular structure of one of the two independent molecules of trimeric bis(tetramethyldiethyldimethylaminodiphenyl)aluminum azide. Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and bond angles (in degrees). Ellipsoids are shown on the 25% probability level. Selected structural parameters of the second independent molecule are quoted after the data for the first independent molecule. Selected bond lengths: Al1-N1 1.822(3), Al1-N2 1.814(3), Al2-N1 1.821(3), Al2-N2 1.815(3), Al3-N1 1.830(3), Al3-N2 1.823(3), Al4-N1 1.820(3), Al4-N2 1.817(3), Al5-N1 1.831(3), Al5-N2 1.824(3), Al6-N1 1.822(3).
Fig. 2a. The molecular structure of trimeric bis(2,2,6,6-tetramethylpiperidino)aluminum cyanide(2). Thermal ellipsoids are represented on a 25% probability level. Only one orientation of the site disordered tmp group N9C60-C68 is shown. Selected bond lengths (in Å): Al1-N1 2.041(3), Al2-N2 2.034(3), Al3-N3 2.009(3), Al1-C3 2.033(3), Al2-N6 1.829(2), Al2-N6 1.829(2), Al1-N5 1.827(2), Al2-N6 1.829(2), Al2-N6 1.829(2), Al3-N8 1.821(3), Al3-N9 1.828(3), C1-N1 1.169(4), C2-N2 1.167(4), C3-N3 1.161(4), N4-C10 1.496(4), N4-C14 1.495(4), N5-C20 1.494(4), N5-C24 1.499(4), N6-C30 1.500(4), N6-C34 1.492(4), N7-C40 1.503(4), N7-C44 1.508(4), N8-C50 1.502(4), N8-C54 1.490 (4), N9-C60 1.502(4), N9-C64 1.487(4). – Selected bond angles (in degrees): Al1-N2-C1 166.2(2), Al2-N2-C2 169.1(2), Al3-N3-C3 165.0(3), Al1-C3-N3 165.6(3), Al2-C1-N1 165.2(3), Al3-C2-N2 166.8(3), N1-Al1-C3 84.3(1), C1-Al2-N2 84.3(1), C2 Al3-N3 83.9(1), N4-Al1-N5 126.9(1), N4-Al1-N1 117.5(1), N4-Al1-C3 99.9(1), N5-Al1-N1 129.7(1), N5-Al1-C2 118.2(1), N1-Al1-C3 84.3(1), N6-Al2-N7 125.8(2), N6-Al2-N2 111.4(1), N6-Al2-C1 105.5(1), N7-Al2-N2 107.6(1), N7-Al2-C1 114.5(1), C1-A12-N2 84.1(1), N8-Al3-N9 126.0(1), N8-Al3-C2 110.5(1), N8-Al3-N3 104.5(1), N9-Al3-C2 109.7(1), N9-Al3-N3 114.5(1), C2-Al3-N3 83.9(1), Al1-N4-C10 127.3(2), Al1-N4-C14 117.1(2), C10-N4-C14 115.5(2), Al1-N5-C20 127.1(2), Al1-N5-C24 114.5(2), Al2-N6-C30 116.8(2), Al2-N6-C34 127.2(2), C30-N6-C24 115.7(2), Al2-N7-C40 121.2(2), Al2-N7-C44 115.7(1), C40-N7-C44 117.8(2), Al3-N8-C50 116.5(2), Al2-N8-C54 127.3(2), C50-N8-C54 113.8(2), Al3-N9-C60 118.2(2), Al3-N9-C64 124.8(2), C60-N9-C64 116.0(3). Interplanar angles (in degrees): C3A1/N1/C10/N4/C14 75.5, C3A1/N1/C20/N5/C24 75.5, C10/N4/C14/C20/N5/C24 87.8, C1A2/N2/C30/N6/C34 73.4, C1A2/N2/C40/N7/C44 87.1, C30/N6/C34/C40/N7/C44 73.4, C1A3/N3/C50/N8/C54 74.6, C1A3/N3/C60/N9/C64 81.1, C50/N8/C54/C60/N9/C64 113.3.

from 90.5 to 91.9(2)°, i.e. they are close to 90°, while the exocyclic N-Al-N bond angles are much wider with 129.6 to 131.4(1)°, a result of the bulky tmp groups. As expected, the NNN groups are almost linear [177.0 to 179.0(4)°]. More interesting are the N-N-Al bond angles. They are of three types. One type comprises angles from 152.0 to 156.5(3)°, the other type is much smaller with 141.5(3) to 144.9(3)°, and the third one is unusually small with only 127.2(3)°. There is no obvious reason for this asymmetry. The N-N bond lengths seem to be a little shorter than in NaN3 [23]. There are also three types of Al-N bonds. The first refers to the tmp groups which span a range from 1.814 to 1.829(3) Å, the others (to the azido groups) fall in the range of 1.927 to 1.973(3) Å. Four of these are almost equal [1.946 to 1.951(3) Å] while the Al1-N13 bond is the shortest with 1.927(3) Å and Al3-N9 is the longest [1.973(3) Å]. Their lengths lie between those of covalent Al-N bonds (average 1.62 Å) [18, 24] and coordinative Al-N bonds (≈ 2.0 Å) [25]. Thus, the Al3N9 rings show no symmetry at all.

The molecular structure of the cyanide 2 is depicted in Fig. 2. There are four trimeric units in the monoclinic unit cell of space group P21/n. The tmp2Al units are bridged by the CN groups. Assignment to C and N atoms were based on the U i values and Al-C and Al-N distances, respectively [26]. Still, some ambiguity remains. Therefore, we will not discuss Al-C and Al-N bond lengths for the nine-membered rings. As expected, the Al-N bonds to the tmp groups span a narrow range from 1.821(3) to 1.842(3) Å, similar to those of 1, although on average they are shorter in 1. The respective N-Al-N bond angles comprise the range from 125.8(1) to 126.9(1)°, i.e. they are similar to those of 1. All tmp groups show the chair conformation with planar N atoms in a C2NAl environment. In contrast to 1 the endocyclic N/C-Al-N/C bond angles are sharper than 90°, with 83.9(1), 84.1(1) and 84.0(1)°. NAIC planes form interplanar angles with their neighbouring NAIC planes of less than 8°.

Fig. 2b. Molecular structure of 2 showing the non planar ring structure and the orientation of the NC2 units of the tmp groups.

Knabel – H. Nöth · Synthesis and Structures of Some Aluminum Pseudohalides
Fig. 3. The molecular structure of the bis(diamidocarboxylato)aluminum bromide (3). Thermal ellipsoides are shown with 25% probability. Selected bond lengths (in Å) and bond angles (in degrees). Al1-Br1 2.031(8), Al1-O1 1.899(2), Al1-O2 1.910(2), Al1-N1 1.930(2), Al1-N2 1.934(2), N1-C1 1.312(3), N2-C2 1.308(3), C1-N4 1.404(3), C2-N3 1.413(3), N1-Si1 1.760(2), N2-Si2 1.757(2), N3-C10 1.501(3), N4-C23 1.509(3). – Br1-Al1-O1 105.31(7), Br1-Al1-O2 106.22(7), Br1-Al1-N1 111.20(6), Br1-Al1-N2 110.50(7), O1-Al1-O2 148.47(9), O1-Al1-N2 99.60(8), O2-Al1-N1 98.79(9), N2-Al1-N1 138.31(9), N1-Al1-Si1 132.7(1), N2-Al1-Si2 135.1(1), O1-C1-N1 112.5(2), O1-C1-N4 121.4(2), N1-C1-N4 126.2(1), C1-N1-Si1 138.0(2), O2-C2-N3 121.7(2), C2-N2-Si2 136.3(2), C10-N3-C14 119.4(2), C19-N4-C23 118.8(2). Interplanar angles (in degrees): O1C1N1/O2C2N2 135.7, C19N4C23/O1C1N1 104.3, O2C2N2/C10N3C14 85.7, C19N4C23/Si1N1C1 94.5, C10N3C14/Si2N2C2 92.2. 

In contrast to 2 the cyanide 4 is a tetramer featuring a twelve-membered ring system. It crystallizes in the triclinic space group P1̅. The molecule has a crystallographic centre of inversion, and the molecule has, therefore, C1 point group symmetry. The CN groups, which are site disordered with SOF 0.5, bridge the tBu2Al groups. This kind of structure has also been observed for Me3SiAl molecules (E = Ga, In, or Au) [27]. Due to the steric requirement of the tert-butyl groups the C-Al-C bond angles are wide with 127.06(9) and 128.5(1)°, while the endocyclic bond angles are 95.3(5) and 95.1(3), respectively. Two of the Al-C-N bond angles are almost linear [174.0(9), 176.4(9)]° while the other pair is less wide with 153.7(9) and 164.4(9)°.

The core structure of the spirocyclic compound 3 shows a distorted tetragonal pyramid with a central pentacoordinated Al atom. The two O-C-N planes are bent against each other by 135.6°. The tmp groups are present in the chair conformation with pyramidal N atoms (sums of bond angles at N3 and N4 are 347.7° and 347.0°, respectively). Their C2N planes stand practically orthogonal to the respective NCO planes. On the other hand, the Me3Si groups bearing N atoms are planar. It is interesting to note that the C-N and the C-O bond lengths are almost of equal lengths. This shows that CN-π-bonding plays an important role, because the CN bonds are shorter than those found on average for amidinates (1.333 Å) [28]. On the other hand, the CO bonds are somewhat longer than average C=O bond lengths (1.23 Å) [28]. As expected, the Al-N bonds are longer than the Al-O bonds, but there is not much difference in the Al-N bonds lengths to tetra-
coordinated Al atoms e.g. [Al(NMe₂)₃]²⁺: 1.961(6) for the AlNAl bridge and 2.106(4) Å for the terminal Al-N bonds [29]. The Al-Br bond is 2.031 Å, and this is significantly shorter than in the AlBr₄⁻ anion [2.291(1)–2.490(1) Å] [30]. A longer Al-Br bond was expected to be present in a compound with pentacoordinated Al atoms, also because the Al-Br bond in the hexacoordinated cation AlBr₂(THF)₄⁺ is 2.4366(8) Å [30]. The Al-Br bond lengths of 3 actually corresponds with the Al-Br bond length found for monomeric tmp₂AlBr [2.309(2) Å] with tricoordinated Al [19]. Thus the general rule that bond lengths increase with increasing coordination number is not obeyed in this case [23].

Discussion

Substituent exchange between tmp₂AlBr and trimethylsilyl pseudohalides proved to be the method of choice for the preparation on tmp₂AlX and Bu₂AlX (X = N₃, CN). In case of tmp₂AlBr and Me₂SiNCO₁, insertion into the Al-N bond occurs to give the spirocyclic compound 3. Therefore, Me₂SiNCO behaves like CO₂, which adds to the Al-N bonds of aluminum amides with formation of the respective Al amidinates [20]. The expectation, that 1 and 2 might be monomeric like tmp₂AlCl or tmp₂AlBr as a result of the sterically demanding tmp group, could not be verified. There is also no dimerization as found for tmp₂AlF [20], which might have been possible for the azide if it would bridge two Al atoms in an α, α-bridging manner similar to compound D. Thus it is quite clear, that the trimerization of 1 in an α, γ-manner is sterically determined, and the smallest possible unit resulting from linear azide groups would be a trimer, which is indeed realized. This holds also for the cyanide 2. Although the azide Bu₂AlNCl could be prepared, its structure could not be determined. Most likely it is a trimer or a tetramer as shown for Bu₂AlClN, 5. Thus, the bulky Bu group does not prevent the association of the monomeric molecules, and it is rather surprising that this compound shows the same degree of oligomerization as the methyl analogues of Al, Ga and Au [27].

The comparatively short Al-N bonds in 1 and 2 are not due to π-bonding but rather to the planar N atoms, which have a smaller effective covalent radius than tetracoordinated N atoms. The observed Al-N distances fall well into the range observed for many other tmp₂AlX compounds [17]. However, it is surprising that the tmp N-atoms of the spirocyclic 3 are pyramidal and that there is obviously no C-N π-bonding, as supported by the interplanar angle C₃N/NCO of 112°. This is due to steric interactions of the trimethylsilyl group with the tmp substituent.

The few examples presented here show that tmp₂Al compounds are structurally much more versatile than many other (R₂N)₂Al compounds [31]. We will report on other examples shortly.

Experimental Section

All experiments were conducted under anhydrous conditions using the Schlenk technique. Solvents were dried by conventional methods. The preparation of tmp₂AlBr is reported elsewhere [19]. Me₂SiN₃, Me₂SiCN, Me₂SiNCO, and Me₂SiNCS were commercial chemicals. IR: Nicolet-FT-Spectrometer, NMR: Bruker AC 200 and 400; references: SiMe₄, C₆D₆, 1M aqueous AlCl₃ solution (ext.). MS: Atlas CH4, 70 eV. X-ray: Siemens P4 diffractometer equipped with an area detector and a low temperature device LT2, Mo-Kα-radiation, graphite monochromator. Elemental analysis: Low C and N values may result from incomplete combustion due to Al₂O₃ and AlN formation.

Trimeric bis(2,2,6,6-tetramethylpiperidino)aluminum azide (1)

tmp₂AlBr (2.00 g, 5.15 mmol) was dissolved in toluene (70 ml). To the stirred solution was added Me₃SiN₃ (1.00 ml, 8 mmol). The resulting suspension was stirred over night, the solid isolated by filtration, and dried in vacuo. Yield 1.50 g (90%). M.p. 90 °C (dec.). The yellow filtrate was cooled to –4 °C. After 2 d some crystals suitable for an X-ray structure determination were obtained.

1H NMR (in C₆D₆): 1.30 (t, 3J(1H1H) = 3 Hz, 3.5-CH₃), 1.43 (s, C(CH₃)₂), 1.54 ppm (m, 4-CH₂). In addition small amounts of Me₂SiN₃ (–0.05) and a large quantity of Me₂SiBr (0.10 ppm) were observed in the filtrate, both in the ¹H NMR spectra. e.g. δ²⁹Si = 15.0 (Me₂SiN₃), 24.9 ppm (Me₂SiBr). δ²⁷Al = 99.4 ppm (h/2 = ca. 2000 Hz). C₆H₁₄H₁₀N₁₅Al₁₃ (1048.51 g mol⁻¹): calc. C 61.86, H 10.38, N 20.04; found C 58.26, H 9.65, N 19.12.

Trimeric bis(2,2,6,6-tetramethylpiperidino)aluminum cyanide (2)

To a stirred solution of tmpAlBr (2.15 g, 5.55 mmol) in toluene (70 ml) was added Me₂SiCN (1.00 ml, 8 mmol). A white precipitate formed rapidly. After stirring over night the solid was isolated by filtration and dried in vacuo. Yield 1.60 g (87%). M.p. 210 °C (dec.). From this yellowish filtrate settled some single crystals in the form of prisms at
From the first filtrate settled colorless prisms within two days suitable for X-ray diffraction studies.

1H NMR (in C6D6): δ = 0.32 (H2C=Si, 18 H), 1.24–1.46 ppm (very br., 36 H, tmp). – 13C[1H] NMR (C6D6): δ = 1.0 SiC, 17.7 (4-CH2), 29.1 (br, C(CH2)2, tmp), 39.0 (3,5-CH2), 78.8 ppm (C(CH2)2), – 29Si[1H] NMR (C6D6): δ = 1.3 ppm. – 27Al NMR (C6D6): δ = 56.0 ppm (br). IR (Nujol), ν = weak bands at 2624, 2606, 2588, 2408, 2199; 2586 (m), 2145 (m), 1579 (m), 1521 (s), 1476 (m), weak bands at 1366, 1458, 1449, 1427; 1394 (s), 1382 (s), 1373 (s), 1342 (s), 1291 (m), 1252 (s), 1232 (m), 1170 (m), 1128 (m), weak bands at 1082, 1063, 977, 974; 1028 (m), 954 (m), 931 (m), 844 (s), 778 (m), 763 (m), 648 (m cm−1). C26H54N4O2BrSi2 (643.78 g mol−1): calcd. C 52.24, H 8.46, N 9.08; found C 51.92, H 9.08, N 8.65.

**Tetrameric di(tert-butyl)aluminum cyanide (4)**

tmpAlBr (1.10 g, 5.00 mmol) was dissolved in toluene (40 ml). To the stirred solution was added 1.00 ml of Me3SiCN (0.800 g, 8.00 mmol, 60% excess), and stirring was continued over night. A light yellow solution resulted

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**Table 1. Crystallographic data and data related to data collection and structure solution of compounds 1–4.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td>Chem. formula</td>
<td>C45H36Al3SiN30</td>
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<tr>
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<td>1000.46</td>
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<td>Space group</td>
<td>P-1</td>
<td>P21(1)/n</td>
<td>P21(1)/n</td>
<td>P-1</td>
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<td>a, [Å]</td>
<td>13.8603(2)</td>
<td>11.2531(3)</td>
<td>13.5188(2)</td>
<td>8.933(1)</td>
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<tr>
<td>b, [Å]</td>
<td>22.4500(1)</td>
<td>21.4344(1)</td>
<td>14.2476(2)</td>
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<tr>
<td>c, [Å]</td>
<td>22.5734(2)</td>
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<td>12.688(1)</td>
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<tr>
<td>α (°)</td>
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<td>90.00</td>
<td>69.22(1)</td>
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<tr>
<td>β (°)</td>
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<td>98.182(1)</td>
<td>107.202(1)</td>
<td>71.71(1)</td>
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<tr>
<td>γ (°)</td>
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<td>1.346</td>
<td>0.121</td>
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<td>0.0369</td>
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<tr>
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<td>0.0598/0.8192</td>
<td>0.100/0.000</td>
<td>0.053/0.000</td>
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<tr>
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<tr>
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</table>

a w−1 = σ2F2 + (aP)2 + yP; P = (F2 + 2F2)/3.

**Spiro[3,3,4][4-bromo-2,6-di(2′,2′,6′,6′-tetramethylpiperidino)]1,5-bis(trimethylsilyl)-4-alumina-1,5-dioxa-3,7-dioxahexane (3)**

To a stirred solution of tmp2AlBr (2.00 g, 5.15 mmol) in toluene (70 ml) was added Me3SiNCN (2.0 ml, 15.0 mmol, 60% excess). A suspension formed which was stirred over night. The solid was isolated by filtration and crystallized from hot toluene (30 ml). Yield 2.70 g (84%). M.p. > 220 °C.
from which about 50% of the volatile material was removed in vacuo. The remaining solution was kept at −4 °C. The crystals formed within two days were isolated. Yield 0.72 g (86%). M.p. > 360 °C. – IR (only s and m bands): ν = 2941 (s), 2921 (s), 2910 (s), 2869 (s), 2640 (s), 2769 (m), 2708 (s), (86%). M.p. > 360 °C. – C 36H72N4Al4 (668.93 g mol\(^{-1}\)). – C 36H72N4Al4 (668.93 g mol\(^{-1}\)).

1H NMR (C\(_6\)D\(_6\)): δ = 3.15 (C(CH\(_3\))), 33.8 (C(CH\(_2\))), C of CN not detected. – \(^{27}\)Al NMR (C\(_6\)D\(_6\)): δ = 141.0 (\(\theta_{1/2} = ca. 3600 \text{ Hz}\)). – IR (only s and m bands): ν = 2941 (s), 2921 (s), 2910 (s), 2869 (s), 2640 (s), 2769 (m), 2708 (s), 2212 (s), 1362 (s), 1004 (s), 938 (m), 815 (s), 614 (s), 558 (s), 396 (m) (cm\(^{-1}\)). – C\(_6\)H\(_2\)N\(_4\)Al\(_4\) (668.93 g mol\(^{-1}\)): calcd. C 64.46, H 10.45, N 8.38; found C 62.33, H 10.45, N 8.26.

\[ 1H \text{ NMR (C}_6\text{D}_6): \delta = 3.15 (\text{C(CH}_3)), 33.8 (\text{C(CH}_2)), \text{C of CN not detected.} \]

\[ ^{27}\text{Al NMR (C}_6\text{D}_6): \delta = 141.0 (\theta_{1/2} = \text{ca. 3600 Hz}). \]

\[ \text{IR (only s and m bands): } \nu = 2941 (s), 2921 (s), 2910 (s), 2869 (s), 2640 (s), 2769 (m), 2708 (s), 2212 (s), 1362 (s), 1004 (s), 938 (m), 815 (s), 614 (s), 558 (s), 396 (m) (\text{cm}^{-1}). \]

\[ \text{C}_6\text{H}_2\text{N}_4\text{Al}_4 (668.93 \text{ g mol}^{-1}): \text{calcd. C} 64.46, \text{H} 10.45, \text{N} 8.38; \text{found C} 62.33, \text{H} 10.45, \text{N} 8.26. \]

\[ \text{X-ray structure determinations} \]

The selected crystal was covered with perfluoroether oil and mounted on top of a glass fiber, fixed to the goniometer head. The crystal was then cooled to −80 °C and the unit cell determined from the reflections observed on five sets of 15 frames each (program SMART [32]). Data collection was performed in the hemisphere mode of this program head. The crystal was then cooled to 132 K. knabel – h. noth

\[ \text{Acknowledgements} \]

We thank Fonds der Chemischen Industrie and the University of Munich for the support of this study. We also acknowledge the help by Mr. P. Mayer and Mrs. E. Kiesewetter for recording NMR and IR data, as well as of Dr. P. Mayer who collected the data set for compound 4 with a Noyon diffractometer operating with a rotating anode.


[26] It was expected that the Al-C bonds are longer than the Al-N bonds. Calculations in which the positions of the C and N atoms of the CN groups were exchanged did not influence the R2 value. Therefore, the atoms with the closer distances to Al were named N atoms.


[34] SHELXTL, Bruker Analytical Instruments, Madison, Version 5.1.