

# Synthesis and Structures of Some Aluminum Pseudohalides

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Z. Naturforsch. **60b**, 155 – 163 (2005); received August 27, 2004

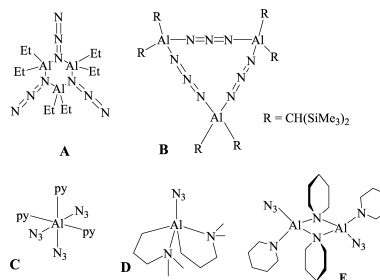
Dedicated to Professor Michael Veith on the occasion of his 60<sup>th</sup> birthday

The reactions of bis(2,2,6,6-tetramethylpiperidino)aluminum bromide ( $\text{tmp}_2\text{AlBr}$ ) with  $\text{Me}_3\text{SiN}_3$  or  $\text{Me}_3\text{SiCN}$  lead to trimeric  $\text{tmp}_2\text{AlN}_3$  and  $\text{tmp}_2\text{AlCN}$ , respectively, while the reaction with  $\text{Me}_3\text{SiOCN}$  produces the bicyclic compound  $[\text{tmpCON}(\text{SiMe}_3)_2]_2$ , **3**. Similarly, di(*tert*-butyl)aluminum bromide reacts with  $\text{Me}_3\text{SiCN}$  to give tetrameric  $(\text{Me}_3\text{C})_2\text{AlCN}$ , **4**. The compounds  $(\text{Me}_3\text{C})_2\text{AlN}_3$  and  $(\text{Me}_3\text{C})_2\text{AlOCN}$ , 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(tetramethylpiperidino)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.  $\text{Al}(\text{N}_3)_3$  [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  $\text{Et}_2\text{AlN}_3$  is also trimeric, it possesses  $\alpha, \gamma$ -bridging azide groups [13] as depicted by **B**. On the other hand, the association of the aluminium azides can be prevented by donor molecules, *e.g.* pyridine, to give compounds of type **C** [14]. Another variation is realized for bis(dimethylaminopropyl)aluminium 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  $\text{NaAl}(\text{N}_3)_4 \cdot 4 \text{ THF}$  [17]. Both cations are hexacoordinated by two THF molecules



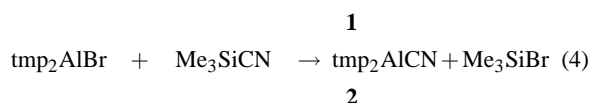
and four azido groups building a two dimensional network.

## 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  $\text{tmp}_2\text{AlF}$  is dimeric with bridging fluorine atoms [19], while the other three bis(tetramethylpiperidino)aluminium halides are monomeric [20]. Thus it was of interest to prepare and determine the structures of bis(tetramethylpiperidino)aluminum pseudohalides to see whether these are monomeric or associated.

$\text{NaN}_3$  was reacted with  $\text{tmp}_2\text{AlBr}$  [20] in an attempt to synthesize  $\text{tmp}_2\text{AlN}_3$ . 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  $\text{tmp}_2\text{AlN}_3$  is soluble in toluene. From the solid, which was isolated, no  $\text{tmp}_2\text{AlN}_3$  could be extracted by a number of non-polar and polar solvents. In case of  $\text{Et}_2\text{O}$  or THF as the solvent the product in solution proved to be a small amount of  $\text{tmpH}$  by  $^1\text{H}$  NMR spectroscopy. So, most likely, an insoluble aluminate  $\text{Na}[\text{AlN}_3\text{Br}(\text{tmp})_2]$  (eq. 2) or a mixture of aluminates are formed.



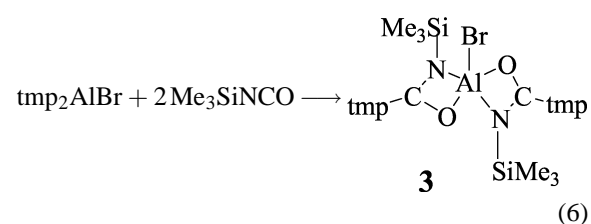
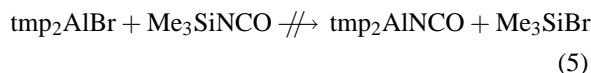
However, the reaction according to eq. (3) proceeded quantitatively within a day in toluene solution. This type of reaction was successful in the synthesis of several other aluminium azides [9, 10]. **1** precipitated from the solution. Though **1** is only sparingly soluble, the filtrate yielded single crystals of **1** at  $-4^\circ\text{C}$  in low yield within a few days.

The cyanide  $\text{tmp}_2\text{AlCN}$ , **2**, was obtained in analogy to **1** 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  $-4^\circ\text{C}$ .

Compounds **1** and **2** are trimeric. They do not add bases such as pyridine or  $\text{PMe}_3$  in order to form more soluble complexes. **2** also did not dissolve in  $\text{Et}_2\text{O}$ , THF or *tert*-butyl(methyl) ether, even under reflux conditions. Only small amounts of  $\text{tmpH}$  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  $\text{tmp}_2\text{AlBr}$  was first reacted with a Lewis base, e.g. forming the adduct  $\text{tmp}_2\text{AlBr}\cdot\text{py}$ , no reaction occurred after subsequent addition of  $\text{Me}_3\text{SiCN}$ .

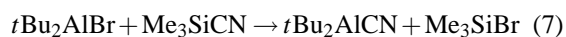
When  $\text{Me}_3\text{SiOCN}$  was treated with  $\text{tmp}_2\text{AlBr}$  in toluene solution no reaction according to eq. (5) was observed as the stoichiometry was not 1:1 but 2:1. The reaction proceeded as shown in eq. (6) to produce a bicyclic compound with a pentacoordinated Al atom.

On a first glance this is surprising. However, because  $\text{Me}_3\text{Si-N}=\text{C}=\text{O}$  is a  $\text{CO}_2$  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 ( $-78^\circ\text{C}$  to  $100^\circ\text{C}$ ). In contrast,  $\text{Me}_3\text{Si-NCS}$  did not react with  $\text{tmp}_2\text{AlBr}$ .



The tmp group mimics in its steric demand the *t*Bu<sub>2</sub>N 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 N<sub>3</sub> 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  $\text{tmp}_2\text{AlF}$  with fluoride bridges [19].

Sterically more demanding than two tmp groups are two *t*Bu groups attached to an Al atom. Therefore, we also studied the reactions of *t*Bu<sub>2</sub>AlBr with  $\text{Me}_3\text{Si}$ -pseudohalides. The result of the reaction of *t*Bu<sub>2</sub>AlBr with  $\text{Me}_3\text{SiCN}$  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  $-4^\circ\text{C}$ . In contrast, the azide  $\text{tBu}_2\text{AlN}_3$ , **5**, which was prepared similarly from  $\text{Me}_3\text{SiN}_3$  and *t*Bu<sub>2</sub>AlBr, was obtained only as an oil. From the reaction of *t*Bu<sub>2</sub>AlBr with  $\text{Me}_3\text{SiNCO}$  a waxy material resulted, probably impure *t*Bu<sub>2</sub>AlOCN, which could also not be crystallised. Therefore, the latter two compounds could not be characterized structurally by X-ray methods. Their  $^{27}\text{Al}$  NMR spectra proved the presence of tetra-coordinated Al atoms showing a single signal, but the  $^1\text{H}$  NMR spectra displayed many more signals than expected for the pure compounds.



### NMR spectra

The low solubility of **1** and **2** in deuterated solvents made it difficult to obtain  $^{27}\text{Al}$  and even  $^1\text{H}$  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  $\delta^{27}\text{Al}$  only for **1** at 99.4 ppm but not for **2**.  $^1\text{H}$  NMR signal for the tmp group could be observed for both compounds: They are, as expected, rather similar, showing only single signals for all  $\text{CMe}_2$  groups, indicating free rotation about the respective Al-N bonds. On the other hand, no problems arose in recording the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  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  $\text{CMe}_2$  protons of  $\text{tmp}_2\text{Al}$  compounds are, in general, well resolved. On the other hand, four  $^1\text{H}$  NMR signals were found for the  $\text{CMe}_2$  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  $\text{Me}_3\text{Si}$  groups are represented by a single and sharp  $^1\text{H}$  NMR signal at 1.0 ppm. The  $^{13}\text{C}$  NMR spectrum of **3** showed the carbamide C atom at 178.8 ppm, and its  $^{27}\text{Al}$  NMR signal was observed at 56.0 ppm. This lies in the range typical for pentacoordinated aluminum atoms [21]. Moreover, the  $^{29}\text{Si}$  NMR signal was observed at 1.3 ppm in accord with other silyl substituted aminates.

While compound  $t\text{Bu}_2\text{AlCN}$ , **4**, exhibits a single  $^1\text{H}$  resonance at 1.24 ppm for the *tert*-butyl group and two  $^{13}\text{C}$  NMR signals, the  $^{13}\text{C}$  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].  $\delta^{27}\text{Al}$  at 131.0 ppm ( $h_{1/2} = 3600$  Hz) for **4** points to the presence of a tetra-coordinated Al atom.  $^{27}\text{Al}$  resonances for  $(t\text{Bu}_2\text{AlX})_n$  compounds ( $\text{X} = \text{OR}, \text{NR}_2$ ) range from 146 to 172 ppm [21, 22]. For  $t\text{Bu}_2\text{AlN}_3$ , the  $^{27}\text{Al}$  chemical shift of 145.8 ppm ascertains the presence of tetra-coordinated Al centers which are also observed for  $(t\text{Bu}_2\text{AlNCO})_n$  ( $\delta^{27}\text{Al} = 141$  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

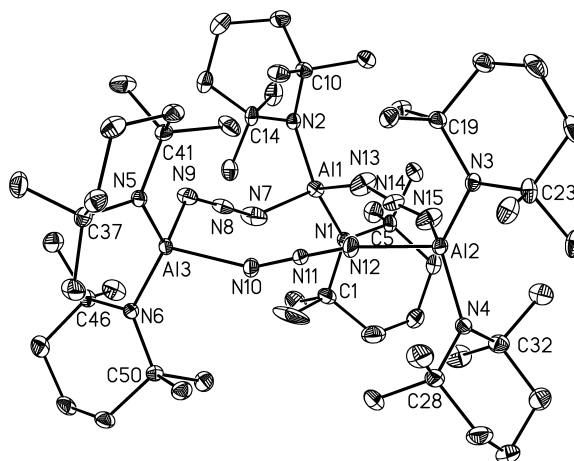


Fig. 1. The molecular structure of one of the two independent molecules of trimeric bis(tetramethylpiperidino)aluminum azide. Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and bond angles (in degrees). Ellipsoids are shown on the 25% probability level. Selected structural parameters 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-N3 1.818(3), Al2-N4 1.821(3), Al3-N5 1.821(3), Al3-N6 1.823(3), Al1-N7 1.947(4), Al1-N13 1.927(3), Al2-N12 1.946(3), Al2-N15 1.951(3), Al3-N9 1.973(4), Al3-N10 1.948(3), N7-N8 1.164(4), N8-N9 1.185(4), N10-N11 1.152(4), N11-N12 1.156(4), N13-N14 1.123(4), N14-N15 1.167(4), N1-C1 1.498(4), N1-C5 1.500(4), N1-C10 1.506(4), N2-C14 1.497(4), N3-C19 1.519(4), N3-C23 1.508(4), N4-C28 1.487(4), N4-C32 1.504(5), N5-C37 1.504(4), N5-C41 1.507(4), N6-C46 1.507(4), N6-C50 1.494(4). – Al4-N16 1.825(3), Al4-N17 1.829(3), Al5-N18 1.817(3), Al5-N19 1.825(3), Al6-N20 1.925(3), Al6-N21 1.815(3), Al4-N22 1.936(3), Al4-N25 1.935(4), Al5-N24 1.951(3), Al5-N30 1.952(3), Al6-N27 1.959(3), Al6-N28 1.968(3), N22-N23 1.146(4), N23-N24 1.165(4), N30-N29 1.155(4), N29-N28 1.157(4), N27-N26 1.167(4), N26-N25 1.164(4). – Selected bond angles: N1-Al1-N2 129.6(1), N3-Al2-N4 131.4(1), N5-Al3-N6 130.2(1), N7-Al1-N13 90.5(2), N12-Al2-N15 91.9(2), N9-Al3-N10 90.7(2), N1-Al1-N7 113.6(2), N1-Al1-N13 106.5(2), N2-Al1-N7 101.9(2), N2-Al1-N13 107.8(2), N3-Al2-N12 106.9(1), N3-Al2-N15 109.3(1), N4-Al2-N12 107.7(1), N4-Al2-N15 103.6(1), N5-Al3-N9 110.1(1), N5-Al3-N10 108.5(1), N6-Al3-N9 103.6(1), N6-Al3-N10 106.6(1).

showed that **1** and **2** are trimers, while **4** is a tetramer. The aluminum azide **1** crystallizes in the triclinic space group  $P\bar{1}$  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  $\text{Al}_3\text{N}_9$  ring structure. The endocyclic N-Al-N bond angles range

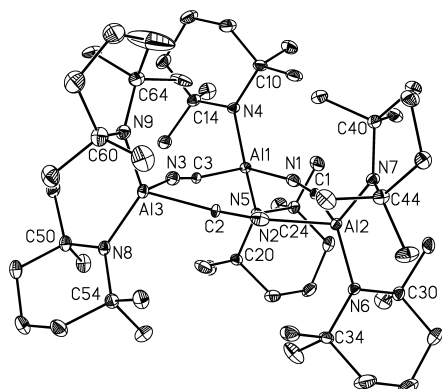


Fig. 2a. The molecular structure of trimeric bis(2,2,6,6-tetramethylpiperidino)aluminum cyanide(2). Thermal ellipsoids are represented on a 25% probability level. Only one orientation of the site disordered tmp group N9C60–C68 is shown. Selected bond lengths (in Å): Al1–N1 2.041(3), Al2–N2 2.034(3), Al3–N3 2.009(3), Al1–C3 2.033(3), Al2–C1 2.003(3), Al3–C2 2.005(3), Al1–N4 1.829(2), Al1–N5 1.827(2), Al2–N6 1.829(2), Al2–N7 1.842(3), 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(1), 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–Al2–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 117.7(2), C20–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 115.8(2), Al3–N9–C60 118.2(2), Al3–N9–C64 124.8(2), C60–N9–C64 116.0(3). Interplanar angles (in degrees): C3Al1N1/C10N4C14 75.5, C3Al1N1/C20N5C24 95.5, C10N4C14/C20N5C24 78.8, C1Al2N2/C30N6C34 73.4, C1Al2N2/C40N7C44 87.1, C30N6C34/C40N7C44 61.6, C2Al3N3/C50N8C54 74.6, C2Al3N3/C60N9C64 81.1, C50N8C54/C60N9C64 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 an-

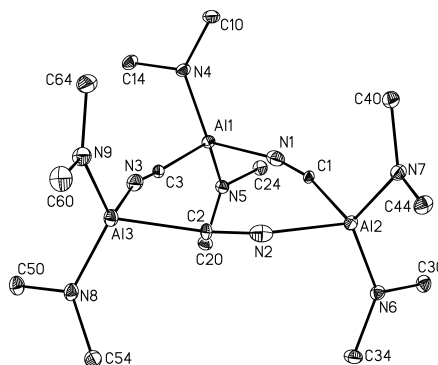


Fig. 2b. Molecular structure of **2** showing the non planar ring structure and the orientation of the NC<sub>2</sub> units of the tmp groups.

gles 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 NaN<sub>3</sub> [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 Al<sub>3</sub>N<sub>9</sub> 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 *P*2<sub>1</sub>/*n*. The tmp<sub>2</sub>Al units are bridged by the CN groups. Assignment to C and N atoms were based on the *U*<sub>i</sub> 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 C<sub>2</sub>NAl 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°.

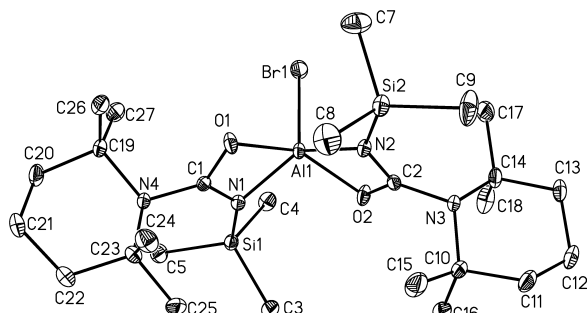


Fig. 3. The molecular structure of the bis(diamidocarboxylato)aluminum bromide (**3**). Thermal ellipsoids are shown with 25% probability. Selected bond lengths (in Å) and bond angles (in degrees): Al1–Br1 2.031(8), Al1–O1 1.899(2), Al1–O2 1.910(2), Al1–N1 1.930(2), Al1–N2 1.934(2), N1–C1 1.312(3), N2–C2 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), N3–C14 1.506(3), N3–C19 1.516(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–N1 69.46(8), O2–Al1–N2 69.18(8), O1–Al1–O2 148.47(9), O1–Al1–N2 99.60(8), O2–Al1–N1 98.79(9), N2–Al1–N1 138.31(9), Al1–N1–Si1 132.7(1), Al1–N2–Si2 135.1(1), O1–C1–N1 112.5(2), O2–C2–N2 113.4(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. Sum of bond angles at N3 347.7°, at N4 347.0°.

In contrast to **2** the cyanide **4** is a tetramer featuring a twelve-membered ring system. It crystallizes in the triclinic space group  $P\bar{1}$ . The molecule has a crystallographic centre of inversion, and the molecule has, therefore,  $C_i$  point group symmetry. The CN groups, which are site disordered with SOF 0.5, bridge the  $t\text{Bu}_2\text{Al}$  groups. This kind of structure has also been observed for  $\text{Me}_2\text{ECN}$  molecules ( $E = \text{Ga}, \text{In}, \text{or Au}$ ) [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  $\text{C}_2\text{N}$  planes stand prac-

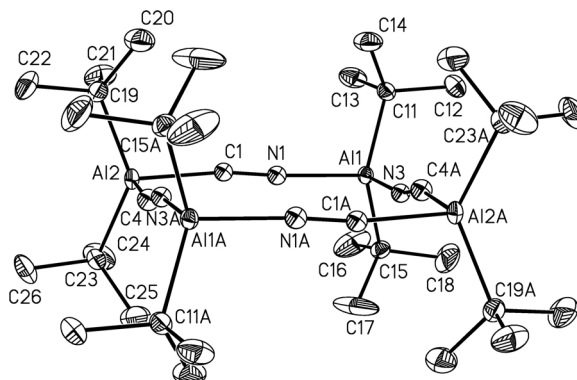


Fig. 4a. The molecular structure of tetrameric di(*tert*-butyl)aluminum cyanide (**4**). Thermal ellipsoids represent 25% probability. Selected bond lengths (in Å): Al1–C2 2.02(2), Al1–C11 1.962(2), Al1–C15 1.967(2), Al1–N1 1.98(1), Al2–C1 2.000(8), Al2–N2 1.989(8), Al2–C19 1.966(2), Al2–C23 1.973(2), Al1–N3 1.982(8), Al1–C3 2.01(1), Al2–N4 2.003(7), Al2–C4 1.982(9). Selected bond angles (in degrees): C11–Al1–C15 127.08(9), C11–Al1–N1 167.7(4), C11–Al1–C2 107.7(9), C11–Al1–N3 109.9(3), C11–Al1–C3 104.2(3), C15–Al1–C3 110.8(3), C15–Al1–N1 108.3(4), C15–Al1–N3 104.8(3), C15–Al1–C2 106.4(5), C19–Al2–C23 128.5(1), C19–Al2–C1 104.0(3), C19–Al2–N2 109.8(3), C23–Al2–C1 109.6(39), C23–Al2–N2 104.5(3).

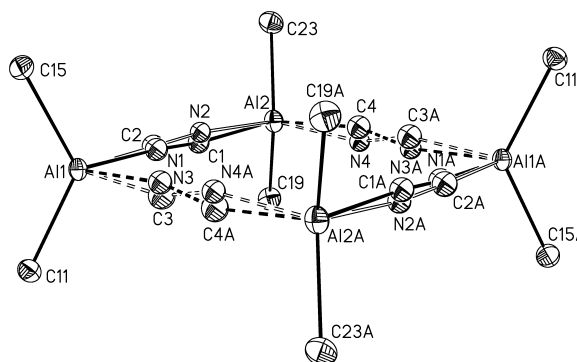


Fig. 4b. Core structure of compound **4** showing the positions of the disordered CN groups.

tically orthogonal to the respective NCO planes. On the other hand, the  $\text{Me}_3\text{Si}$  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– $\pi$ -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.  $[\text{Al}(\text{NMe}_2)_3]_2$ : 1.961(6) for the Al–Al 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  $\text{AlBr}_4^-$  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  $\text{AlBr}_2(\text{THF})_4^+$  is 2.4366(8) Å [30]. The Al–Br bond lengths of **3** actually corresponds with the Al–Br bond length found for monomeric  $\text{tmp}_2\text{AlBr}$  [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  $\text{tmp}_2\text{AlBr}$  and trimethylsilyl pseudohalides proved to be the method of choice for the preparation on  $\text{tmp}_2\text{AlX}$  and  $t\text{Bu}_2\text{AlX}$  ( $\text{X} = \text{N}_3, \text{CN}$ ). In case of  $\text{tmp}_2\text{AlBr}$  and  $\text{Me}_3\text{SiNCO}$ , insertion into the Al–N bond occurs to give the spirocyclic compound **3**. Therefore,  $\text{Me}_3\text{SiNCO}$  behaves like  $\text{CO}_2$ , 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  $\text{tmp}_2\text{AlCl}$  or  $\text{tmp}_2\text{AlBr}$  as a result of the sterically demanding tmp group, could not be verified. There is also no dimerization as found for  $\text{tmp}_2\text{AlF}$  [20], which might have been possible for the azide if it would bridge two Al atoms in an  $\alpha, \alpha$ -bridging manner similar to compound **D**. Thus it is quite clear, that the trimerization of **1** in an  $\alpha, \gamma$ -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  $t\text{Bu}_2\text{AlN}_3$  could be prepared, its structure could not be determined. Most likely it is a trimer or a tetramer as shown for  $t\text{Bu}_2\text{AlCN}$ , **5**. Thus, the bulky  $t\text{Bu}$  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  $\pi$ -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  $\text{tmp}_2\text{AlX}$  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  $\pi$ -bonding, as supported by the interplanar angle  $\text{C}_2\text{N}/\text{NCO}$  of  $112^\circ$ . This is due to steric interactions of the trimethylsilyl group with the tmp substituent.

The few examples presented here show that  $\text{tmp}_2\text{Al}$  compounds are structurally much more versatile than many other  $(\text{R}_2\text{N})_2\text{Al}$  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  $\text{tmp}_2\text{AlBr}$  is reported elsewhere [19].  $\text{Me}_3\text{SiN}_3$ ,  $\text{Me}_3\text{SiCN}$ ,  $\text{Me}_3\text{SiNCO}$ , and  $\text{Me}_3\text{SiNCS}$  were commercial chemicals. IR: Nicolet-FT-Spectrometer, NMR: Bruker AC 200 and 400; references:  $\text{SiMe}_4$ ,  $\text{C}_6\text{D}_6$ , 1M aqueous  $\text{AlCl}_3$  solution (ext.). MS: Atlas CH4, 70 eV. X-ray: Siemens P4 diffractometer equipped with an area detector and a low temperature device LT2,  $\text{Mo-K}\alpha$ -radiation, graphite monochromator. Elemental analysis: Low C and N values may result from incomplete combustion due to  $\text{Al}_2\text{O}_3$  and AlN formation.

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

$\text{tmp}_2\text{AlBr}$  (2.00 g, 5.15 mmol) was dissolved in toluene (70 ml). To the stirred solution was added  $\text{Me}_3\text{SiN}_3$  (1.00 ml 7.70 mmol). The resulting suspension was stirred over night, the solid isolated by filtration, and dried *in vacuo*. Yield 1.50 g (90%). M.p.  $90^\circ\text{C}$  (dec.). The yellow filtrate was cooled to  $-4^\circ\text{C}$ . After 2 d some crystals suitable for an X-ray structure determination were obtained.

$^1\text{H}$  NMR (in  $\text{C}_6\text{D}_6$ ): 1.30 (t,  $^3J(^1\text{H}^1\text{H}) = 3\text{ Hz}$ , 3,5- $\text{CH}_2$ ), 1.43 (s,  $\text{C}(\text{CH}_3)_2$ ), 1.54 ppm (m, 4- $\text{CH}_2$ ). In addition small amounts of  $\text{Me}_3\text{SiN}_3$  ( $-0.05$ ) and a large quantity of  $\text{Me}_3\text{SiBr}$  (0.10 ppm) were observed in the filtrate, both in the  $^1\text{H}$  as well as the  $^{29}\text{Si}$  NMR spectra, e.g.  $\delta^{29}\text{Si} = 15.0$  ( $\text{Me}_3\text{SiN}_3$ ), 24.9 ppm ( $\text{Me}_3\text{SiBr}$ ).  $-\delta^{27}\text{Al} = 99.4$  ppm ( $h_{1/2} = \text{ca. } 2000\text{ Hz}$ ).  $\text{C}_{54}\text{H}_{108}\text{N}_{15}\text{Al}_3$  ( $1048.51\text{ g}\cdot\text{mol}^{-1}$ ): calcd. 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  $\text{tmp}_2\text{AlBr}$  (2.15 g, 5.55 mmol) in toluene (70 ml) was added  $\text{Me}_3\text{SiCN}$  (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.  $210^\circ\text{C}$  (dec.). From the yellowish filtrate settled some single crystals in the form of prisms at

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

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Chem. formula	C <sub>108</sub> H <sub>216</sub> Al <sub>6</sub> N <sub>30</sub>	C <sub>57</sub> H <sub>108</sub> Al <sub>3</sub> N <sub>9</sub>	C <sub>26</sub> H <sub>54</sub> AlBrN <sub>4</sub> O <sub>2</sub> Si <sub>2</sub>	C <sub>18</sub> H <sub>36</sub> Al <sub>2</sub> N <sub>2</sub>
Form. wght.	2096.99	1000.46	617.80	334.45
Cryst. size [mm]	0.10 × 0.30 × 0.30	0.20 × 0.30 × 0.30	0.30 × 0.40 × 0.40	0.16 × 0.18 × 0.34
Cryst. system	triclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> -1
<i>a</i> , [Å]	13.8603(2)	11.251(3)	13.5188(2)	8.933(1)
<i>b</i> , [Å]	22.4500(1)	21.4344(1)	18.2950(2)	11.976(1)
<i>c</i> , [Å]	22.5734(2)	24.8391(3)	14.2476(2)	12.688(1)
$\alpha$ , [°]	62.538(1)	90.00	90.00	69.22(1)
$\beta$ , [°]	83.758(1)	98.182(1)	107.202(1)	71.71(1)
$\gamma$ , [°]	76.43	90.00	90.00	85.38(1)
<i>V</i> , [Å <sup>3</sup> ]	6058.6(1)	5929.29(8)	3366.18(8)	1204.3(2)
<i>Z</i>	2	4	4	2
$\rho$ (calcd.), [Mg/m <sup>3</sup> ]	1.149	1.121	1.219	0.922
$\mu$ [mm <sup>-1</sup> ]	0.110	0.107	1.346	0.121
<i>F</i> (000)	2304	2208	1320	368
Index range	–17 ≤ <i>h</i> ≤ 17 –28 ≤ <i>k</i> ≤ 28 –27 ≤ <i>l</i> ≤ 27	–13 ≤ <i>h</i> ≤ 13 –28 ≤ <i>k</i> ≤ 27 –33 ≤ <i>l</i> ≤ 26	–17 ≤ <i>h</i> ≤ 17 –20 ≤ <i>k</i> ≤ 23 –18 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10 –14 ≤ <i>k</i> ≤ 14 –14 ≤ <i>l</i> ≤ 15
2 $\theta$ [°]	58.32	58.80	58.58	51.62
Temp, [K]	193	193(2)	193	200
Refl. collected	35218	34115	18690	9331
Refl. unique	19056	11599	6627	4311
Refl. observed (4 $\sigma$ )	10161	7734	5512	2640
<i>R</i> (int.)	0.0582	0.0519	0.0228	0.0452
No. variables	1345	664	339	237
Weighting scheme <sup>a</sup> <i>x/y</i>	0.0607/0.6945	0.0598/9.8192	0.100/0.000	0.053/0.000
GOOF	0.987	1.018	1.019	0.682
Final <i>R</i> (4 $\sigma$ )	0.0606	0.0690	0.0369	0.0426
Final <i>wR</i> 2	0.1240	0.1486	0.1212	0.1052
Larg. res. peak [e/Å <sup>3</sup> ]	0.356	0.929	0.392	0.213

<sup>a</sup>  $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$ ;  $P = (F_o^2 + 2F_c^2)/3$ .

–4 °C which were used for the X-ray structure determination. – <sup>1</sup>H NMR (in C<sub>6</sub>D<sub>6</sub>): 1.35 (m, 3, 5-CH<sub>2</sub>), 1.40 (s, C(CH<sub>3</sub>)<sub>2</sub>), 1.64 (m, 4-CH<sub>2</sub>). – IR (nujol/hostafion):  $\tilde{\nu}$  = 3006 (m), 2989 (s), 2924 (s), 2866 (s), 2182 (m), 2135 (w), 2102 (w), 1650 (w), 1629 (w), 1570 (w), 1460 (m), 1380 (m), 1362 (m), 1348 (w), 1236 (s), 1203 (w), 1178 (m), 1130 (s), 1082 (w), 1064 (m), 1032 (w), 995 (m), 980 (m), 938 (st), 916 (m), 899 (m), weak bands at 869, 850, 835, 803, 761, 755, 745, 730, 709, 694, 664, 647, 637, 594, 583, 570, 555, 546, 529(m), 502 (m) 441, 423, 393, 380, 365 (cm<sup>-1</sup>). – C<sub>57</sub>H<sub>108</sub>N<sub>9</sub>Al<sub>3</sub> (1000.50 g mol<sup>-1</sup>): calcd. C 68.43, H 10.88, N 12.60; found C 67.47, H 9.84, N 11.44.

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

To a stirred solution of tmp<sub>2</sub>AlBr (2.00 g, 5.15 mmol) in toluene (70 ml) was added Me<sub>3</sub>SiNCO (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 the first filtrate settled colorless prisms within two days suitable for X-ray diffraction studies.

<sup>1</sup>H NMR (in C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.32 (H<sub>3</sub>CSi, 18 H), 1.24–1.46 ppm (very br., 36 H, tmp). – <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.0 SiC, 17.7 (4-CH<sub>2</sub>), 29.1 (br, C(CH<sub>3</sub>)<sub>2</sub>, tmp), 39.0 (3,5-CH<sub>2</sub>), 78.8 ppm (C(CH<sub>3</sub>)<sub>2</sub>). – <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.3 ppm. – <sup>27</sup>Al NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 56.0 ppm (br). IR (Nujol),  $\tilde{\nu}$  = 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), 1343 (s), 1291 (m), 1252 (s), 1232 (m), 1170 (m), 1128 (m), weak bands at 1082, 1063, 997, 974; 1028 (m), 954 (m), 931 (m), 918 (m), 844 (s), 778 (m), 763 (m), 648 (m) cm<sup>-1</sup>. C<sub>26</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>BrSi<sub>2</sub> (643.78 g mol<sup>-1</sup>): calcd. C 52.24, H 8.46, N 8.70; found C 51.92, H 9.08, N 8.65.

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

tmp<sub>2</sub>AlBr (1.10 g, 5.00 mmol) was dissolved in toluene (40 ml). To the stirred solution was added 1.00 ml of Me<sub>3</sub>SiCN (0.800 g, 8.00 mmol, 60% excess), and stirring was continued over night. A light yellow solution resulted

from which about 50% of the volatile material was removed *in vacuo*. The remaining solution was kept at  $-4\text{ }^{\circ}\text{C}$ . The crystals formed within two days were isolated. Yield 0.72 g (86%). M.p.  $> 220\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 1.24$  ( $\text{CH}_3$ ). –  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 31.5$  ( $\text{C}(\text{CH}_3)_3$ , 33.8 ( $\text{C}(\text{CH}_3)_3$ ), C of CN not detected. –  $^{27}\text{Al}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 141.0$  ( $h_{1/2} = \text{ca. } 3600\text{ Hz}$ ). – IR (only s and m bands):  $\tilde{\nu} = 2941$  (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) ( $\text{cm}^{-1}$ ). –  $\text{C}_{36}\text{H}_{72}\text{N}_4\text{Al}_4$  ( $668.93\text{ g mol}^{-1}$ ): calcd. C 64.46, H 10.45, N 8.38; found C 62.33, H 10.45, N 8.26.

#### 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  $-80\text{ }^{\circ}\text{C}$  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 at two different setting of  $\chi$  by changing  $\phi$  by  $0.3^{\circ}$  between each collected frame. Data on a total of 1280 frames were reduced (program SAINT [33]). The structures were solved by direct methods implemented in the program package SHELXTL [34]. Non hydrogen atoms were refined with

anisotropic thermal parameters and hydrogen atoms placed in calculated positions. In the refinement of the cyanides **2** and **4** the positions with the smaller  $U_i$  values and shorter Al–X distances were considered to be N atoms. In case of compound **4** our model has split positions for the atoms of the CN groups. Refinement of the occupancy converged close to 0.5 for each atom. Therefore, in the final refinement, the occupancy was fixed at 0.5. Fig. 4b shows the result. The crystallographic data and information about data collection and structure solution are summarized in Table 1. Additional data are deposited with the Cambridge Crystallographic Data Center which can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit @ccdc.cam.ac.uk] free of charge by quoting the journal, the authors and the CCD numbers 248596 to 248599.

#### 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 Nonius diffractometer operating with a rotating anode.

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