# Synthesis and Structures of Bis(tetramethylpiperidino)aluminum Halides – X-Ray Crystal Structures of tmp$_2$AlX (X = Cl, Br, I) and [tmp$_2$Al($\mu$-F)]$_2$☆

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*N*-Lithio-2,2,6,6-tetramethylpiperidine [Li(tmp)] reacts with AlX$_3$ (X = Cl, Br) in diethyl ether/ *n*-hexane solution to generate the products of substitution and ether cleavage, [tmpAl(X)($\mu$-OEt)]$_2$ (**1a**, X = Cl; **1b**, X = Br). However, when the reaction is allowed to proceed in *n*-hexane alone, an almost quantitative yield of compounds tmp$_2$AlX (**2a**, X = Cl; **2b**, X = Br; **2c**, X = I) is obtained. According to $^{27}$Al-NMR spectroscopy, mass spectroscopy, cryoscopy, and X-ray crystal structure determinations, these compounds are monomeric in the solid state, in solution, and in the gas phase. **2b** reacts with AgBF$_4$ yielding the fluoride-bridged dimer (tmp$_2$AlF)$_2$, **2d**, as shown by X-ray crystal structure determination.

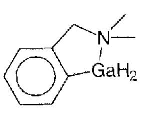
In the 1960s, the first monomeric tris(amino)aluminum compounds stabilized by bulky amino substituents, e.g. Al(N*i*Pr$_2$)$_3$[1] and Al[N(SiMe$_3$)$_2$]$_3$[2], were characterized. Less bulky amino groups led to oligomeric, nitrogen-bridged species[3]. Additionally, some dimeric mono- and bis(amino)aluminum halides have also been synthesized[4]. All such compounds are characterized by a planar Al$_2$N$_2$ ring[3,5].

The 2,2,6,6-tetramethylpiperidino group as a substituent of aminoboranes and borinium cations exerts a remarkable stabilizing effect[6]. This effect is not solely of a steric nature; B–N $\pi$ bonding, as demonstrated by hindered rotation about the B–N bond, adds to the stability of these compounds. The latter is not true of Al–N bonds, since in this case there is free rotation about the bond[4]. However, we have demonstrated that the steric requirement of the tmp group prevents oligomerization of tmp$_2$AlH via Al–N bonds[7] and it should be noted that Linti et al.[8] have recently shown that monomeric bis(amino)gallium halides can be prepared by using tmp as a substituent.

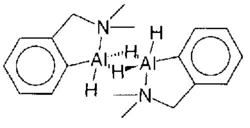
However, there are significant differences between the chemistry of aluminum and gallium. For instance, AlMe$_3$ exists as a dimer, whereas GaMe$_3$ is a monomer[9]. In contrast to the hydride-bridged dimer tmp$_2$AlH[7], the gallium hydride tmp$_2$GaH[10] is monomeric.

Another notable difference concerns the aluminum and the gallium compounds **1** and **2**, which were synthesized by Cowley et al.[11]. X-ray crystal structures revealed a monomeric nature of the gallium hydride **1**, while the aluminum compound **2** was shown to be a hydride-bridged dimer.

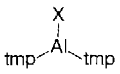
It was, therefore, of interest to study compounds tmp$_2$AlX **2a**–**d** (X = F, Cl, Br, I) in order to find out whether these exist as monomers or as dimers. We report herein on the preparation and characterization of these compounds.



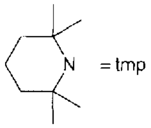
**1**



**2**



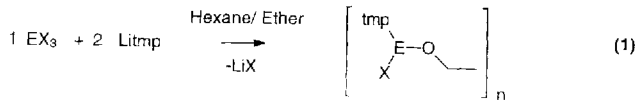
**2a-d**



## Synthesis and NMR-Spectroscopic Characterization

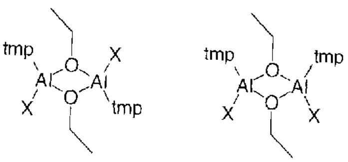
Attempts to prepare tmp$_2$AlX compounds by the reaction of two equivalents of Li(tmp) with one equivalent of AlX$_3$ (X = Cl, Br) in a diethyl ether/*n*-hexane mixture led to the exclusive formation of the ether-cleavage products tmpAl(X)(OEt) (**1a**, X = Cl; **1b**, X = Br), which proved to be dimeric, oxygen-bridged species. Ether cleavage, depending on the reaction conditions, has also been observed in the synthesis of the homologous gallium and boron compounds: tmpGa(Cl)(OEt)[10] is dimeric with bridging ethoxy groups, whereas tmpB(Cl)(OEt)[6] shows no tendency to dimerize.

The formation of **1a** and **1b** can be deduced from $^{27}$Al-NMR spectroscopy. Signals at $\delta$ = 87 (**1a**) and $\delta$ = 85 (**1b**), with half-height widths of 2.300 Hz, are indicative of an asymmetrically tetracoordinated aluminum center[11], while two discrete sets of signals for the ethoxy- and tmp groups



(1)

| E | X | n |  |
|---|---|---|---|
| B | Cl | 1 | **1c** |
| Al | Cl | 2 | **1a** |
| Al | Br | 2 | **1b** |
| Ga | Cl | 2 | **1d** |



X = Cl, Br

in the $^{13}$C-NMR spectra suggests the presence of a 1 : 1 ratio of *cis* and *trans* isomers in solution.

Semiempirical geometry optimization (AM1 basis set[12]) revealed a very small difference of 0.98 kcal/mol (**1a**), (1.06 kcal/mol for **1b**) in the heats of formation of these *cis* and *trans* isomers. Thus, the presence of isomers in solution is readily understood.

Upon concentration and cooling of the respective solutions to −20°C, **1a** and **1b** are obtained as colourless crystals, soluble in many aprotic organic solvents. They are present in the solid state as *trans*-isomers, as ascertained by X-ray crystal structure determination.

Ether cleavage can be avoided, and a straightforward preparation of tmp$_2$AlX can be achieved, if a freshly prepared suspension of Li(tmp) is allowed to react with the appropriate powdered aluminum trihalide (X = Cl, Br, I) in hexane. This leads to the quantitative formation of **2a**−**2c**, as shown in equation (2).

$$2\ \text{Litmp} + 1\ \text{AlX}_3 \xrightarrow[-2\ \text{LiX}]{\text{Hexane}} \underset{\mathbf{2}}{\text{tmp}_2\text{AlX}} \quad \frac{\text{X = Cl Br I}}{\mathbf{2a\ 2b\ 2c}} \qquad (2)$$

The monomeric nature of these compounds in solution can be deduced not only from the chemical shifts of the $^{27}$Al-NMR signals, but also from the extremely broad appearance of the signals (**2a**: δ = 134, 13.700 Hz; **2b**: δ = 130, 9.100 Hz; **2c**: 130, = 10.000 Hz). The signal width at $h_{1/2}$ is a valuable indicator for the symmetry around the aluminum core[11], since low local symmetry leads to broad signals[11,13]. Similar $h_{1/2}$ data have been found for the monomeric bis(aryloxy)aluminum alkyl compounds *i*bu-Al(−O−2,6-*t*Bu$_2$C$_6$H$_3$)$_2$ (11.500 Hz)[13], *i*BuAl(−O−2,6-*t*Bu$_2$-4-Me-C$_6$H$_2$)$_2$ (13.000 Hz)[13] and MeAl(−O−2,6-*t*Bu$_2$-4-Me-C$_6$H$_2$)$_2$[13]. Nevertheless, $h_{1/2}$ values of tricoordinated Al compounds are rarely found in the literature. These derivatives exhibit the same local symmetry as the tmp$_2$AlX compounds (tricoordinated aluminum, A$_2$AlX system).

Due to the broad signals, no accurate values for the $^{27}$Al-NMR chemical shifts of compounds **2** can be given. Different phasing parameters led to a variation of the chemical shifts by up to 20 ppm, whereas the width at half height remained almost constant. $^{1}$H- and $^{13}$C-NMR data show only one set of signals for the tmp groups of these compounds, a behavior fitting for the monomeric state in solution with free rotation of the tmp group. The monomeric nature of the bis(amino)aluminum halides **2** in solution was also ascertained by cryoscopic molecular mass determination in cyclohexane. Low energy mass spectroscopy (20 eV, 50 to 70°C) was used to investigate the gas phase behavior of **2a**−**2c**. Peaks for the molecular ions ($M^{+\bullet}$) of these compounds were observed in 9 to 19% relative intensity. This proves that **2a**−**2c** are monomeric in the gas phase, since no indication of the presence of a dimer was observed. The most intense peaks were those of the fragments with mass M − 15 ($(M - CH_3)^+$). Although compounds **2a**−**2c** are obviously monomeric in the gas phase and in solution, the question remained as to whether this was also true in the solid state. Therefore, X-ray crystal structure determinations were performed (vide infra).

Special efforts were made to synthesize and characterize the fluoro derivative, tmp$_2$AlF **2d**. Due to the strong Al−F bond and the smaller radius of fluorine, the structure of **2d** may be different from that of the other halides.

It seemed very unlikely that tmp$_2$AlF **2d** could be prepared from AlF$_3$ and Li(tmp), since AlF$_3$ is a high-melting ionic solid (m.p. 1290°C)[16] with a coordination number of 6 at aluminum. Moreover, AlF$_3$ is completely insoluble in hydrocarbon solvents and, indeed, no reaction occurred.

However, the fluoride **2d** was obtained as the product of the reaction of **2b** with AgBF$_4$ in *n*-hexane. The tetrafluoroborate, though detectable in solution (δ$^{11}$B = 17.7 ppm), is unstable and loses BF$_3$ according to equation (3).

$$2\ \underset{\mathbf{2b}}{\text{tmp}_2\text{AlBr}} + 2\ \text{AgBF}_4 \xrightarrow{\text{hexane}} 2\ \text{tmp}_2\text{AlBF}_4 \xrightarrow{-2\,\text{BF}_3} \underset{\mathbf{2d}}{(\text{tmp}_2\text{AlF})_2} \qquad (3)$$

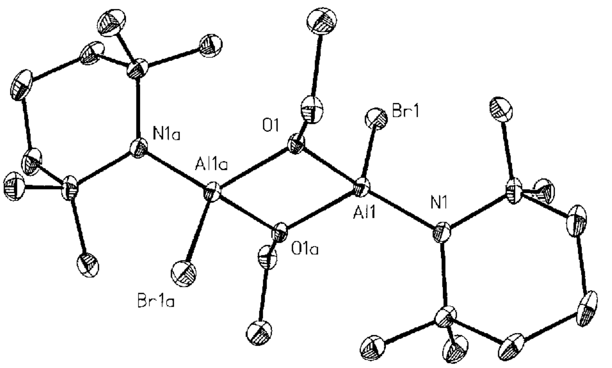
Since **2d** is insoluble in aprotic organic solvents, no solution-NMR spectra could be recorded for its characterization, nor could its degree of association be determined by cryoscopy. Possibly the monomeric nature of **2b** leads to monomeric **2d** which, according to its X-ray crystal structure determination, crystallizes from the solution as a dimer.

## Crystal Structures

X-ray crystal structure determinations were performed to characterize the new compounds, to ascertain their nature in the solid state, and to obtain bonding parameters for the discussion of their structures.

**1a** and **1b** are isomorphous and crystallize in the monoclinic space group *P*2$_1$/*n*. A four membered, planar, and crystallographically centrosymmetric Al$_2$O$_2$ ring [*d*(Al−O) = 1.827(6) Å, O−Al−O 81.3(2)°] with terminal tmp ligands in a *trans* orientation [*d*(Al−N) = 1.811(7) Å (**1a**); 1.810(3) Å (**1b**)] is the most important structural feature. The Al−O bonding parameters compare well with recently published data for (H$_2$Al−O*t*Bu)$_2$[12a] [*d*(Al−O) = 1.810(3), 1.815(3) Å and O−Al−O 81.0(2)°]. The Al−N bond length is rather short, but within the range found for terminal amino groups at tetracoordinated aluminum centers[4]. The geometry around the nitrogen atom is almost planar, indicated by the sum of the bond angles being close to 360° (357.0 and 357.5°, respectively). Due to steric hindrance, the angle N−Al−X is widened beyond the tetrahedral angle. We find 117.0(2)° for the chloride **1a** and 117.7(1)° for the bromide **1b**. Therefore, the geometry around the aluminum center is distorted tetrahedral.

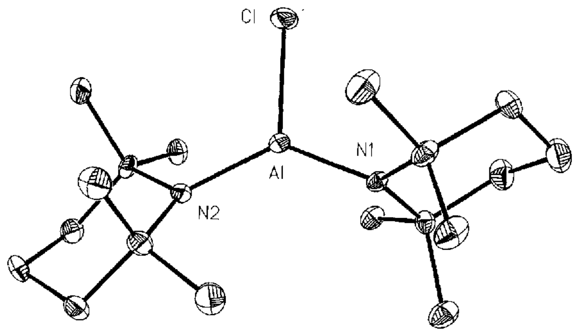
Figure 1. Molecular structure of **1b** in the solid state; thermal ellipsoids are shown at a 25% probability level; selected atom distances (in Å) and bond angles (in deg.)[a]



[a] Al1−N1 1.810(3), Al1−O1 1.835(3), Al1−O1A 1.840(3), Al1−Br1 2.316(1); Al1−O1−Al1A 99.3(1), O1−Al1−O1A 80.7(1), N1−Al1−Br1 117.7(1), N1−Al1−O1 117.6(1), N1−Al1−O1A 124.4(1). **1a** exhibits the same configuration as **1b** and is therefore not depicted as ORTEP. Its molecular parameters are: Al1−N1 1.815(7), Al1−N2 1.808(7), Al1−O1 1.827(6), Al1−O2 1.827(6), Al1−Cl1 2.143(3); Al1−O1−Al2 98.9(3), O1−Al1−O2 81.3(2), N1−Al1−Cl1 117.0(2), N2−Al2−Cl2 118.1(2), N1−Al1−O1 116.7(3), N1−Al1−O2 125.1(3).

The high solubility of **2a**−**2c** in all the tested aprotic solvents, including pentane and hexane, caused problems in growing single crystals. Nevertheless, a few crystals suitable for X-ray structure analysis were isolated in each case. **2a** and **2b** are isomorphous and crystallize in the tetragonal space group $P4_2/n$, whereas **2c** was found to be triclinic, space group $P\bar{1}$. Bonding parameters are listed in Table 1.

Figure 2. Molecular structure of **2a** in the solid state; thermal ellipsoids are shown at a 25% probability level; **2b**−**c** exhibit the same configuration as **2a** and are therefore not depicted as ORTEP



The aluminum atoms in **2a**−**2c** reside in a planar environment made up by two nitrogen atoms and one halogen atom (sum of bond angles at Al: 360°). The nitrogen atoms of the tmp ligands, which exhibit the half-chair conformation, show an almost planar geometry. The sum of the bond angles ranges from 356.7 to 357.9°. We observe two significantly different Al−N bond lengths in each molecule. In fact, the shorter ones represent some of the shortest distances yet found for *d*(Al−N). Morevoer, the shorter bond length [*d*(Al−N1)] correlates with the larger torsion angle X−Al−N1−C1. In comparison with other Al−X distances, the Al−X bond length is rather long. For steric reasons the bond angle N1−Al−N2 (**2a** 130.1°; **2b** 130.4°; **2c** 129.5°) is larger than the expected ideal trigonal-planar value of 120°.

Table 1. Bonding parameters of $tmp_2AlX$ compounds

| $tmp_2AlX$ | X = F | X = Cl | X = Br | X = I |
|---|---|---|---|---|
| [Å] | | | | |
| Al–X | 1.829(1)<br>1.835(1) | 2.144(2) | 2.309(2) | 2.571(1) |
| Al–N1 | 1.832(2) | 1.785(4) | 1.782(6) | 1.788(3) |
| Al–N2 | 1.832(2) | 1.810(4) | 1.812(6) | 1.803(3) |
| [°] | | | | |
| N1–Al–N2 | 128.6(1) | 130.1(2) | 130.4(3) | 129.5(1) |
| X–Al–N1 | 108.5(1) | 113.3(2) | 112.1(2) | 111.0(1) |
| X–Al–N2 | 110.9(1) | 116.6(2) | 117.3(2) | 119.3(1) |
| Al–N1–C1 | 127.7(2) | 124.4(3) | 124.6(5) | 126.2(2) |
| Al–N1–C5 | 115.8(2) | 115.2(3) | 113.9(4) | 113.6(2) |
| [°] | | | | |
| Σ (Al) | – | 360.0 | 359.8 | 359.9 |
| Σ (N1) | 359.5 | 357.6 | 357.5 | 357.9 |
| Σ (N2) | 359.5 | 356.7 | 356.9 | 357.1 |
| [°] | | | | |
| X–Al–N1–C1 | – | 66.2 | 66.0 | 65.2 |
| N2–Al–N1–C5 | – | 84.3 | 88.7 | 89.3 |
| X–Al–N2–C10 | – | 30.8 | 31.1 | 35.6 |
| N1–Al–N2–C14 | – | 52.1 | 46.9 | 48.8 |

**2d** crystallizes in the monoclinic space group *C*2/*c* and is isomorphous with the hydride $(tmp_2AlH)_2$[7]. The crystallographic data for the unit cells are almost identical (see Table 2).

Figure 3. Molecular structure of **2d** in the solid state; thermal ellipsoids are shown at a 25% probablity level

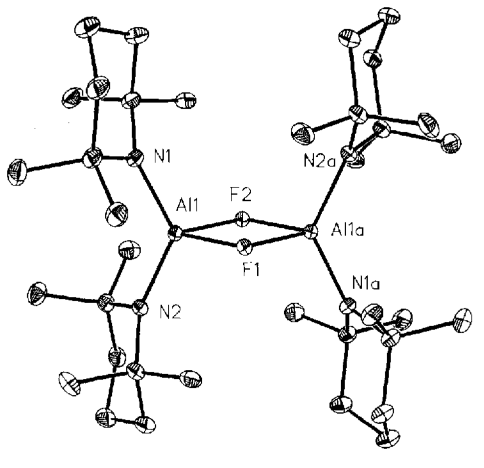


Table 2. Crystallographic data for **2d** and $(tmp_2AlH)_2$

| compound | *a*[Å] | *b*[Å] | *c*[Å] | β[°] | *d*(Al–N) [Å] | N–Al–N [°] |
|---|---|---|---|---|---|---|
| $(tmp_2AlH)$ | 21.414 | 7.945 | 24.231 | 113.76 | 1.832(2) | 127.0 |
| $(tmp_2AlF)$ | 21.496 | 7.922 | 24.575 | 113.67 | 1.832(2) | 128.6 |

The molecular structure of **2d** is depicted in Figure 3. It is a centrosymmetric dimer containing fluoride bridges in the solid state. The compound exhibits Al−F bond lengths

[1.829(1) and 1.835(1) Å] in the normal range found for Al−F−Al bridges[14,22]. The geometry at the nitrogen atoms is almost planar (sum of the bond angles 359.5°) and the tmp ligands exhibit the half-chair conformation. In contrast to **2a**−**2c**, there are no differences in the Al−N bond lengths. The Al−N distance in **2d** [1.832(2) Å] is comparable to that in other aluminum amides with tetracoordinate aluminum atoms and tricoordinate nitrogen atoms[4]. As expected, $(tmp_2AlH)_2$ shows the same Al−N bond length [1.832(2) Å][7]. The bond angle N−Al−N is only slightly smaller than in **2a**−**2c** [**2d**: 128.6(1)°].

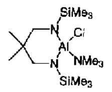
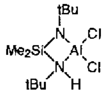
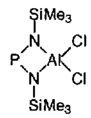
The shortest Al−N bond lengths reported in the literature are 1.770(2) Å for cyclo-$Me_2NCH_2CH_2N(Et)AlCl_2$[17a], 1.78(2) Å for $Al[N(SiMe_3)_2]_3$[2], and 1.782(4) Å for $[MeAlN(2,6\text{-}i\text{Pr}_2C_6H_3)]_3$[17]. Some authors explain these short distances in terms of partial pp(π) bonding, by analogy with the corresponding boron-nitrogen systems[17a]. This requires that the plane $C_2NAl$ of the shorter bond is coplanar or close to planarity with the $XAlN_2$ plane. However, the shorter bond length Al−N is associated with the tmp ligand with the bigger torsion angle X−Al−N1−C1 (65 to 66°). This precludes an efficient overlap of the nitrogen $p_z$ orbital with the aluminum $p_z$ orbital. Therefore, it would seem very unlikely that pp(π) interaction is a factor in the bond shortening. Steric hindrance combined with ionic interaction, as proposed by Power et al.[18], seems to give a better explanation for the short bond length for the amino group with the larger torsion angle X−Al−N−C, since for a highly polar bonding situation the stability increases as the Al−N bond length becomes shorter. This is the case for **2a**−**2c**, where the molecule adopts a conformation with one tmp group almost orthogonal to the $N_2AlX$ plane. This also reduces steric repulsion in the molecule. The observed torsion angles of 65 to 66° for the tmp groups attached via the shorter Al−N bonds seem to be the result of a compromise between the polar character of the Al−N bond and the steric requirements of the tmp ligand.

pπ(N)-σ*(X) interaction, as proposed by Barron et al.[13], should lead to a bond lengthening for Al−X and a bond shortening for Al−N, a behavior consistent with our data. Indeed, we observe Al−X bond lengths approximately 2 to 9 pm longer than for other terminal Al−X bonds in tetracoordinated aminoaluminum halides[4], and short Al−N distances.

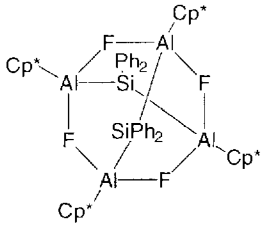
Bond shortening is at its most pronounced when the torsion angle X−Al−N−X approaches 90°. In this situation, the best overlap results for the pπ(N)-σ*(X) orbitals. In the case of **2a**−**2c**, the shorter Al−N bond length is found for the tmp group where the torsion angle X−Al−N−C has the smallest deviation from 90° (about 65 to 66°). Therefore, pπ(N)-σ*(X) interactions may account for the Al−N bond shortening and Al−X bond lengthening.

The boron homologues of **2a**−**2c** can be readily transformed into ionic compounds by replacing the halogen atoms with bigger, non-nucleophilic ligands such as $BF_4^-$ or $AlCl_4^-$. Under these circumstances, biscoordinated borinium salts $[tmp_2B]^+X^-$ ($X = BF_4^-$, $AlCl_4^-$, etc.) are generated[6]. If this holds true for the compounds **2a**−**2c**, the N1−Al−N2 bond angle must change from the ideal trigonal-planar value (120°) to 180°. The observed values for the $tmp_2AlX$ compounds of about 130° may reflect an increased polarity of the Al−X bond, in line with a tendency to form the biscoordinated ionic species $tmp_2Al^+$. In this way, the aluminum center would become more Lewis acidic, and the coulombic attraction between the anion ($R_2N^-$) and the cation ($Al^+$) would be increased. This assumption would also explain the long Al−X distances and short Al−N bond lengths.

Table 3. Aluminium halogen bond lengths for $tmp_2AlX$ and other aminoaluminum halides

| Compound | Cl | Br | I | Ref. |
|---|---|---|---|---|
| $tmp_2AlX$ | 2.144(2) Å | 2.309(2) Å | 2.571(1) Å | this publication |
| $(Me_2NAlX_2)_2$ | 2.106(4) Å | 2.260(5) Å | 2.478(5) Å<br>2.505(8) Å | X = Cl[21]<br>X = Br, I[5] |
| $[Me_3SiN(H)AlCl_2]_2$ | 2.098(3) Å | – | – | [20] |
|  | 2.086(2) Å | – | – | [16a] |
|  | 2.122(2) Å | – | – | [17a] |
|  | 2.111(1) Å | – | – | [17b] |

A fine example of the special behavior of compounds containing aluminum and fluorine atoms has recently been provided by Roesky et al.[14] for compound **4**, the product of the reaction of $(Cp^*Al)_4$ and $Ph_2SiF_2$. Both elements, Si and F, exhibit high bond energies M−F (SiF: 543 kJ/mol[15]; AlF: 659−672 kJ/mol[15]). In the mentioned reaction, Si−F bond cleavage occurs leading to formation of the Al−F−Al bridged aluminum-silicon-fluorine cluster compound **4**.



**4**

For $[(Cp^*AlF)_2SiPh_2]_2$[14] an Al−F bond length of 1.846 Å is reported, while for $(Me_2AlF)_4$ the value is 1.81 Å[22]. Both are close to the 1.829(1) and 1.835(1) Å observed in **2d**. The bond angle N1−Al−N2 [128.6(1)°] for **2d** is quite open for a tetracoordinated aluminum atom, and this is most likely to be due to the steric demand of the tmp ligand. It should be noted that there is only a small difference (ca. 2°) between this value and the N−Al−N bond angles in the tricoordinated species **2a**−**c**.

For $(tmp_2AlH)_2$ an Al−Al distance of 2.680(2) Å has been found. This compares well with other four-membered $Al_2X_2$ rings (X = C, H)[9] where Al−Al separations of 2.52 to 2.70 Å have been determined by X-ray crystallography. Even the dialane(4) $[(Me_3Si)_2CH]_4Al_2$ exhibits only a slightly shorter Al−Al bond length [2.660(1) Å][19]. For **2d**, this distance is 2.870(2) Å. Therefore, any bonding interaction between the aluminum nuclei can be excluded.

## Conclusion

Attempts to prepare $tmp_2AlX$ (X = Cl, Br) in $Et_2O$ as solvent lead to the exclusive formation of the ether cleavage products **1a** and **1b**. However, reaction of Li(tmp) with $AlX_3$ in *n*-hexane leads to the bis(tetramethylpiperidino)aluminium halides $tmp_2AlX$ (X = Cl, Br, I), **2a−c**, which are monomeric in the solid state, in solution and in the gas phase. In contrast, $tmp_2AlF$, **2d**, exists as a dimer. Dimerization occurs via Al−F−Al bridges and not via the usually observed Al−N−Al bridges. Since the bond length Al−N for the tetracoordinated species **2d** is elongated only slightly, π-bonding in the tricoordinated species **2a−c** can be excluded, and a high polarity of this bond or an anomeric effect provides a better explanation for the short Al−N bond length. Obviously, dimerization of the bis(tetramethylpiperidino)aluminum halides is controlled by the steric requirements of the halogen atom. The small fluoride ligand allows dimerization, while chloride, bromide, and iodide prevent it. Compounds **2a−b** in particular are suitable starting materials for a larger range of mononuclear $tmp_2AlX$ compounds, and this will be described and discussed in forthcoming reports.

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## Experimental Section

All manipulations were performed using Schlenk techniques under a dinitrogen atmosphere. All solvents were rigorously dried prior to use and stored under $N_2$. − NMR: Bruker ACP 200, Jeol GSX400 and Jeol GSX270. − IR: Nicolet FT-IR spectrometer model 6000, CsI plates, nujol. − MS: Varian Atlas CH7 spectrometer.

*Synthesis of 2,2,6,6-Tetramethylpiperidino Lithium:* One equivalent of tmp-H (e.g. 7.06 g, 50 mmol) (Merck) was dissolved in 50 ml of *n*-hexane. Then, 1.05 equivalents of a 1.6 M solution of *n*-BuLi in *n*-hexane (e.g. 32.8 ml of a 1.6 M solution, 52.5 mmol) was added with stirring at ambient temperature. Evolution of Bu-H was observed. The resulting suspension was heated to reflux for one hour. After cooling, the suspension was used directly, without isolation of Li(tmp), assuming a 100% conversion.

*Dimeric 2,2,6,6-Trimethylpiperidinoethoxyaluminum Chloride* (**1a**): A solution of $AlCl_3$ (2.66 g, 20 mmol) in 25 ml of $Et_2O$ was added at −20°C to a freshly prepared suspension of Li(tmp) (5.88 g, 40 mmol) in 40 ml of *n*-hexane and the mixture was stirred overnight. After filtration of the insoluble material (LiCl), all volatile components were removed from the filtrate in vacuo. The residue was dissolved in 30 ml of toluene and stored at −20°C for several days. The resulting crystals were collected (3.54 g, 35.7%). − $^1H$ NMR ($CDCl_3$, 270 MHz): δ = 1.30 (t, 8H, tmp-β-$CH_2$), 1.34 (s, 24H, tmp-$CH_3$), 1.52−1.59 (m, 4H, tmp-γ-$CH_2$), 4.19 (q, 4H, O-$CH_2$), 1.50 (t, 6H, $CH_2$-$CH_3$). − $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 17.0, 17.6 ($CH_2$-$CH_3$), 17.9, 18.3 (O-$CH_2$), 34.3, 34.6 (tmp-$CH_3$), 41.0, 41.7 (tmp-β-$CH_2$), 52.0 (NC), 62.5, 63.5 (O-$CH_2$). − $^{27}Al$ NMR ($CDCl_3$, 70 MHz): δ = 85 ($\Delta_{1/2}$ = 2200 Hz). − $C_{22}H_{46}Al_2Cl_2N_2O_2$ (495.46): calcd. Al 10.9, Cl 14.3; found Al 10.0, Cl 15.0.

*Dimeric 2,2,6,6-Tetramethylpiperidinoethoxyaluminum Bromide* (**1b**): A solution of $AlBr_3$ (2.67 g, 10 mmol) in 25 ml of $Et_2O$ was added at −20°C to a freshly prepared suspension of Li(tmp) (3.23 g, 22 mmol) in 40 ml of *n*-hexane and the mixture was heated to reflux for three hours. After cooling and filtration of the insoluble material (LiBr), the filtrate was stored overnight at −20°C. The precipitated crystals were collected (0.62 g, 21%). m.p. 153−156°C. − $^1H$ NMR ($C_6D_6$, 270 MHz): δ = 1.33 (t, 8H, tmp-β-$CH_2$), 1.50 (s, 24H, tmp-$CH_3$), 1.52−1.62 (m, 4H, tmp-γ-$CH_2$), 4.05 (q, 4H, O-$CH_2$), 1.31 (t, 6H, $CH_2$-C$H_3$). − $^{13}C$ NMR ($C_6D_6$, 100 MHz): δ = 17.0, 17.6 ($CH_2$-$CH_3$), 17.9, 18.3 (O-$CH_2$), 34.3, 34.6 (tmp-$CH_3$), 41.0, 41.7 (tmp-β-$CH_2$), 52.0 (N-C), 62.5, 63.5 (O-$CH_2$). − $^{27}Al$ NMR ($C_6D_6$, 70 MHz): δ = 85 ($\Delta_{1/2}$ = 2320 Hz). − IR: ν(Al−Br) range: 431, 364 $cm^{-1}$. − $C_{22}H_{46}Al_2Br_2N_2O_2$ (584.40): calcd. C 45.22, H 7.93, N 4.79, Al 9.2, Br 27.3; found C 44.91, H 8.13, N 4.68, Al 9.0, Br 28.0.

*Bis(2,2,6,6-tetramethylpiperidino)aluminum Chloride* (**2a**): $AlCl_3$ powder (8.4 g, 63.1 mmol) was added to a freshly prepared suspension of Li(tmp) (18.6 g, 126.2 mmol) in 250 ml of *n*-hexane (−78°C). The mixture was allowed to warm to room temperature and was then heated to reflux for 20 hours. After cooling and filtration of the insoluble material (LiCl), the filtrate was concentrated to a volume of 100 ml and stored at −78°C for some days. Isolation of the precipitate afforded 8.9 g (41%) of crystalline **2a**. − Molar mass (in cyclohexane): 347 g/mol, calcd. for the monomer, 343. − $^1H$ NMR ($CDCl_3$, 270 MHz): δ = 1.34 (t, 8H, tmp-β-$CH_2$), 1.39 (s, 24H, tmp-$CH_3$), 1.55−1.65 (m, 4H, tmp-γ-$CH_2$). − $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 17.9 (tmp-γ-$CH_2$), 34.0 (tmp-$CH_3$), 39.6 (tmp-β-$CH_2$), 51.9 (N-C). − $^{27}Al$ NMR ($CDCl_3$, 70 MHz): δ = 134 ($\Delta_{1/2}$ = 13700 Hz). − $C_{18}H_{36}AlClN_2$ (342.9): calcd. C 63.04, H 10.58, N 8.17, Cl 10.3; found C 61.37, H 11.22, N 7.62, Cl 9.7.

*Bis(2,2,6,6-tetramethylpiperidino)aluminum Bromide* (**2b**): $AlBr_3$ powder (42.8 g, 160.5 mmol) was added to a freshly prepared suspension of Li(tmp) (47.1 g, 321 mmol) in 400 ml of *n*-hexane (−78°C). The mixture was allowed to warm to room temperature and was then heated to reflux for 15 hours. After cooling and filtration of the insoluble material (LiBr), the filtrate was reduced to a volume of 150 ml in vacuo and stored at −78°C for some days. Isolation of the precipitate afforded 31.8 g (52%) of crystalline **2b**, m.p. 86−89°C. − Molar mass (in cyclohexane): 361 g/mol, calcd. for the monomer, 387. − $^1H$ NMR ($C_6D_6$, 270 MHz): δ = 1.30 (t, 8H, tmp-β-$CH_2$), 1.44 (s, 24H, tmp-$CH_3$), 1.52−1.62 (m, 4H, tmp-γ-$CH_2$). − $^{13}C$ NMR ($C_6D_6$, 100 MHz): δ = 18.2 (tmp-γ-$CH_2$), 34.3 (tmp-$CH_3$), 39.9 (tmp-β-$CH_2$), 52.5 (N-C). − $^{27}Al$ NMR ($C_6D_6$, 70 MHz): δ = 130 ($\Delta_{1/2}$ = 9150 Hz). − IR: ν(Al−Br) range: 401 $cm^{-1}$. − MS: *m/z*: 386/388 [$tmp_2Al^{79/81}Br^{+\bullet}$]. − $C_{18}H_{36}AlBrN_2$ (387.38): calcd. C 55.81, H 9.37, N 7.26, Al 7.0, Br 20.6; found C 53.27, H 9.28, N 6.63, Al 6.1, Br 20.4.

*Bis(2,2,6,6-tetramethylpiperidino)aluminum Iodide* (**2c**): $AlI_3$ powder (9.8 g, 23 mmol) was added to a freshly prepared suspension of Li(tmp) (6.7 g, 46 mmol) in 200 ml of *n*-hexane (−78°C). The mixture was allowed to warm to room temperature and was then heated to reflux for 20 hours. After cooling and filtration of the insoluble material (LiI), the filtrate was reduced to a volume of 50 ml in vacuo and stored at −78°C for some days. Isolation of the precipitate afforded 5.2 g (27%) of crystalline **2c**, m.p. 150−152°C. − Molar mass (in cyclohexane): 421 g/mol, calcd. for the monomer, 434. − $^1$H NMR ($C_6D_6$, 270 MHz): $\delta$ = 1.29 (t, 8H, tmp-β-$CH_2$), 1.47 (s, 24H, tmp-$CH_3$), 1.52−1.62 (m, 4H, tmp-γ-$CH_2$). − $^{13}$C NMR ($C_6D_6$, 100 MHz): $\delta$ = 18.1 (tmp-γ−$CH_2$), 34.4 (tmp-$CH_3$), 40.0 (tmp-β-$CH_2$), 52.8 (N-C). − $^{27}$Al NMR ($C_6D_6$, 70 MHz): $\delta$ = 130 ($\Delta_{1/2}$ = 10000 Hz). − IR: ν(Al−I) range: 337 cm$^{-1}$. − MS: *m/z*: 434 $[\mathrm{tmp_2Al^{127}I}]^{+\bullet}$. − $C_{18}H_{36}AlIN_2$ (434.38): calcd. C 49.77, H 8.05, N 6.45, Al 6.2, I 29.2; found C 47.94, H 8.00, N 6.02, Al 5.9, I 28.1.

*Dimeric Bis(2,2,6,6-tetramethylpiperidino)aluminum Fluoride* **2d**: A solution of **2b** (1.94 g, 5.0 mmol) in 30 ml of *n*-hexane was added to a cooled (−30°C) suspension of $AgBF_4$ (Aldrich) (1.11 g, 5.7 mmol) in 20 ml of *n*-pentane. The mixture was allowed to warm to room temperature and was then stirred overnight. After filtration of the insoluble material (AgBr), the concentrated filtrate (20 ml) was stored at −20°C for some days, affording 0.41 g **2d** (23%), m.p. >314°C (decomp.). Since **2d** was found to be completely insoluble in all the tested solvents, no NMR spectra could be obtained. − $C_{36}H_{72}Al_2F_2N_4$ (652.96): calcd. C 66.22, H 11.11, N 8.58, Al 8.26; found C 62.72, H 10.99, N 8.18, Al 7.9.

*X-ray Crystal Structure Determinations:* Data collection for X-ray structure determinations was performed on Syntex P4 or Syntex R3 four-circle diffractometers using graphite-monochromated Mo-$K_\alpha$ (0.71073 Å) radiation. Single crystals were mounted in Lindemann capillaries and sealed under argon atmosphere. All calculations were performed on PC's using the Siemens SHELXTL-Plus or SHELX-93 software packages. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions by a riding model using fixed isotropic parameters. Crystallographic data and relevant details of the data collection and refinement are compiled in Table 3. Further details on the crystal structure determination are deposited at the Cambridge Crystallographic Data Centre and may be requested by quoting the depository number 100429, the names of the authors, and the journal citation.

☆ Dedicated to Prof. Dr. *G. Huttner* on the occasion of his 60th birthday.

[1] J. K. Ruff, *J. Am. Chem. Soc.* **1961**, *83*, 2835−2839.

[2] G. M. Sheldrick, W. S. Sheldrick, *J. Chem. Soc. (A)* **1969**, 2279−2282.

[3] M. Cesari, S. Cucinella, in *The Chemistry of Inorganic Homo- and Heterocycles* (Eds.: I. Haiduc, D. B. Sowerby), Academic Press, London, Vol. 1, **1987**, 176−190.

[4] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides, Synthesis, Structures, Physical and Chemical Properties*, Ellis Horwood Publishers, New York, **1980**, 99−114 and 191−200.

[5] A. Ahmed, W. Schwarz, H. Hess, *Z. Naturforsch.* **1978**, *33b*, 43−46.

[6] S. Weber, *PhD Thesis*, University of Munich, **1984**.

[7] C. Klein, H. Nöth, M. Tacke, M. Thomann, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 886−888; *Angew. Chem.* **1993**, *105*, 923−926.

[8] G. Linti, R. Frey, K. Polborn, *Chem Ber.* **1994**, *127*, 1387−1393.

[9] Ch. Elschenbroich, A. Salzer, *Organometallchemie*, Teubner Studienbücher, 3. Auflage, Stuttgart, **1993**.

[10] R. Frey, *PhD Thesis*, University of Munich, **1995**.

[11] J. Mason, *Multinuclear NMR*, Plenum Press, New York and London, **1987**, 259−278.

[12] Performed with the program *Hyperchem*, V3.0, Autodesk, **1993**. [12a] M. Veith, S. Faber, H. Wolfanger, V. Huch, *Chem. Ber.* **1996**, *129*, 381−384.

[13] M. D. Healy, M. P. Power, A. R. Barron, *Coord. Chem. Rev.* **1994**, *130*, 63−135.

[14] S. Schulz, T. Schoop, H. W. Roesky, L. Häming, A. Steiner, R. Herbst-Irmer, *Angew. Chem.* **1995**, *107*, 1015−1016; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 919.

[15] R. T. Sanderson, *Polar Covalence*, Academic Press, New York, **1983**, 155.

[16] A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin and New York, **1985**, 875. − [16a] C. Klein, *PhD Thesis*, University of Munich, **1994**.

[17] K. M. Waggoner, H. Hope, P. P. Power, *Angew. Chem.* **1988**, *100*, 1765−1766; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1699. − [17a] M. J. Zawortko, J. L. Atwood, *Inorg. Chem.* **1980**, *19*, 268−270. − [17b] S. Pohl, *Chem. Ber.* **1979**, *112*, 3159−3165.

[18] P. P. Power, P. J. Brothers, R. J. Wehmschulte, M. M. Olmstead, K. Ruhlandt-Senge, S. R. Parkin, *Organometallics* **1994**, *13*, 2792−2799.

[19] W. Uhl, *Z. Naturforsch.* **1988**, *43b*, *1113−1118*.

[20] S. J. Schauer, G. H. Robinson, *J. Coord. Chem.* **1993**, *30*, 197−214.

[97024]