

A Contribution to the Chemistry of 2,2,6,6-Tetramethylpiperidino Aluminium Compounds

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Dedicated to Prof. Dr. Dr. h. c. mult. H. W. Roesky on the occasion of his 70th birthday

tmpAlBr_2 (tmp = 2,2,6,6-tetramethylpiperidino) was prepared from AlBr_3 and tmp_2AlBr at 90 °C in the absence of a solvent, but could not be crystallised from toluene or hexane because it reacted with the solvents to form $\text{tmpH}\cdot\text{AlBr}_3$ in high yield. $\text{tmpH}\cdot\text{AlMeCl}_2$, obtained from the components, decomposes at elevated temperatures but no tmpAlCl_2 could be isolated. Attempts to generate the cation $[\text{tmp-Al-tmp}]^+$ from tmp_2AlBr or tmp_2AlCl by halide abstraction with $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Ph}_3\text{C}(\text{SnCl}_5)$ or SbCl_5 or from tmp_2AlR (R = Me, Ph) and $\text{B}(\text{C}_6\text{F}_5)_3$ have failed. An unexpected reaction occurred on treatment of $\text{tmp-B}=\text{P}(\text{tBu})\text{AlBr}_3$ with BH_3 in THF which led to the formation of $[\text{AlBr}_2(\text{thf})_4][\text{AlBr}_4]$. The attempted synthesis of $\text{tBu}_2\text{Al}(\text{tmp})$ from tBu_2AlBr and $\text{Li}(\text{tmp})$ gave a product which, on exposure to CO_2 at dry ice temperature, yielded the salt $[(\text{tBuAl})_2(\text{O}_2\text{C}(\text{tmp}))_3][\text{tBu}_3\text{Al-Br-AltBu}_3]$ in low yield. All isolated products were characterized by NMR spectroscopy and by X-ray determination of their molecular structures.

Key words: Tetramethylpiperidino Alanes, Tetramethylpiperidino Aluminiumdihalides, Dibromo-tetrakis(tetrahydrofuran)aluminium Tetrabromoaluminate, Bis(tri-tert-butylaluminium)bromide Anion, X-Ray Structure

Introduction

2,2,6,6-Tetramethylpiperidino aluminium compounds tmp_2AlX (tmp = 2,2,6,6-tetramethylpiperidino) opened the door to a rich chemistry [1–5]. The compounds tmp_2AlF and tmp_2AlH [1, 2] are dimeric *via* AlFAl or AlHAl bridges in contrast to bis(dialkylamino)aluminium hydrides and halides [6–11] which dimerize *via* AlNAI bridges. However, most tmp_2AlX compounds (X = Me, Ph, OR, SR, SeR, TeR, PR_2 , AsR_2) are monomeric including the halides (X = Cl, Br, I) [2, 3, 5]. While dialkylaminodihaloalanes R_2NAIX_2 (R = Me, Pr, Ph, C_5H_{10}); X = Cl, Br) are readily available [8, 11], tmpAlBr_2 is difficult to prepare (*v.i.*). The structures of the tmp_2AlX compounds (X = Cl, Br, I) show fairly wide N-Al-N bond angles suggesting that they may be used as precursors for the generation of linear dicoordinated Al cations $[\text{tmp-Al-tmp}]^+$ by halide abstraction using a strong halide acceptor. This goal has up to date not yet been achieved. New aspects related to tmpAl chemistry are reported here.

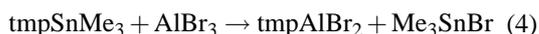
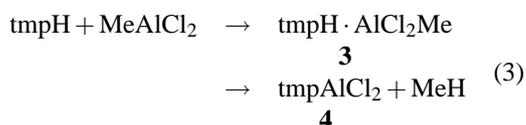
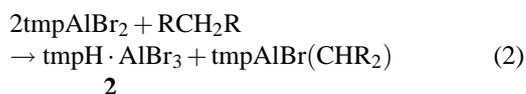
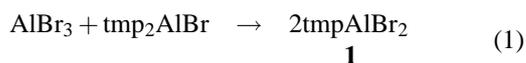
Results

Tetramethylpiperidinoaluminium halides

One might expect that the synthesis of the still unknown tmpAlBr_2 (**1**), could be easily achieved by melting together AlBr_3 with tmp_2AlBr at 90 °C in a 1 : 1 ratio and in the absence of a solvent as shown in eq. (1). This is indeed the case, because **1** dissolved in hexane or toluene provided a single ^{27}Al NMR signal at $\delta = 108$ ppm. These solutions, however, are unstable. After some hours at ambient temperature only a signal at $\delta^{27}\text{Al} = 90$ ppm remains which is due to $\text{tmpH}\cdot\text{AlBr}_3$ (**2**) [4]. Obviously a reaction with the solvents occurs as proposed in eq. (2).

Therefore, we explored other procedures to prepare tmpAlX_2 compounds. One possibility is shown in eq. (3). It was expected that the adduct **3** would readily be formed and loose methane at slightly elevated temperatures to produce **4**. The first step (1) yields **3** in good yield, however, on heating of compound **3** no gas evolution (methane) was noted up to 220 °C. **3** turned into a brown material from which no pure compound

could be isolated.

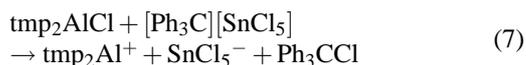
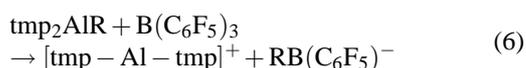
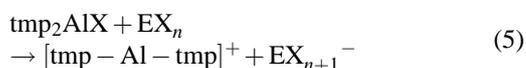


In another attempt to obtain tmpAlBr_2 the well known stannazane cleavage reaction was employed [12, 13] as depicted in eq. (4). On warming the reaction mixture in toluene from -78°C to 20°C this reaction indeed occurs as shown by a dominant ^{27}Al NMR signal at $\delta = 108$ ppm which however lost its intensity with time to make room for the ^{27}Al NMR signal of compound **2** ($\delta = 90$ ppm; reported 88 ppm [4]). This compound was isolated in 60% yield. The solution showed an ^{119}Sn resonance for Me_3SnBr at $\delta^{119}\text{Sn} = 128$ ppm [14].

In spite of many attempts we were unable to isolate and characterize the expected second aluminium compound which must form during the reaction of tmpAlBr_2 with toluene. We had expected that this compound might be $\text{tmpAlBr}(\text{CH}_2\text{Ph})$ a compound that should be soluble in toluene, but no ^{27}Al NMR signal could be detected [15].

Attempts to generate a bis(tetramethylpiperidino)aluminium cation

Bis(2,2,6,6-tetramethylpiperidino) alanes tmp_2AlX ($X = \text{Cl}, \text{Br}, \text{Me}, \text{Ph}$) are potential precursors for the generation of compounds with a dicoordinated bis(tetramethylpiperidino)-aluminium cation. For the halides, a strong halide acceptor may react as shown in eq. (5) while organyl anion acceptors could act as depicted in eq. (6).



No reaction was observed when tmp_2AlCl was treated with SbCl_5 in toluene at -50°C . At room temperature, however, a reaction occurred as suggested by the formation of a red solution and a black solid ($\text{Sb}^?$). In solution, however, the only Al species present was the AlCl_4^- anion ($\delta^{27}\text{Al} = 103$ ppm).

Using the method described by Jordan [16] we treated tmp_2AlR ($R = \text{Me}, \text{Ph}$) with $\text{B}(\text{C}_6\text{F}_5)_3$. No reactions were observed at low temperature by ^{11}B NMR spectroscopy, but under ambient conditions several ^{11}B NMR signals were observed revealing the presence of tetra- and tricoordinated boron compounds in solution (see Experimental Section). No ^{27}Al NMR signals could be observed. Comparison of the ^{11}B chemical shifts of known species related with those observed here suggests the following borates and boranes to be present: $\text{MeB}(\text{C}_6\text{F}_5)_3^-$, $\text{B}(\text{C}_6\text{F}_5)_3$, tmp_2BMe , $\text{MeB}(\text{C}_6\text{F}_5)_2$, and $\text{Me}_2\text{BC}_6\text{F}_5$.

Finally, we treated tmp_2AlCl with $[\text{Ph}_3\text{C}][\text{SnCl}_5]$ expecting a process according to eq. (7), but no reaction was observed in toluene solution.

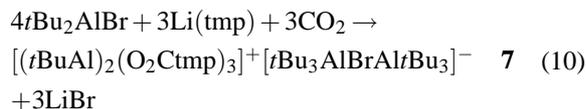
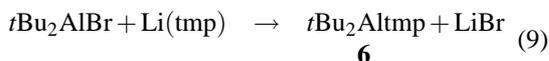
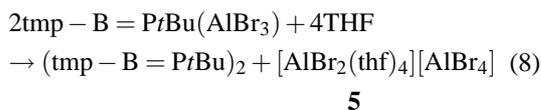
Two unexpected reactions

It has been shown that the amido-phosphinidene borane adduct $\text{tmp-B}=\text{PtBu}(\text{AlBr}_3)$ [17] is a reactive species. Its thermolysis might yield tmpAlBr_2 but produced a mixture of compounds which could not be separated. Addition of an electrophile EX_n to the P atom would be expected to lead to $\text{tmp(X)B-P}(\text{EX}_{n-1})\text{tBu}(\text{AlBr}_3)$ complexes or to a transfer of the tmp group to give tmpAlBr_2 . For this reason compound $\text{tmp-B}=\text{PtBu}(\text{AlBr}_3)$ was treated with $\text{BH}_3 \cdot \text{THF}$ in THF solution. It turned out that the course of the reaction was determined by the THF donor which removed its AlBr_3 component from the AlBr_3 adduct in the form of the salt **5** according to eq. (8).

This reaction occurs only in the presence of toluene as a cosolvent. Compound **5** is an isomer of $\text{AlBr}_3(\text{thf})_2$ [3]. Because it is well known that the BN multiple bond of $\text{tmp-B}=\text{NtBu}$ inserts readily into a BH bond of BH_3 with formation of a four-membered B_2N_2 ring, we assume that the second product is the tetra cyclic (tmp-BH-PtBu-BH_2) adduct (ring closure via a B-N bond) [18]. The conclusion is tentative because no ^{11}B NMR data could be recorded.

In connection with the synthesis and characterization of di(*tert*.butyl)aluminium pseudohalides [19] we tried to synthesize tBu_2Altmp in hexane according to

eq. (9):



In order to obtain crystals of **6**, the solution was kept at -78°C in dry ice. After several weeks crystals had formed but these proved not to be **6** but rather the salt **7**, which obviously was formed according to eq. (10) by slow diffusion of CO_2 into the reaction mixture.

Crystal structures

The new aluminium compounds have been characterized not only by NMR methods and IR spectra but particularly by their molecular structures as determined by X-ray diffraction. In the discussion the relevant features will be compared.

The molecular structure of compound **2** has already been described. The data now obtained agree well with those reported [4].

Crystals of **3** are monoclinic, space group $P2_1/n$ (see Fig. 1). For the tetracoordinated Al atom

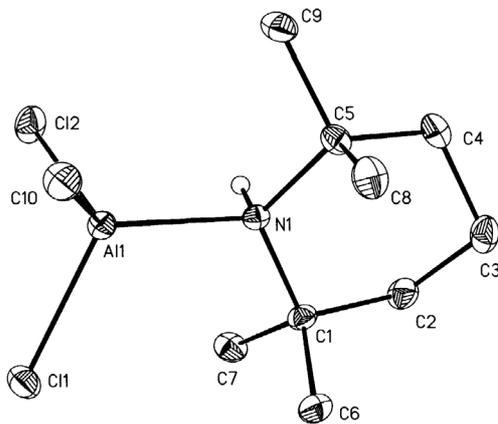


Fig. 1. Molecular structure of compound $\text{tmpH} \cdot \text{AlMeCl}_2$ (**3**). Thermal ellipsoids are presented on a 25% probability level. For selected bond lengths and bond angles see Table 1. Additional bond angles ($^\circ$): C1-N1-C5 116.84(1), C1-N1-Al1 117.84(9), C5-N1-Al1 113.51(9), C10-Al1-Cl11 104.52(5), C10-Al1-Cl12 113.23(6), Cl1-Al1-Cl12 105.94(3).

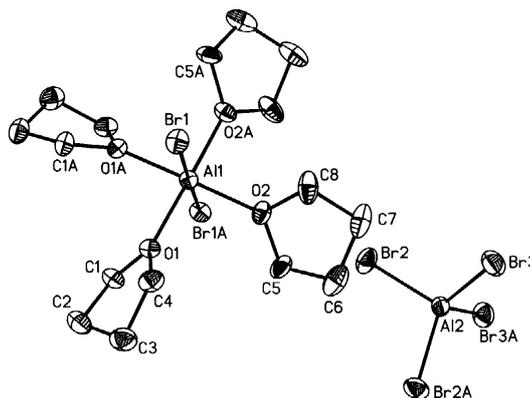


Fig. 2. Structure of the ions of the salt $[\text{AlBr}_2(\text{thf})_4][\text{AlBr}_4]$ (**5**). Thermal ellipsoids are presented on a 25% probability level. Selected bond lengths (\AA) and bond angles ($^\circ$): Al1-Br1 2.4366(8), Al1-O1 1.929(6), Al1-O2 1.942(7), O1-C1 1.48(1), O1-C4 1.48(1), Al2-Br2 2.290(2), Al2-Br3 2.292(2). – O1-Al1-O1A 89.1(4), O1-Al1-O2 90.1(3), O1-Al1-O2A 179.2(3); O1-Al1-Br1 90.5(2), O2-Al1-Br1 89.6(2), Br1-Al1-Br1A 178.9(2), Al1-O1-C1 125.0(5), Al1-O1-C4 125.9(5), Al1-O2-C5 125.7(5), Al1-O2-C8 125.9(6), C1-O1-C4 109.1(7), C5-O2-C8 108.4(7), Br2-Al2-Br3 109.32(6), Br2B-Al1-Br3 109.79(5), Br3-Al2-Br3B 110.9(2), Br2-Al2-Br2B 107.7(2).

there are strong deviations from a tetrahedral array due to the presence of methyl group. Thus, the “tetrahedral angles” range from $96.56(4)^\circ$ for N1-Al1-Cl2 to $119.90(6)^\circ$ for C10-Al1-N1. The twist angle H1-N1-Al1-Cl2 is -8.3° . Intermolecular N-H \cdots Cl hydrogen bonds (H1 \cdots Cl2 = 2.863 \AA ; N1-H1-Cl2 = 160.5°) connect two molecules of **3** in the unit cell.

The salt **5** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$ (see Fig. 2). Both Al atoms are located at a crystallographic twofold axis. The Al atom in the cation $[\text{AlBr}_2(\text{thf})_4]^+$ has a tetragonal bipyramidal coordination sphere with four O atoms in a slightly distorted AlO_4 plane as shown by two different Al-O bond lengths (1.926(6) and 1.942(7) \AA) and O1-Al-O1A and O2-Al-O2 bond angles of $89.1(4)$ and $90.1(3)^\circ$, respectively. The two Br atoms are in *trans* position to each other showing Br1-Al1-O bond angles of $90.5(2)$ and $89.6(2)^\circ$. As expected, the Al1-Br1 bond length is longer with 2.4366(8) \AA than the Al2-Br bonds (2.290(2), 2.292(2) \AA) at the almost perfectly tetrahedrally coordinated Al2 atom [20].

The molecular structure of the salt **7** is depicted in Fig. 3. The compound crystallizes in the orthorhombic space group $Pccn$ with $Z = 4$. Both the cation and the anion show C_2 symmetry. The

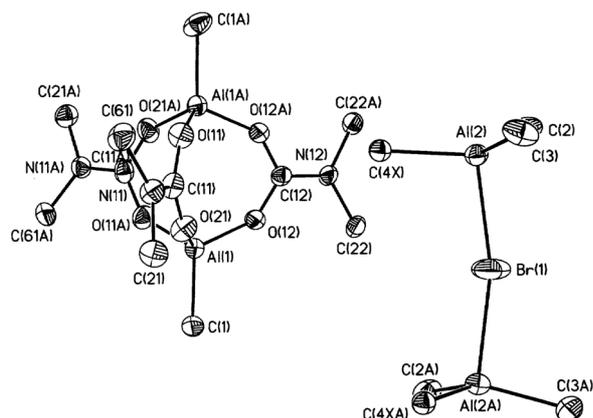


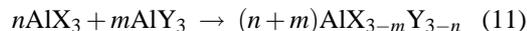
Fig. 3. Molecular structure of the components of compound $[(AltBu)_2(O_2Ctmp)_3]-(tBu_3Al)Br(AltBu_3)$ (**7**). Thermal ellipsoids represent a 25 probability level. The Me groups of *t*Bu have been omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Al1-C1 1.970(7), Al1-O12 1.763(4), Al1-O21 1.757(5), Al1-O11A 1.770(4), C11-N11 1.312(7), C11-O21 1.288(7), C11-O11 1.298(7), N11-C61 1.534(8), C12-N12 1.305(9), N12-C22 1.534(6), N12-C22B 1.534(6), C12-O12 1.289(5), Al2-C2 2.013(7), Al2-C3 2.019(7), Al2-C4X 2.01(1). – O12-Al1-O21 106.9(2), O12-Al1-O11B 107.9(2), O12-Al1-C1 112.8(2), O21-Al1-O11B 104.9(2), O21-Al1-C1 112.7(3), O11B-Al1-C1 111.2(3), Al2-Br1-Al2A 164.5(1), Br1-Al2-C2 102.74(2), Br1-Al2-C3 98.6(2), Br1-Al2-C4 107.6(4), C2-Al2-C3 114.5(3), C2-Al2-C4 124.2(5), C3-Al2-C4 105.9(5).

cation $[(tBuAl)_2(O_2Ctmp)_3]^+$ has a tricyclic structure containing tetracoordinated Al and trigonal planar N atoms. The smallest angle at atom Al1 is 104.9(2)° for O21-Al1-O11B, the widest is found with 111.2(3)° for the angle O11A-Al1-C1. The angles at the carbamate C and N atoms are close to 120° [119.3(5) to 120.8(6)°, and 119.1(5) to 121.5(5)°, respectively]. C=O bond lengths are on average 1.293(7) Å for C11-O11 and C11-O21, while the C11-N11 bond is only slightly longer with 1.312(7) Å. These data are typical for a carbamate ligand which coordinates to a metal centre by its two O atoms in accord with delocalized π -bonds [21].

Typical for the $[tBu_3Al-Br-AltBu_3]^-$ anion is the Al2-Br1-Al2A bond angle of 164.5(1)°. The Al-C bonds in this anion are slightly longer than in the cation [2.013(7), 2.01(1) and 2.019(7) Å versus 1.970(7) Å]. Steric interaction between the *t*Bu groups widens the C-Al2-C bond angles as shown for C2-Al2-C3 = 114.5(3)°, and C3-Al2-C4 = 123.9(5)° while sharp bond angles of 102.7(2)° and 98.6(2)° are found for C2-Al2-Br1 and C3-Al2-Br1, respectively.

Discussion

Substituent exchange between AlX_3 and AlY_3 species is in general a common route to mixed species $AlX_{3-m}Y_{3-n}$ as depicted in eq. (11):



This kind of reaction either leads to pure compounds AlX_2Y or $AlXY_2$ depending on stoichiometry, or to an equilibrium mixture of all components depending on the nature of X and Y [18]. For instance the reaction of Al_2Br_6 with $[Al(NMe_2)_3]_3$ leads to $[BrAl(NMe_2)_2]_2$ (1 : 2 reaction) or to $[Br_2AlNMe_2]_2$ (2 : 1 reaction) [7]. Since we had not been successful in preparing tmpAlX₂ halides (X = Cl, Br) by allowing AlX_3 to react with Li(tmp) we now obtained tmpAlBr₂ from the components AlBr₃ and tmp₂AlBr. Its ²⁷Al NMR data ($\delta = 108.9$ ppm, $h_{1/2} = 210$ Hz) suggest that the compound is dimeric having a tmp(Br)Al(μ -Br)₂Al(Br)tmp structure. This argument is based particularly on the line width as monomeric tmp₂AlBr shows a line width of 9100 Hz [3]. The signal of the Al atom of **2** is 10 ppm at higher field than that of dimeric Me₂NAlBr₂ [19]. Also, the Al atom of **2** is better shielded by 22 ppm compared to tmp₂AlBr which is, however, not a strong additional criterion as the shielding of the dimeric compounds Me₂NAlX₂ and (Me₂N)₂AlX (X = Cl, Br, I) are not strongly dependent on the nature and number of halogen atoms.

The structure suggested for compound **2** with bromide bridges is more likely than one with tmp bridges also for steric reasons. So far all compounds carrying a tmp group have no bridging tmp groups, exceptions being species of the type tmp-BR-N*t*Bu-AlX₂ with strong Lewis acidic AlX₂ groups and of small steric requirements [15]. The ability of **2** to deprotonate toluene to give compound **3** can only be understood if the amino group is a strong base and this excludes a tetracoordinated tmp N atom in a bridging position.

Compound **3** has been prepared from tmpH and AlBr₃ previously and its structure determined. The adduct tmpH·AlMeCl₂, **5**, is a new member in the series of tmpH adduct of aluminum halides [4]. This merits a short comparison of structural parameters which are summarized in Table 1.

All compounds crystallize in the monoclinic space group $P2_1/n$ except tmpH·AlH₂Cl [4]. The iodide is exceptional in that it contains two independent molecules in the asymmetric unit. Typical for all molecules are dihedral angles H-N-Al-X close to 0°.

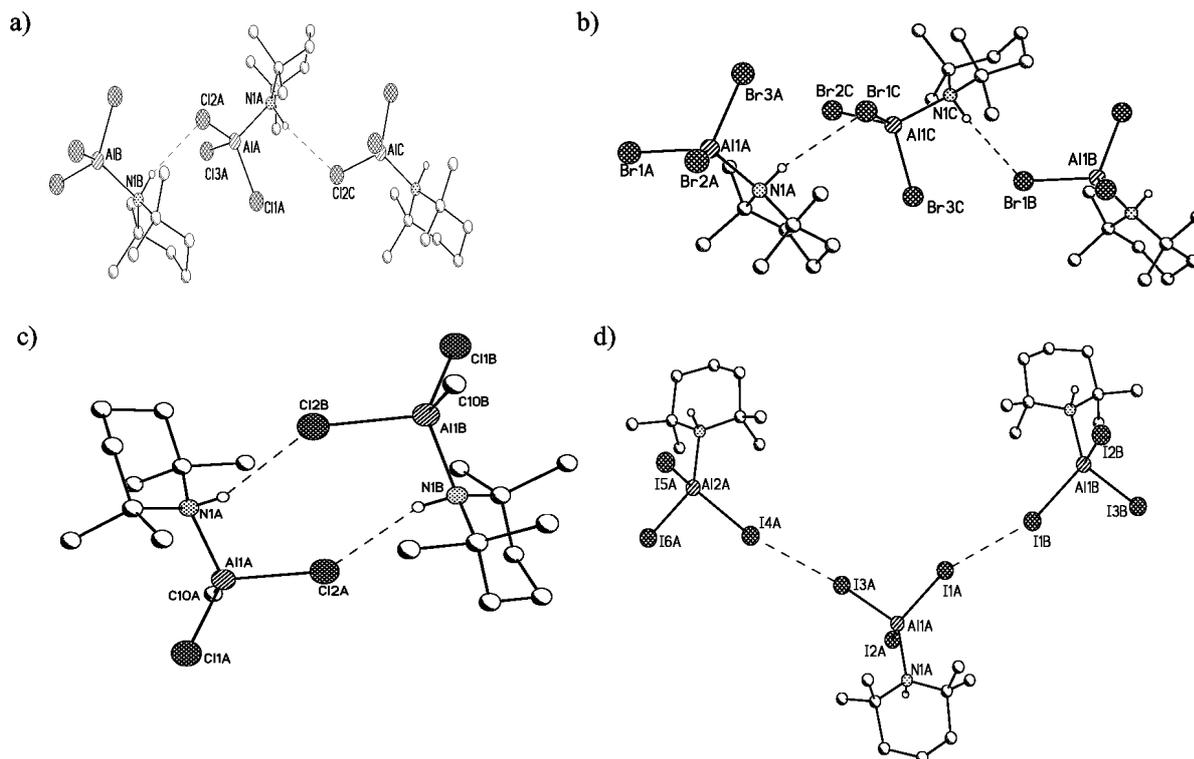


Fig. 4. Hydrogen bonding and I...I contacts in tmpH AlX₂Y compounds a) tmpH·AlCl₃; b) tmpH·AlBr₃; c) tmpH·AlI₃ and d) tmpH·AlCl₂Me.

Table 1. Comparison of structural data of compounds tmpH·AlX₃.

	X = Cl	X = Br	X = I	X = I	X = Me,Cl (3)
Al-N	2.014(2)	2.009(5)	2.038(9)	2.031(9)	2.039(1)
Al-X1	2.129(1)	2.280(2)	2.540(3)	2.532(3)	2.156(4)
Al-X2	2.136(1)	2.283(2)	2.535(3)	2.535(3)	2.169(5)
Al-X3	2.129(1)	2.310(2)	2.532(3)	2.523(3)	1.950(2) (Me)
N-Al-X1	99.86(7)	100.5(1)	99.00(3)	119.7(3)	114.10(4)
N-Al-X2	115.39(8)	116.0(1)	118.6(3)	98.3(3)	98.56(4)
N-Al-X3	116.72(3)	117.9(1)	119.2(3)	118.6(3)	119.90(6) C
H-N-Al-X	0 (Cl1)	2.3 (Br2)	-1.8 (I2)	0.3 (I5)	-8.3 (Cl2)

The Al-N bond lengths seem to increase in the order Br < Cl < I and are longest for compound **3** but, they do not differ much taking into account the 3σ criterion. Although the Al-X bonds differ within each molecule they fall in the range of those observed in other amine adducts of aluminium trihalides [22]. Moreover, the Al-Cl bond lengths in **3** are longer than in tmpH·AlCl₃ and this is true also for the AlN bond lengths indicating that MeAlCl₂ is a weaker Lewis acid than AlCl₃.

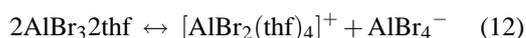
It is also worth noting that the N-Al-Cl2 bond angle in **3** is quite acute with 98.56° while the N-Al-C bond angle of 119.90(6)° is wide. Consequently, the C-Al-Cl

bond angles also differ considerably [105.94(4) and 113.23(5)°].

Finally, there are considerable differences in the intermolecular interactions between the adducts. Fig. 4 shows that tmpH·AlCl₃ and tmpH·AlBr₃ molecules are associated into chains in the solid state *via* N-H-X hydrogen bonds while no N-H-I hydrogen bonds are present in tmpH·AlI₃, I...I contacts are found instead. On the other hand, the N-H-Cl hydrogen bridges in compound **3** lead to dimeric units. The N-H...X hydrogen bonds induce a lengthening of the respective Al-X bonds.

Although the chemistry of tmp-B≡P-*t*Bu has been studied in some detail [23] this holds not for its Lewis acid adducts *e.g.* tmp-B=P(*t*Bu)AlBr₃ [19]. Several reactions can be envisaged for its behavior towards BH₃ in THF solution: a) addition of BH₃ at the B=P double bond to generate tmp-BH-P(BH₂)(*t*Bu)AlBr₃ with a four-membered ring containing a tetracoordinated BH₂ group attached to the tmp N atom in analogy to tmp-BX-N*t*Bu-EX_n [18]; b) replacement of AlBr₃ by BH₃ to give tmp-B=P(*t*Bu)BH₃ which in turn may form a

four membered ring tmp-BH-P(*t*Bu)-BH₂ via a B-N bond, and c) abstraction of AlBr₃ by THF with generation of AlBr₃·thf and (tmp-B=P*t*Bu)₂ [23]. This latter reaction was observed, but the product did not prove to be AlBr₃·2thf [3] but the salt [AlBr₂(thf)₄][AlBr₄] (**5**). The adduct AlBr₃·2thf has been obtained by an ether displacement reaction from AlBr₃·DME with THF [3]. This reaction corresponds to the base displacement from (Me₂Si)₂NH·AlCl₃ with THF to give AlCl₃·2thf [24]. However, an AlBr₃ solution in THF leads to the formation of an ion pair, and the Fuoss-Krauss plot [25] is in accord with the eq. (12)



This result agrees with those found by Derroult *et al.* for AlCl₃ solutions in THF [26], and the formation of [AlCl₂(thf)₄]⁺[AlCl₄]⁻ has been ascertained by Atwood *et al.* [27], in the reaction of AlCl₃ in toluene with THF. This corroborates with our observation that the bromide **5** can only be obtained from tmp-B=P(*t*Bu)AlBr₃ and THF in the presence of toluene. Both ionic compounds have rather similar structures.

It is well known that CO₂ inserts like CS₂ [28] into the AlN bonds of aluminium amides to form aluminium carbamates. For instance, MeAl(tmp₂) adds CO₂ to give [MeAl(O₂Ctmp)₂]₂ with pentacoordinated Al atoms and bridging carbamate groups [5]. However, a rather unusual behavior is observed in the attempt to prepare *t*Bu₂Altmp from *t*Bu₂AlBr and Li(tmp). It is difficult to suggest a route to the formation of compound **7**, but certainly a ligand exchange which produces Al*t*Bu₃ which adds to eliminated LiBr with formation of the anion [*t*Bu₃AlBrAl*t*Bu₃]⁻ explains at least the formation of this anion. That aluminum trialkyls add to alkali metal halides to give R₃AlXAl₃⁻ anions is best known for X=F [29, 30]. In these anions the Al-F-Al unit is linear. It is surprising that the Al-Br-Al bond angle in **7** is quite open (164.5°) as the corresponding Al-Br-Al bond angle in the anions of type Al₂Br₇⁻ are close to a tetrahedral bond angle (about 108°) [31]. However, to our knowledge the new type of the cationic counterpart is, unique.

Obviously, the chemistry of tetramethylpiperidino-alanes offers unique reaction pathways because the bulkiness of its amino group rules out others.

Experimental Section

All experiments were conducted by using the Schlenk technique with Ar as a protecting gas. tmp₂AlBr and

tmp₂AlCl were prepared as described in [3]. All other reagents were obtained by literature methods or were of commercial origin. Solvents were made anhydrous by standard methods.

IR: Perkin Elmer FT 360, NMR: JEOL 400 with SiMe₄ as internal standard (¹H, ¹³C), and aqueous Al(NO₃)₃ as external standard (²⁷Al). X-ray structures: Siemens P4 diffractometer equipped with an area detector and an LT2 low temperature device, Mo-K_α radiation, graphite monochromator.

2,2,6,6-Tetramethylpiperidino aluminium dibromide (**1**), and tetramethylpiperidine aluminium tribromide (**2**)

a) A mixture of AlBr₃ (7.38 g, 27.6 mmol) and tmp₂AlBr (10.7 g, 27.6 mmol) was heated *in vacuo* to 90 °C. A slightly brownish melt formed which solidified at ambient temperature to the raw product **1**. Addition of toluene (100 ml) dissolved much of the solid leaving a small residue (0.2 g). The ²⁷Al NMR spectrum of the solution showed a single signal at δ = 108.7 ppm (*h*_{1/2} = 100 Hz). The solution was first reduced in volume *in vacuo* by 50% and then cooled to -30 °C. After 24 h the crystals were collected (yield: 12.0 g, 54%) and identified as **2** as shown by its X-ray structure. The supernatant solution no longer showed the ²⁷Al signal at 108.7 ppm, but a new signal at 80 ppm (**2**) besides some other weaker signals.

b) A solution of AlBr₃ (0.62 g, 2.04 mmol) in hexane (50 ml) was added to tmp₂AlBr (0.62 g, 2.04 mmol) while stirring. After the addition, the clear solution showed two signals in the ²⁷Al NMR spectrum at δ = 108 and 80 (*h*_{1/2} = 30 Hz) in an intensity ratio of ~ 1 : 4. From the concentrated solution crystals separated on cooling to -30 °C. These proved to be **2** by X-ray diffraction.

2,2,6,6-Tetramethylpiperidine-methyldichloroalane (**3**)

A solution of tmpH (1.70 ml, 10.09 mmol) in toluene (10 ml) was cooled to -78 °C. While stirring a solution of MeAlCl₂ in toluene (10 ml, 1.0 M) was added. Then the reaction mixture was allowed to attain room temperature, and its volume was reduced to ~ 5 ml. From this solution crystals of **3** settled after cooling to -30 °C. Yield: 2.7 g (9.2 mmol, 92%), m.p. > 220 °C. - ¹H NMR (C₆D₆): δ = 0.12 (s, 3H, MeAl), 0.66 (m, 2H, CH₂-3), 0.93 (m, 4H, CH₂-2,4), 1.12 (s, 6H, N(CH₃)₂), 1.39 (s, 6H, N(CH₃)₂). - ¹³C{¹H} NMR: δ = 15.7 (C-3), 23.6 (C-2,4), 33.6 C(CH₃)₂, 40.3 [C(CH₃)₂], 57.8 (CMe₂), AlC not observed. - ²⁷Al NMR: δ = 104.4 (*h*_{1/2} = 80 Hz). - C₁₀H₂₂AlCl₂ (254.18): calcd. C 47.25, H 8.72, N 5.31; found C 46.39, H 8.49, N 5.37.

Reaction of tmp₂AlCl with antimony pentachloride

To a solution of tmp₂AlCl (820 mg, 2.40 mmol) in toluene (20 ml) was added at -50 °C a solution of SbCl₅ (0.72 g,

2.40 mmol) in toluene (10 ml). NMR spectra showed no reaction at this temperature. At room temperature the solution turned orange, and after 3 d a dark red solution was present containing a black precipitate (most likely Sb). A ^{27}Al NMR spectrum revealed the presence of AlCl_4^- at $\delta = 103.0$ ppm ($h_{1/2} = 25$ Hz).

Reaction of tmp_2AlBr with tris(pentafluorophenyl)borane

To a solution of tmp_2AlBr (30 mg, 0.08 mmol) in toluene (1 ml) was added $\text{B}(\text{C}_6\text{F}_5)_3$ (40 mg, 0.08 mmol) dissolved in toluene (5 ml). The mixture was stirred for three weeks and samples taken for NMR investigation once a week. No reaction was observed both by ^{11}B and ^{27}Al NMR. Addition of some diethyl ether did not induce a reaction.

Reaction of tmp_2AlMe with tris(pentafluorophenyl)-borane

To tmp_2AlMe (30 mg, 0.09 mmol) dissolved in toluene (1 ml) was added a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (40 mg, 0.08 mmol) in toluene (5 ml). After stirring for some days no reaction was observed by ^{11}B and ^{27}Al NMR. The solution was then kept at reflux for 24 h. Subsequently several ^{11}B NMR signals were observed ($\delta = -25.2$ (?), -12.0 ($\text{MeB}(\text{C}_6\text{F}_5)_3^-$), 41.6 (main signal, br, $\text{B}(\text{C}_6\text{F}_5)_3$), 45.6 (tmp_2BMe), 71.0 ($\text{MeB}(\text{C}_6\text{F}_5)_2$), 80.8 ($\text{Me}_2\text{BC}_6\text{F}_5$) ppm), but no signal in the ^{27}Al NMR spectrum.

Reaction of tmp_2AlPh with tris(pentafluorophenyl)-borane

A mixture of tmp_2AlPh (50 mg) and $\text{B}(\text{C}_6\text{F}_5)_3$ (70 mg, 0.013 mmol) in toluene (20 ml) showed no reaction at -50 °C. After the suspension had attained room temperature it was stirred for 24 h. Then its ^{11}B NMR spectrum showed the absence of $\text{B}(\text{C}_6\text{F}_5)_3$. The solution was reduced stepwise in its volume at room temperature. No crystals appeared on cooling to -78 °C. After removal of all the solvent a sticky oil remained. Neither a bulb to bulb microdistillation nor attempts to get crystals from hexane or diethyl ether solution lead to a pure product.

NMR of the residue: ^1H NMR (in d_8 -toluene): $\delta = 1.34$ (m, CH_2 -2,4), 1.38 (s, $\text{C}(\text{CH}_3)_2$), 1.67 (m, CH_2 -3), 7.02 (m), 7.26 (m), 7.35 (t, $^3J(\text{H,H}) = 4$ Hz), 7.98 (d, $^3J(\text{H,H}) = 4$ Hz). – ^{11}B NMR: $\delta = -14.4$ (40%, $\text{tmpB}(\text{C}_6\text{F}_5)_3^-$), -13.9 (5%, ?), -5.2 (55%, $\text{B}(\text{C}_6\text{F}_5)_4^-$). – No ^{27}Al NMR signal detectable.

Reaction of 2,2,6,6-tetramethylpiperidino(*tert*-butylphosphinidene)borane aluminium tribromide adduct with borane in THF

To a yellow solution of $\text{tmp-B}(\text{PrBu})\text{AlBr}_3$ (100 mg, 0.2 mmol) in toluene (10 ml) was added at -30 °C with stirring a solution of BH_3 in THF (0.20 ml of a 1 M solution). On warming to ambient temperature the yellow color

had disappeared. After reduction of the volume of the solution to 5 ml and cooling to -30 °C colorless prisms formed within 2 d (Yield of **4**: 90 mg, 0.16 mmol, 80%); m. p. 110 °C dec. – ^{27}Al NMR (in C_6D_6): $\delta = 10.2$ (broad), 54.2 ($h_{1/2} = 230$ Hz). – IR (nujol, hostraflon): $\nu = 2425$ w, 2489 w, 1629 w, 1509 w, 1480 w, 1470 m, 1450 st, 1430 w, 1419 w, 1370 w, 1358 st, 1326 m, 1301 m, 1251 st, 1209 w, 1195 st, 1175 st, 1140 w, 1043 st, 987 w, 952 st, 914 w, 863 st, 834 w, 694 m, 682 m, 599 m, 570 m, 433 st, 407 st, 326 w (cm^{-1}).

Reaction of di(*tert*-butyl)aluminiumbromide with lithium (2,2,6,6-tetramethylpiperidide) and CO_2

To tmpH (0.71 g, 5 mmol) was added dropwise and with stirring a solution of LiBu in hexane (3.2 ml, 1.56 M, 5.0 mmol). After keeping the solution for 1 h at reflux the yellow solution was diluted with hexane (20 ml) and cooled in dry ice. Then a solution of $t\text{Bu}_2\text{AlBr}$ (1.10 g, 5 mmol) dissolved in hexane (20 ml) was added and the mixture slowly warmed to ambient temperature. After stirring over night the white solid that had formed (LiBr) was removed by filtration. Then $\sim 50\%$ of the solvent were removed in vacuo and the solution stored in dry ice. After several weeks 90 mg (5%) of colorless crystals of **7** had formed, which were characterized by X-ray structure determination. – ^1H NMR (CDCl_3): $\delta = 0.95$ (CMe_3), 1.25 (m, CH_2 -2,4), 1.35 (m, CH_2 -3), 1.51 (s, CCH_3)₂. – $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 17.7$ (CH_2 -4), 29.9 ($\text{C}(\text{CH}_3)_3$), 30.9 ($\text{C}(\text{CH}_3)_2$), 31.8 ($\text{C}(\text{CH}_3)_2$), 37.6 (CH_2 -2,4), 33.4 (CMe_3), 51.6 (CMe_2). – ^{27}Al NMR: $\delta = 53$ ($h_{1/2} = 3500$ Hz), 154 ($h_{1/2} = 3000$ Hz).

X-ray structure determinations

Table 2 shows relevant crystallographic data and gives information on data collection and structure solution. Selected crystals were mounted on a glass fibre and placed on the goniometer head. After cooling to -80 °C five sets of 15 frames were recorded, and the unit cell determined from the strongest reflections using the program SMART [32]. Data collection (1200 frames) was performed in the hemisphere mode of the program SMART. The data were reduced with the program SAINT [32] and the structures solved with direct methods as implemented in SHELX97 [33]. Non hydrogen atoms were refined anisotropically, the hydrogen positions were placed in calculated positions except NH hydrogens. Their positions were taken from the difference Fourier plot and refined isotropically. In compound **7** the Me groups of one *t*Bu group in the anion were refined in split positions. Additional data are deposited with the Cambridge Crystallographic data centre and can be obtained via www.ccdc.cam.ac.uk/data_request/cif or E-mail: deposit@ccdc.cam.ac.uk from the Director free of charge by quoting the CCD numbers 273041 - 274043 and the literature citation.

Compound	3	5	7
Chem. formula	C ₁₀ H ₂₂ AlCl ₂ N	C ₁₆ H ₃₂ Al ₂ Br ₆ O ₄	C ₆₂ H ₁₂₆ Al ₄ BrN ₃ O ₂
Form wght.	254.17	488.98	1197.49
Cryst. size [mm]	0.20 × 0.20 × 0.22	0.30 × 0.30 × 0.40	0.35 × 0.28 × 0.19
Cryst. system	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2/ <i>c</i>	<i>Pccn</i>
<i>a</i> [Å]	8.2785(5)	11.0956(9)	14.2980(7)
<i>b</i> [Å]	14.2676(8)	13.2397(1)	19.634(1)
<i>c</i> [Å]	11.5332(7)	14.404(1)	26.003(2)
α [°]	90.00	90.00	90.00
β [°]	92.424(1)	107.060(1)	90.00
γ [°]	90.00	90.00	90.00
<i>V</i> [Å ³]	1361.0(1)	2022.8(3)	7299.5(7)
<i>Z</i>	4	2	4
ρ (calcd.) [mg/m ³]	1.240	1.606	1.090
μ [mm ⁻¹]	0.509	6.025	0.655
<i>F</i> (000)	544	948	2616
Index range	-11 ≤ <i>h</i> ≤ 9 -17 ≤ <i>k</i> ≤ 18 -14 ≤ <i>l</i> ≤ 14	-14 ≤ <i>h</i> ≤ 11 -16 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 17	-16 ≤ <i>h</i> ≤ 16 -22 ≤ <i>k</i> ≤ 22 -29 ≤ <i>l</i> ≤ 29
2 θ [°]	57.72	57.90	47.96
Temp. [K]	183	193(2)	200(2)
Refl. collected	7729	11267	36118
Refl. unique	2525	3329	5705
Refl. observed (4 σ)	2175	2211	2833
<i>R</i> (int)	0.0168	0.0449	0.0794
No. variables	136	191	341
Weighting scheme ^a	0.0143/0.064	0.0370/0.0330	0.1000/0.000
<i>x/y</i>			
GOOF	1.044	1.096	1.172
Final <i>R</i> (4 σ)	0.0275	0.0643	0.0817
Final <i>wR</i> 2	0.0685	0.1682	0.2087
Larg. res. peak [e/Å ³]	0.232	0.940	1.152

Table 2. Relevant crystallographic data, and information concerning data collection and structure solution of compounds **3**, **5**, and **7**.

$$^a w^{-1} = \sigma^2 F_0^2 + (xP)^2 + yP; P = (F_0^2 + 2F_c^2)/3.$$

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| [1] C. Klein, H. Nöth, M. Tacke, M. Thomann, <i>Angew. Chem.</i> 105 , 923 (1993); <i>Angew. Chem. Int. Edit. Engl.</i> 32 , 886 (1993). | [9] A. Ahmed, W. Schwarz, H. Hess, <i>Z. Naturforsch.</i> 33b , 43 (1978). |
| [2] I. Krossing, H. Nöth, H. Schwenk-Kircher, <i>Chem. Ber. Receuil</i> 130 , 1047 (1997). | [10] J. K. Gilbert, J. D. Smith, <i>J. Chem. Soc. (A)</i> 233 (1968). |
| [3] I. Krossing, H. Nöth, H. Schwenk-Kircher, <i>Europ. J. Inorg. Chem.</i> 927 (1988). | [11] P. Wolfgardt, PhD Thesis, University of Munich (1975). |
| [4] I. Krossing, H. Nöth, H. Schwenk-Kircher, T. Seifert, C. Tacke, <i>Europ. J. Inorg. Chem.</i> 1925 (1998). | [12] K. Jones, M. F. Lappert, <i>Proc. Chem. Soc.</i> 22 (1964). |
| [5] K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kircher, M. Schmidt-Amelunxen, T. Seifert, <i>Europ. J. Inorg. Chem.</i> 1095 (1998). | [13] H. Nöth, P. Otto, W. Storch, <i>Chem. Ber.</i> 118 , 3020 (1985). |
| [6] W. Marconi, A. Mazzei, F. Bonati, M. de Malde, <i>Gazz. Chim. Ital.</i> 92 , 1062 (1962). | [14] T. A. Gorge, M. F. Lappert, <i>Chem. Comm.</i> 14 , 463 (1966). |
| [7] A. Mazzei, F. Bonati, W. Marconi, G. Manara, G. Castelfranchi, <i>Ital. Patent</i> 684 (1967). | [15] Provided that this compound is monomeric one has to expect a very broad signal. This could be the reason why we failed to spot a second Al compound. |
| [8] J. K. Ruff, <i>J. Org. Chem.</i> 83 , 2835 (1961). | [16] C. E. Radzewich, I. A. Guzei, R. F. Jordan, <i>J. Am. Chem. Soc.</i> 121 , 8673 (1999). |

- [17] K. Knabel, T. M. Klapötke, H. Nöth, R. T. Paine, I. Schwab, *Europ. J. Inorg. Chem.* 1099 (2005).
- [18] U. Braun, B. Böck, H. Nöth, I. Schwab, M. Schwartz, S. Weber, U. Wietelmann, *Eur. J. Inorg. Chem.* 3612 (2004).
- [19] K. Knabel, H. Nöth, *Z. Naturforsch.* **60b**, 1 (2005).
- [20] R. Staudigl, H. Nöth, *Inorg. Chem.* **21**, 706 (1986).
- [21] A. J. Downs (ed): *The Chemistry of Aluminium, Gallium, Indium and Thallium*, pp. 481–485, Chapman and Hall, New York (1993).
- [22] J. L. Atwood, G. A. Koutsantonis, F. G. Lee, L. Raston, *Chem. Comm.* 91 (1994) and lit. cited therein.
- [23] P. Kölle, G. Linti, H. Nöth, G. L. Wood, C. K. Narula, R. T. Paine, *Chem. Ber.* **121**, 871 (1988).
- [24] A. H. Cowley, M. C. Cushner, R. E. Davies, P. Riely, *Inorg. Chem.* **20**, 1179 (1981).
- [25] I. Krossing, PhD thesis, University of Munich (1997).
- [26] J. Derouault, M. T. G. Forel, *Inorg. Chem.* **16**, 3207 (1977).
- [27] N. C. Means, C. M. Means, S. G. F. Bott, J. L. Atwood, *Inorg. Chem.* **26**, 1466 (1986).
- [28] P. Konrad, H. Nöth, *Chem. Ber.* **116**, 32 (1983).
- [29] G. Allegra, G. Perego, *Acta Crystallogr.* **16**, 185 (1963).
- [30] J. L. Atwood, W. R. Newberry III, *J. Organomet. Chem.* **66**, 185 (1974).
- [31] E. Rytter, B. E. D. Rytter, J. Krogh Moe, *Acta Crystallogr.* **8**, 1541 (1973).
- [32] SMART, SAINT, Siemens Analytical Instruments, Version 5.2, Madison (1995).
- [33] SHELX 97, G. W. Sheldrick, University of Göttingen (1997).