

Synthesis and Structure of an Aluminium-Nitrogen Heteronorborene with Bulky *t*-Butyl Substituents and the Crystal Structure of Tri(*t*-butyl)aluminium

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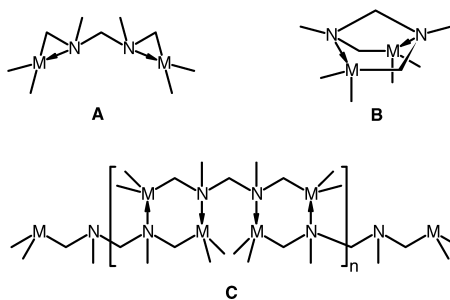
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The reaction of bis(lithiomethyl-methylamino)methane with di-*t*-butylaluminium chloride leads to the formation of 3,3,6,6-tetra-*t*-butyl-1,4-dimethyl-3,6-dialumina-1,4-diaza-norborene by simultaneous formation of two metal-carbon and two metal nitrogen bonds accompanied by two ring closure reactions. The compound was identified by an NMR analysis (^1H , ^{13}C , ^{27}Al) and by determination of its crystal structure. Despite the high steric demand of the *t*-butyl groups, the norbornane-basket structure is favoured over potential isomers containing three-membered rings and over polymeric aggregation. The crystal structure of tri(*t*-butyl)aluminium has been determined. $^t\text{Bu}_3\text{Al}$ crystallizes as a monomer, with the molecules interconnected by weak secondary $\text{Al}\cdots\text{C}$ contacts (2.95 Å) leading to a slight deviation of the AlCl_3 units from a planar coordination geometry at the Al atoms.

Key words: Aluminium, Tri(*t*-butyl)aluminium, Heterocycles, Donor-Acceptor Bonds, Crystal Structure

Introduction

We have recently reported the first synthesis of compounds with saturated Al-C-N and Ga-C-N linkages [1,2], which we studied in the course of our attempt to understand the fundamentals of systems with donor and acceptor centres in geminal positions. These investigations revealed different types of aggregation, either *intramolecular* with formation of three-membered ring systems as in compounds containing *BCN* [3], *BNN* [4], *AlCN* [5] and *AlNN* [6] but also *SiON* [7], *GeON* [8] and *SnON* [9] units (geminal donors and acceptors printed *italics*) or *intermolecular* with formation of dimers with cyclohexane-like six-membered rings as in $[\text{Me}_2\text{Al}(\text{CH}_2\text{PMe}_2)]_2$ and $[\text{Al}(\text{CH}_2\text{PMe}_2)_3]_2$ [10], $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$ [11], $[\text{Me}_2\text{Al}(\text{CH}_2\text{NMe}_2)]_2$ and $[\text{Me}_2\text{Ga}(\text{CH}_2\text{NMe}_2)]_2$ [1], as well as the sulphur systems $[(\text{H}_2\text{BCH}_2\text{SMe})_2]$ [12], $[(\text{Me}_2\text{ECH}_2\text{SMe})_2]$ (E = Al, Ga, In) [13]. Compounds which contain two *ECN* functions joined by a common bridging unit were also studied. The compounds $[\text{Me}_2\text{ECH}_2\text{N}(\text{Me})]_2\text{CH}_2$ (E = Al, Ga) were found to be intramolecularly aggregated into heteronorborene systems (Scheme 1 C). Three modes of aggregation of these systems are depicted in



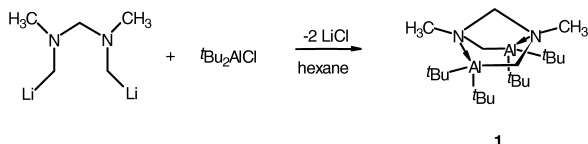
Scheme 1.

Scheme 1. These are two three-membered rings (A), six-membered rings in either polymeric arrays (C) or in the above mentioned norbornane-like structure (B). The question arose, whether it is possible to change the mode of aggregation by increasing the sterical requirement of the substituents at the metal atoms by replacing the metal bound methyl groups by the more bulky *t*-butyl groups.

Results

Synthesis and structure of a *t*-butyl substituted dialumina-diaza-norborene

For the synthesis of the 2,5-di-*t*-butyl-3,6-dimethyl-2,5-dialumina-3,6-diaza-norborene we reacted a sus-



Scheme 2.

pension of the dilithiated aminal $[\text{LiCH}_2(\text{Me})\text{N}]_2\text{CH}_2$, first reported by Karsch [14], with di-*t*-butylaluminium chloride and its gallium analogue. The reaction with the aluminium compound yielded the desired $[\text{tBu}_2\text{AlCH}_2\text{N}(\text{Me})]_2\text{CH}_2$ (**1**) in low yields of only 20% isolable material, whereas with the respective gallium chloride no similar compound could be isolated.

Compound **1** was identified by ^1H , ^{13}C and ^{27}Al NMR spectroscopy and by single crystal X-ray crystallography. In the proton NMR spectra the patterns typical of norbornane units are observed: two sets of signals for the two non-equivalent geminal *t*-butyl groups at the aluminium atom and the geminal hydrogen atoms of the methylene units connecting the Al and N atoms. The ^{27}Al NMR spectrum contains a single broad signal at 158 ppm with a half width of 4550 Hz, which is typical for a four-coordinate Al atom in an organoaluminium compound with a nitrogen donor substituent.

A crystal suitable for X-ray diffraction was obtained by cooling a hexane solution of **1**. This crystal belongs to the polar trigonal space group $P3_221$. The molecules in the crystal have C_2 symmetry (with the C_2 axis passing through the aminal carbon atom), and are thus chiral. The investigated crystal was a racemic twin.

As **1** adopts the same type of intramolecular aggregation as the two heteronorborenes $[\text{Me}_2\text{ECH}_2\text{N}(\text{Me})]_2\text{CH}_2$ (E = Al, Ga) [1] which bear methyl instead of *t*-butyl groups at the metal atoms, it becomes clear that this increase of steric bulk was not sufficient to change the type of aggregation in **1**.

Compound **1** can be described as consisting of a six-membered $\text{Al}_2\text{C}_2\text{N}_2$ ring in boat conformation, with the two N atoms at the bow and stern positions of the boat bridged by a methylene unit. This leads to small endocyclic angles at the aluminium atoms [$84.1(1)^\circ$] and wider angles at the methylene groups in the six-membered ring [$107.8(1)^\circ$] relative to the hydrocarbon norbornane, which has C-C-C angles at the methylene groups of 102.7° in its six-membered rings [15]. These small angles at the Al atoms lead to a strongly distorted tetrahedral coordination geometry. This is also manifest from the C(10)-Al-C(20) angle enclosed by

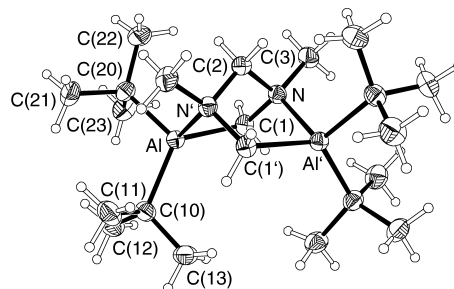


Fig. 1. Molecular structure of $(\text{tBu}_2\text{AlCH}_2\text{MeN})_2\text{CH}_2$ (**1**). Selected interatomic distances and angles (\AA , $^\circ$) for **1**: Al-C(1) 2.035(1), Al-C(10) 2.034(2), Al-C(20) 2.033(1), Al-N 2.044(2), N-C(1) 1.522(2), N-C(2) 1.476(2), N-C(3) 1.475(2), C(10)-C(11) 1.528(3), C(10)-C(12) 1.526(3), C(10)-C(13) 1.523(3), Al-C(1)-N 107.8(1), Al'-N-C(1) 112.6(1), Al'-N-C(2) 100.3(1), Al'-N-C(3) 114.6(1), C(1)-Al-C(10) 125.8(1), C(1)-Al-C(20) 108.4(1), C(10)-Al-C(20) 113.0(1), N-C(1)-N' 107.0(2), C(2)-N-C(3) 109.4(2), Al-C(10)-C(11) 109.1(2), Al-C(10)-C(12) 111.3(2), Al-C(10)-C(13) 115.1(1).

the two *t*-butyl groups at $113.0(1)^\circ$ and the extremely wide angle C(1)-Al-C(10) at $125.8(1)^\circ$ to the *endo*-*t*-butyl group whereas the angle C(1)-Al-C(20) to the *exo*-*t*-butyl group is comparatively small at $108.4(1)^\circ$.

There is a large difference in the C-N bond lengths. The endocyclic C(1)-N bonds are much wider [$1.522(2) \text{ \AA}$] than the ones to the N,N-bridging methylene unit C(2)-N [$1.476(2) \text{ \AA}$] or the exocyclic C(3)-N bonds [$1.475(2) \text{ \AA}$].

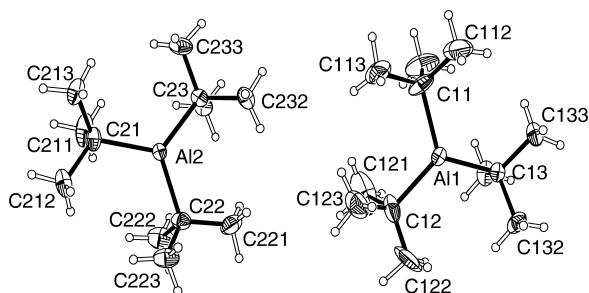
The dative bonds Al-N' at $2.044(2) \text{ \AA}$ are slightly shorter than the Al-N bond in $\text{Me}_3\text{Al} \leftarrow \text{NMe}_3$ at $2.099(10) \text{ \AA}$ [16], while the Al-C bonds to the *t*-butyl groups are $2.035(2) \text{ \AA}$ and thus 0.032 longer than the average Al-C bond length in tri(*t*-butyl)aluminium at 2.003 \AA (see below). It should be noted that in all the discussed structural parameters the trends are very similar to those in the methyl analogue, $[\text{Me}_2\text{AlCH}_2\text{N}(\text{Me})]_2\text{CH}_2$.

Crystal structure of tri(*t*-butyl)aluminium

For the purpose of comparison we determined the crystal structure of tri(*t*-butyl)aluminium. Despite of its wide application in organoaluminium chemistry [17] and its use in the preparation and structural analysis of many Lewis acid-base adducts [18], the crystal structure of this compound has not been reported. References to the aggregation and structures of other aluminium alkyls with bulky substituents can be found in the textbook literature [19], with a statement that AlMe_3 , AlEt_3 , $\text{Al}(\text{tPr})_3$ and

Table 1. Selected bond lengths [Å] and angles [°] for the crystal structure of $\text{Al}[\text{C}(\text{CH}_3)_3]_3$.

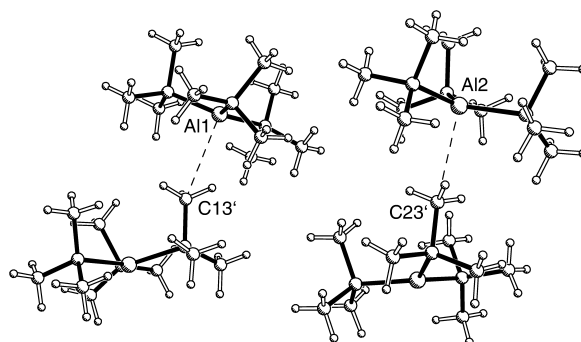
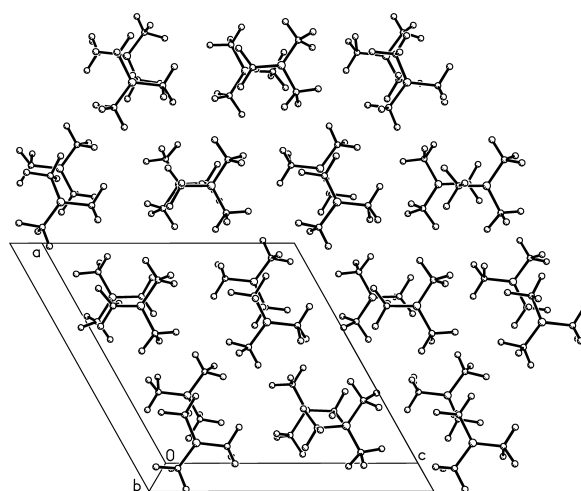
Molecule 1		Molecule 2	
Al(1)–C(11)	1.988(4)	Al(2)–C(21)	1.999(4)
Al(1)–C(12)	2.003(4)	Al(2)–C(22)	2.000(4)
Al(1)–C(13)	2.014(4)	Al(2)–C(23)	2.011(4)
C(11)–C(111)	1.605(7)	C(21)–C(211)	1.546(5)
C(11)–C(112)	1.501(6)	C(21)–C(212)	1.534(6)
C(11)–C(113)	1.515(6)	C(21)–C(213)	1.550(6)
C(11)–Al(1)–C(12)	119.6(2)	C(21)–Al(2)–C(22)	118.9(2)
C(12)–Al(1)–C(13)	119.0(2)	C(22)–Al(2)–C(23)	118.3(2)
C(13)–Al(1)–C(11)	117.3(2)	C(23)–Al(2)–C(21)	117.9(2)
Al(1)–C(11)–C(111)	109.6(3)	Al(2)–C(21)–C(211)	105.1(2)
Al(1)–C(11)–C(112)	111.3(3)	Al(2)–C(21)–C(212)	113.9(3)
Al(1)–C(11)–C(113)	115.5(3)	Al(2)–C(21)–C(213)	115.5(3)
Al(1)···C(13)	2.962(4)	Al(2)···C(23)	2.932(4)

Fig. 2. Molecular structure of the two independent molecules of $t\text{-Bu}_3\text{Al}$ as determined by low-temperature X-ray crystallography.

$\text{Al}(t\text{-Bu})_3$ are dimeric in the solid state. To the best of our knowledge of this series only the crystal structure of AlMe_3 has been determined so far. Crystal structures of other aluminium trialkyls with bulky substituents include those of $\text{Al}(\text{CH}_2\text{Ph})_3$ [20] and $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCH}_2[\text{Al}(\text{CH}(\text{SiMe}_3)_2)_2]$ [21].

$\text{Al}(t\text{-Bu})_3$ crystallizes in the monoclinic space group $P2_1/n$. The investigated crystal was a trilling. The twinning arises owing to the cell dimensions with a and b being almost equal and β close to 120° . There are two independent molecules of $\text{Al}(t\text{-Bu})_3$ in the asymmetric unit. The molecules have a narrow distribution of Al–C bond lengths between 1.988(4) and 2.014(4) Å.

The molecules deviate substantially from C_{3v} symmetry (Fig. 2). This is due to the distorted coordination geometry of the aluminium atoms, which is non-planar, as indicated by the sum of angles at these atoms [355.9° at Al(1) and 355.1° at Al(2)] and the deviations of the Al atom positions from the AlC_3 planes [0.237 Å for Al(1) and 0.257 Å for Al(2)]. The aluminium atoms are thus the vertices of shallow AlC_3 pyra-

Fig. 3. Crystal structure of $t\text{-Bu}_3\text{Al}$ showing the intermolecular $\text{Al}\cdots\text{C}$ interactions: $\text{Al}(1)\cdots\text{C}(13')$ 2.962(4) Å, $\text{Al}(2)\cdots\text{C}(23')$ 2.932(4) Å. The deviations of the Al atoms from the plane through three carbon atoms are: Al(1) 0.237 Å and Al(2) 0.257 Å.Fig. 4. Packing diagram of $t\text{-Bu}_3\text{Al}$.

mids. The geometry of the t -butyl groups is also substantially distorted with three different Al–C–C angles and three different C–C bond lengths for each group (see Table 1).

The aluminium atoms are involved in a type of weak secondary bonding towards methyl groups of neighbour molecules (Fig. 3) the contacts being formed on the top side of the shallow AlC_3 pyramids. These $\text{Al}\cdots\text{C}$ contacts are 2.962(4) and 2.932(4) Å for Al(1) and Al(2), respectively, and thus much shorter than the secondary contacts in GaMe_3 or GaEt_3 [22], which show a related pattern of secondary $\text{Ga}\cdots\text{C}$ bonds. The $\text{Al}\cdots\text{C}$ contacts lead to the formation of a pseudo-polymeric chain aggregate of $\text{Al}(t\text{-Bu})_3$ molecules.

In $\text{Al}(\text{CH}_2\text{Ph})_3$ [20] there are also secondary bonds but these are of a different type and involve $\text{Al}\cdots\text{C}$

contacts to phenyl-carbon (sp^2) atoms, which are shorter and stronger (2.453 Å). The Al atoms in $[(Me_3Si)_2CH]_2AlCH_2[Al(CH(SiMe_3)_2)_2]$ devoid of a π -system [21] are so well shielded that there are no secondary contacts, not even of an intramolecular nature.

The steric bulk of three t Bu groups makes a dimerization of $Al(tBu)_3$ impossible, but with only two of them in an $Al(tBu)_2$ unit, the formation of norbornane type heterocyclic systems is observed by intermolecular aggregation as demonstrated for compound **1**.

Experimental Section

Preparation of **1**

A solution of di- t butylaluminium chloride (0.495 g, 2.5 mmol) in 25 ml of hexane was added to a suspension of bis[(lithiomethyl)(methyl)amino]methane [14] (0.143 g, 1.25 mmol) in 30 ml of hexane at $-78^\circ C$ with vigorous stirring. The mixture was stirred for 1 h at this temperature and then allowed to warm to ambient temperature, at which stirring was continued for 12 h. After filtration and washing the residue with 10 ml of pentane a clear yellowish solution was obtained. The solution was concentrated to a volume of about 20 ml and was kept at $-25^\circ C$ for 1 week. 0.19 g of colourless crystals (most of them hexagonal prisms) was obtained from which the mother liquor was separated with a canula. Yield 20%, decomposition above $160^\circ C$. NMR spectra were recorded in predried C_6D_6 (K/Na alloy) on a JEOL JNM-LA400 spectrometer. 1H NMR δ = 1.05, (s, 18H, $Al(C(CH_3)_3)_2$), 1.28, (s, 18H, $Al(C(CH_3)_3)_2$), 2.05 (s, 6H, NCH_3), 2.49, (s, 2H, $AlCH_2N$), 2.53 (s, 2H, $AlCH_2N$), 2.93 (s, 2H, NCH_2N). $-^{13}C\{^1H\}$ -NMR δ = 16.10 (s, $Al(C(CH_3)_3)_2$), 32.4, (s, $Al(C(CH_3)_3)_2$), 33.6 (s, $Al[C(CH_3)_3]_2$), 37.9 (s, $AlCH_2N$), 45.1 (s, NCH_3), 79.8 (s, NCH_2N). $-^{27}Al$ NMR δ = 158 ($\nu_{1/2}$ = 4550 Hz).

Structure determination of **1**

$C_{21}H_{48}Al_2N_2$, M = 382.57 g mol $^{-1}$, trigonal, $P3_221$, a = 8.8049(2), c = 27.3595(10) Å, V = 1836.91(9) Å 3 , Z = 3, D_c = 1.038 g cm $^{-3}$. 27617 reflections collected on a Nonius

DIP2020 image plate diffractometer [$2\theta_{max}$ = 55° , Mo- K_α radiation, λ = 0.71073 Å, T = 133(2) K] merged to 2808 unique (R_{int} = 0.078). Intensity corrections were applied by means of the program SCALEPACK [23]. Anisotropic refinement of all displacement parameters was applied to non-H-atoms, isotropic to H-atoms. The structure was refined [24] as a racemic twin with equal contributions of both individuals [refined contribution 0.5(2)]. The final refinement converged to R_1 = 0.041 for 2499 data [$F_o > 4\sigma(F_o)$] and wR_2 = 0.086 for all data. Deposition number at the Cambridge Crystallographic Structure Database: CCDC 227410.

Structure determination of $Al[C(CH_3)_3]_3$

A single crystal was grown by establishing a solid liquid equilibrium of a sample of $Al[C(CH_3)_3]_3$, selecting a well formed seed crystal and melting the remainder followed by cooling the sample first by 2 K over 12 h, then more rapidly to $-100^\circ C$. Crystal data: $C_{12}H_{27}Al$, M = 198.32 g mol $^{-1}$, monoclinic, $P2_1/n$, a = 17.713(5), b = 10.112(3), c = 17.725(5) Å, β = $119.37(1)^\circ$, V = 2766.7(14) Å 3 , Z = 8, D_c = 0.952 g cm $^{-3}$. 11339 scattering intensities collected on a Nonius CAD4 diffractometer [$2\theta_{max}$ = 52° , Mo- K_α radiation, λ = 0.71073 Å, T = 173(2) K] merged to 5427 unique (R_{int} = 0.038). A solution was obtained by direct methods in the space group $P2_1/n$. The crystal was refined as a trilling by applying the twin law (0 0 1 0 1 0) with contributions of 0.395(2) and 0.264(2) of the other two twin components. Anisotropic refinement of all displacement parameters was applied to non-H-atoms, H-atoms were calculated in idealized positions and refined in a riding model [24]. Largest residual electron density: min -0.55 , max. 1.07 e Å $^{-3}$. The final refinement converged to R_1 = 0.064 for 4400 data [$F_o > 4\sigma(F_o)$] and wR_2 = 0.188 for all data. Deposition number at the Cambridge Crystallographic Structure Database: CCDC 227409.

Acknowledgements

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