Organoaluminium and -gallium Lewis-Acid Adducts of Tetramethylmethylenediamine

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The compounds Me_3Al-$Me_2NCH_2NMe_2$-$AlMe_3$ (**1**) and Me_3Ga-$Me_2NCH_2NMe_2$-$GaMe_3$ (**2**) were prepared by reacting $Me_2NCH_2NMe_2$ (TMMDA) with two equivalents of the metal trialkyls in hydrocarbon solutions. With the ether adduct $Me_3Ga·OEt_2$ $Me_2NCH_2NMe_2$ reacts to give the mono-adduct $Me_2NCH_2NMe_2$-$GaMe_3$ (**3**). These compounds were characterized by NMR spectroscopy (^{1}H, ^{13}C and ^{27}Al) and by elemental analyses. Crystal structure investigations show **1** and **2** to be monomeric and to a adopt a *trans,trans*-conformation for their M-N-C-N-M backbones. **3** is also monomeric in the solid state, but adopts a *cis,trans*-conformation. Tetramethylformamidinium chloride and also chlorotetramethylformamidinium chloride reacts with lithium aluminium hydride to give the mono-adduct $[Me_2NCH_2NMe_2$-$AlH_3]_2$ (**4**), which is dimeric and can be regarded as a double TMMDA adduct to Al_2H_6 with five-coordinate Al atoms. *Ab initio* calculations on the MP2/6-311G** level of theory have been performed for the model compound H_3N-$H_2Al(\mu$-$H)_2AlH_2$-NH_3 to obtain its molecular structure and vibrational spectrum for comparison with **4** and for the assignment of its vibrational spectrum.

Key words: Aluminium, Gallium, Aminal Adduct, Crystal Structure, *ab initio* Calculations

Introduction

In the course of our studies of compounds with geminal donor and acceptor atoms we have recently reported on the first syntheses of compounds containing saturated Al-C-N and Ga-C-N linkages. These included the simple dimethylaminomethyl compounds $[Me_2NCH_2MMe_2]_2$ (M = Al, Ga, In) [1], the respective isopropyl derivatives $[Me_2NCH_2MMe_2]_2$ (M = Al, Ga) derived from the hexameric lithium alkyl $[iPr_2NCH_2Li]_6$ [2], but also dimetallated compounds derived from the lithiated aminal $LiCH_2N(Me)CH_2N(Me)CH_2Li$ [3]. The latter aggregate as aza-metalla-heteronorbornanes $[R_2CH_2N(Me)CH_2N(Me)CH_2MR_2]$ (R = Me [4], R = *t*Bu [5], Scheme 1).

The *N*-methyl aminals are a rare case of amines, which can be directly deprotonated by strong bases like *tert*-butyl lithium, whereas compounds possessing longer chains between the two nitrogen atoms generally resist deprotonation and *e. g.* dilithiated tetramethylethylendiamine (TMEDA) can only be prepared
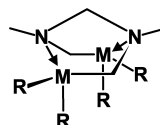
Scheme 1.

from functionalized precursors like stannanes upon transmetallation [6].

The intramolecular aggregation found for the above mentioned aza-metalla-heteronorbornanes points to the possibility, that precoordination of the metallating basic reagent to one nitrogen atom of the aminal helps to deprotonate the methyl groups attached to the other. It was therefore interesting to test, whether other metal alkyls would undergo similar reactions, or whether it would even be possible to establish a direct route to the organoearth metal derivatives of tetramethylmethylendiamine (TMMDA). The first step into this direction is the synthesis of TMMDA adducts with alkylaluminium or gallium compounds. This is what we report about in this contribution. Such adducts are also of interest, as they demonstrate the versability of the co-

ordination chemistry of aminals in contrast to simple trialkylamines on one hand and bidentate amine bases like TMEDA on the other.

Results and Discussion

Synthesis

Upon addition of alkane solutions of trimethyla-luminium and -gallium to alkane solutions of tetra-methylmethylendiamine (TMMDA), the bis-adducts of the metal alkyls **1** and **2** are formed as colourless solids in reasonable yields (Scheme 2). They are air- and moisture-sensitive compounds, which are soluble in all common aprotic organic solvents and can be crystallized from toluene or hexane or sublimed under reduced pressure.
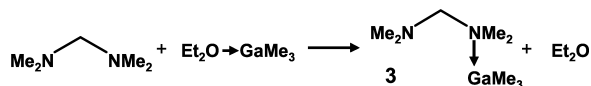
Scheme 2.

These adducts are surprisingly stable upon heating far beyond their melting points (102° for **1**, 82° for **2**) up to 150°, without a sign of liberation of methane, which would be an indication for an intramolecular de-protonation reaction necessary for the formation of the aza-metalla-heteronorbornanes (Scheme 3).
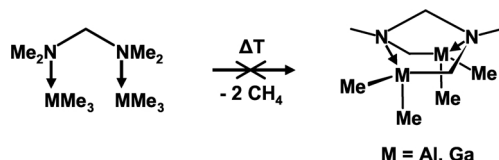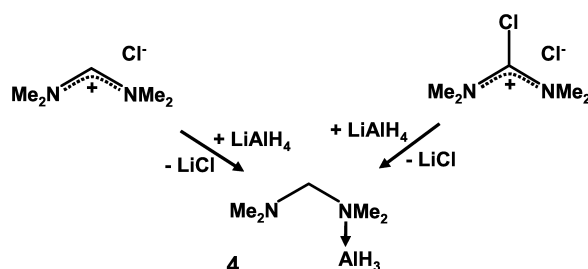
Scheme 3.

If the diethylether adduct of trimethylgallium is em-ployed in the synthesis the formation of the bis-adduct **2** is not observed, but rather the mono-adduct **3** is formed (Scheme 4). This mono-adduct is an oily liq-uid at ambient temperature solidifying at 10 °C as a crystalline mass.

Scheme 4.

Scheme 5.

Alane adducts of trialkylamines are generally syn-thesized by the reaction of lithium aluminium hydride with the corresponding ammonium salts, whereby hy-drogen and lithium chloride are formed [7]. Due to the inaccessibility of ammonium salts of aminals, this syn-thetic route cannot be applied to these systems. Alter-native routes include the reaction of iminium salts with LiAlH$_4$ [8]. In a similar way we reacted tetramethyl-formamidinium chloride with LiAlH$_4$, which leads to the expected reduction of the formamidinium ion and formation of the mono-alane adduct of TMMDA, **4** (Scheme 5). Compound **4** is extremely pyrophoric, but much more stable at ambient temperature than the trimethylamine-alane adduct Me$_3$N-AlH$_3$, which is used among other adducts of alane as a thermolabile precursor for the deposition of thin Al films in CVD processes [9]. In contrast, compound **4** can be sublimed without decomposition and purified in this way.

We also tried to react chloro-tetramethylformamid-inium chloride with LiAlH$_4$ in order to get access to the bis-AlH$_3$ adduct of TMMDA, but this reaction leads also to the mono-adduct **4**, under simultaneous re-duction of the chloro-tetramethylformamidinium unit (Scheme 5).

Spectroscopic characterization

All new compounds were characterized by means of NMR spectroscopy and elemental analyses. The trimethylmetal-adducts **1**, **2** and **3** show three sharp sin-glets in their ^{1}H NMR spectra for the metal bonded methyl, the aminomethyl and the methylene units, with correct relative intensities. The adducts show a pro-nounced low-field shift of the signals of the methylene protons (**1**: 3.86 ppm, **2**: 3.31 ppm and **3**: 3.07 ppm) relative to the corresponding signals of the free aminal (2.49 ppm). The signals of the N-methyl groups are only slightly high-field shifted relative to TMMDA.

Upon coordination to the Lewis base TMMDA, the signals of the methyl groups bonded to the metal atoms
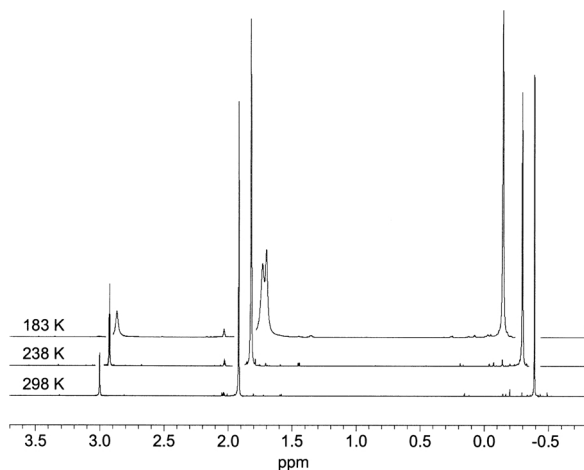
Fig. 1. Variable temperature ^{1}H NMR spectra of compound **3** showing the occurrence of a splitting of the central signal for the NMe$_2$ groups upon cooling.

show a slight high-field shift relative to benzene solutions of Al$_2$Me$_6$ or GaMe$_3$, while the signals of the metal bound carbon atoms in the ^{13}C NMR spectra are markedly high-field shifted.

The occurrence of one resonance for the chemically different Me$_2$N groups in **3** indicates that at ambient temperature the GaMe$_3$ unit rapidly changes between the available nitrogen coordination sites. Upon cooling of a d^8-toluene solution of **3** the single signal observed for the NMe$_2$ groups at ambient temperature splits into two signals indicating that the exchange process is slowed and the coordinated and uncoordinated NMe$_2$ groups give rise to two different signals. Although presumably this happens intramolecularly, an intermolecular mechanism cannot be excluded rigorously on the basis of our data. However, in the case of an intermolecular process one should expect up to four signals for the NMe$_2$ groups, as in addition to the two for the intermolecular process, those for the uncoordinated aminal and the doubly coordinate aminal **2** could also be expected to be observed.

The alane adduct **4** is characterized by Al-H stretching modes detected at 1830, 1709 and 1694 cm^{-1} in the infrared spectrum. Moreover, one observes characteristic bands at 791, 762, 740 and 631 cm^{-1}. The free aminal does not show absorptions in these regions and therefore these bands can only be due to the aluminium hydride part of the compound. The bands at 1709 and 1694 cm^{-1} indicate the presence of Al-H-Al bridges. An Al$_2$H$_6$ unit is a plausible structural motif and in accord with the bands observed, as was later con-
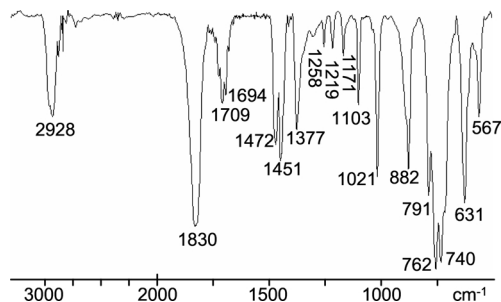

Fig. 2. Infrared spectrum of **4** (transmission mode). The band at 1831 cm^{-1} corresponds to the ν_{as}(AlH$_{terminal}$) mode, those at 1709 and 1694 cm^{-1} to ν_{as}(AlH$_{bridge}$).
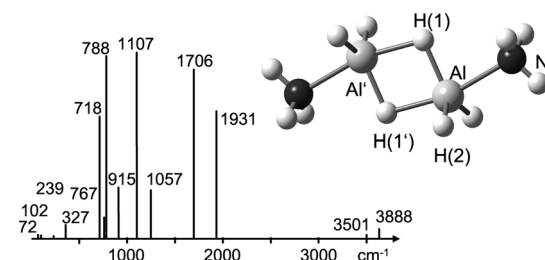
Fig. 3. Molecular structure and schematic vibrational spectrum of H$_3$N-H$_2$Al(μ-H)$_2$AlH$_2$-NH$_3$ as calculated *ab initio* on the MP2/6-311G** level of theory. Calculated bond lengths and angles: Al-N 2.157, Al-H(1) 1.664, Al-H(1') 1.883, Al-H(2) 1.592 Å, Al-H(1')-Al' 100.7, N-Al-H(1') 165.9, H(2)-Al-H(2') 125.2, H(2)-Al-H(1) 117.4°.

firmed by determination of the crystal structure (see below). The bands at lower wave numbers can be assigned to wag, rock and bending motions of the Al$_2$H$_6$ unit.

This occurrence of Al-H stretching bands for both the terminal and bridging hydrogen atoms was not reported in the first communication on tertiary amine stabilized dialanes (*N*-methylpiperidine and benzyldimethylamine bis-adducts of Al$_2$H$_6$) [10]. We therefore wanted to confirm our interpretation, by comparison with the calculated spectrum of a suitable model compound. For this purpose we calculated the structure and vibrational frequencies of H$_3$N-H$_2$Al(μ-H)$_2$AlH$_2$-NH$_3$ *ab initio* at the MP2/6-311G(d,p) level of theory. For this model we predict bands at 1931 cm^{-1} for ν_{as}(AlH$_{terminal}$), at 1706 cm^{-1} for ν_{as}(AlH$_{bridge}$), at 1107 cm^{-1} for ν_{as}(Al$\cdots$H$_{bridge}$) and at 718 cm^{-1} for the δ(AlH$_2$) mode. This confirms our above spectral assignments for **4**. It should also be noted that, expectedly, these data differ from those for Al$_2$H$_6$, with four-coordinate Al atoms, which was very recently observed for matrix isolated dialane

Table 1. Selected bond lengths and angles for **1** (M = Al) and
2 (M = Ga).

Bond lenghts [Å]	**1**	**2**	Bond angles [°]	**1**	**2**
M(1)-N(1)	2.104(2)	2.219(4)	N(1)-C(1)-N(2)	124.2(1)	123.4(4)
M(2)-N(2)	2.112(2)	2.230(4)	C(2)-N(1)-C(3)	109.2(1)	110.7(4)
N(1)-C(1)	1.483(2)	1.482(6)	C(4)-N(2)-C(5)	109.8(2)	110.2(5)
N(1)-C(2)	1.491(2)	1.470(6)	C(1)-N(1)-C(3)	114.8(1)	114.9(4)
N(1)-C(3)	1.485(2)	1.456(6)	C(1)-N(1)-C(2)	114.1(1)	114.7(4)
N(2)-C(1)	1.483(2)	1.477(6)	C(1)-N(2)-C(4)	114.2(2)	115.6(4)
N(2)-C(4)	1.484(2)	1.482(7)	C(1)-N(2)-C(5)	114.6(2)	115.0(4)
N(2)-C(5)	1.482(2)	1.471(7)	M(1)-N(1)-C(1)	103.9(1)	101.2(3)
			M(2)-N(2)-C(1)	103.2(1)	101.3(3)
M(1)-C(6)	1.979(2)	1.974(6)	N(1)-M(1)-C(6)	105.4(1)	101.8(2)
M(1)-C(7)	1.978(2)	1.977(6)	N(1)-M(1)-C(7)	103.3(1)	102.7(2)
M(1)-C(8)	1.979(2)	1.973(6)	N(1)-M(1)-C(8)	102.7(1)	99.9(2)
M(2)-C(9)	1.968(2)	1.967(6)	N(1)-M(1)-C(9)	105.4(1)	100.4(2)
M(2)-C(10)	1.977(2)	1.973(6)	N(1)-M(1)-C(10)	103.3(1)	101.9(2)
M(2)-C(11)	1.972(2)	1.978(6)	N(2)-M(2)-C(11)	102.8(1)	101.4(2)

[ν(AlH$_{terminal}$) 1932 and 1915, ν(AlH$_{terminal}$) 1408, 1268 cm^{-1}] [11].

In the ^{1}H NMR compound **4** shows a marked low-field shift of the signal of the methylene protons, which is even larger than observed for the trimethylmetal adducts **1**, **2** and **3**. The ^{27}Al NMR spectra of **1** and **4** contain signals at chemical shifts of 186 ppm ($\nu_{1/2}$ = 2600 Hz) and 133 ppm ($\nu_{1/2}$ = 1700 Hz), respectively. This points to two different coordination numbers at the Al atoms in solution for **1** and **4**. The low-field shift of **1** indicates a four-coordinate Al atom, while the high-field shift for **4** can be interpreted as five-coordinate. These interpretations are further supported by the crystal structures described in the following section.

Crystal structures

Surprisingly the bis-trimethylmetal adducts **1** and **2** are not isostructural but isomorphous. The bis-trimethyaluminium-adduct **1** crystallizes in the orthorhombic space group *Pbca*, while the corresponding gallium compound **2** crystallizes in the triclinic space group *P*$\bar{1}$. Despite this difference the structures of the two molecules are rather similar as can be deduced from the data presented in Table 1.

For comparison we also attempted to crystallize the free aminal TMMDA, but this solidifies glassy upon cooling. There is, however, a gas-phase structure investigation for TMMDA by electron diffraction [12], which showed that free TMMDA adopts a *gauche,gauche*-conformation. This contrasts the situation in the bis-trimethylmetal adducts **1** and **2**, which
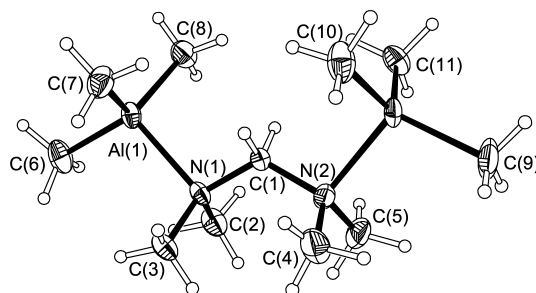
Fig. 4. Molecular structure of **1** as determined by low-temperature X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level.
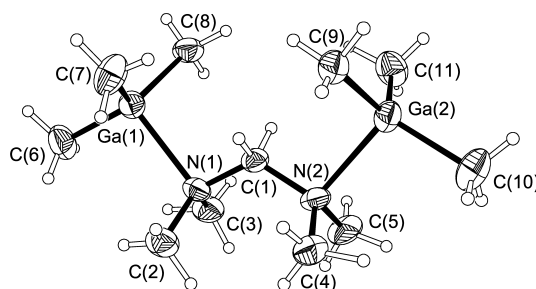
Fig. 5. Molecular structure of **2** as determined by low-temperature X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level.

both show a *trans,trans*-conformation. The trimethyl-metal units are furthermore staggered with respect of the NC$_3$ fragments to which they are bonded.
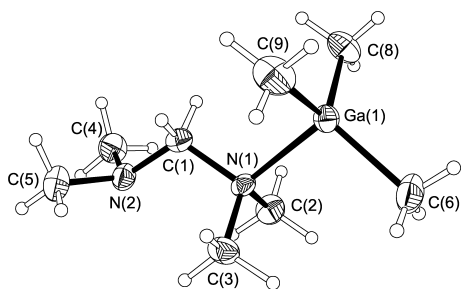
The dative M-N bonds [**1**: 2.104(2) and 2.112(2), **2**: 2.219(4) and 2.230(4) Å] are slightly longer than in the corresponding bis-adducts of tetramethylene-diamine [13] or diazabicyclooctane [14]. They are also longer than in solid Me$_3$N·AlH$_3$ [2.063(7) Å] [15] and solid Me$_3$N·AlMe$_3$ [2.045(1) Å] [16], or than in solid Me$_3$N·GaH$_3$ [2.081 Å] [17] and gaseous Me$_3$N·GaMe$_3$ [2.09(5) Å] [18], respectively.

Expectedly all C-N bonds in **1** and **2** are longer than those observed in the free uncoordinated TMMDA. Upon coordination of the free aminal to the Me$_3$M fragments the N(1)-C-N(2) angle is markedly widened as can be seen from a comparison of these angles in the free TMMDA [115.8(1)°] and the adducts [**1**: 124.2(1) and **2**: 123.4(4)°].

By contrast, the C-N-C angles are almost unchanged between free [110.7(1)°] and coordinated TMMDA [**1**: 109.2(1)−114.6(2)° and **2**: 110.2(4)−115.6(4)°]. In the diaza-dimetalla-norbornanes the N(1)-C-N(2) angles are markedly compressed [106.2(1) (Al) und 106.7(3)° (Ga)] and the M-N distances shorter

Table 2. Selected bond lengths and angles for **3**.

Bond lenghts [Å]		Bond angles [°]	
Ga-N(1)	2.134(2)	N(1)-C(1)-N(2)	114.4(2)
Ga-C(6)	1.984(3)	C(2)-N(1)-C(3)	109.0(2)
Ga-C(7)	1.980(3)	C(4)-N(2)-C(5)	110.8(2)
Ga-C(8)	1.979(3)	C(2)-N(1)-C(1)	109.6(2)
N(1)-C(1)	1.485(3)	C(3)-N(1)-C(1)	110.1(2)
N(1)-C(2)	1.482(3)	C(4)-N(2)-C(1)	113.0(2)
N(1)-C(3)	1.475(3)	C(5)-N(2)-C(1)	113.0(2)
N(2)-C(1)	1.450(3)	Ga-N(1)-C(1)	108.5(1)
N(2)-C(4)	1.457(3)	Ga-N(1)-C(2)	109.9(2)
N(2)-C(5)	1.454(3)	Ga-N(1)-C(3)	109.8(2)

Table 3. Selected bond lengths and angles for **4**.

Bond lengths [Å]		Bond angles [°]	
Al-N(2)	2.078(1)	N(1)-C(1)-N(2)	113.8(1)
N(1)-C(1)	1.451(2)	C(2)-N(1)-C(3)	111.0(1)
N(1)-C(2)	1.460(2)	C(4)-N(2)-C(5)	109.4(1)
N(1)-C(3)	1.456(2)	C(2)-N(1)-C(1)	112.8(1)
N(2)-C(1)	1.494(2)	C(3)-N(1)-C(1)	112.7(1)
N(2)-C(4)	1.480(2)	C(4)-N(2)-C(1)	110.3(1)
N(2)-C(5)	1.474(2)	C(5)-N(2)-C(1)	110.5(1)
Al-H(1)	1.584(16)	Al-H(1)-Al'	104.0(8)
Al-H(1')	1.992(16)	N(2)-Al-H(1')	167.4(8)
Al-H(2)	1.506(15)	H(1)-Al-H(2)	117.2(8)
Al-H(3)	1.510(16)	H(2)-Al-H(3)	122.4(9)

Fig. 6. Molecular structure of **3** as determined by low-temperature X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level.

Fig. 7. Molecular structure of **4** as determined by low-temperature X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level.

[2.028(1) (Al) and 2.124(3) Å (Ga)] than in the corresponding bis-adducts **1** and **2**.

The mono-Me$_3$Ga adduct **3** crystallizes in the monoclinic space group $P2_1/n$. The aminal unit in **3** has a *cis,trans*-conformation and the Me$_3$Ga unit adopts a staggered conformation relative to the attached C$_3$N unit.
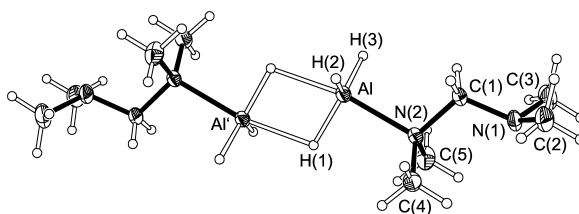
Expectedly, the Ga-N distance in **3** at 2.134(2) Å is shorter than in the bis-adduct **2**. The Ga-C distances in **3** are slightly shorter than in the bis-adduct or than in Me$_3$Ga [1.952(2) – 1.962(2) Å] [19]. In contrast to **1** and **2**, the N-C-N angle in **3** [114.4(2)°] is not widened but slightly compressed relative to that of free TMMDA. This is obviously due to the different conformations and the fact that the *cis,trans*-conformation adopted by **3** does not suffer repulsive forces between the methyl groups of the two NMe$_2$ units in contrast to **1** and **2**, where these methyl groups come close together.

As in **1** and **2** the distortion of the coordination of the Me$_2$N groups upon dative bonding to GaMe$_3$ is also reflected in the larger C-N bond lengths of the group bound to the GaMe$_3$ unit as compared to the other.

The aminal-alane-adduct **4** crystallizes in the triclinic space group $P\bar{1}$. A plot of the molecular structure is provided in Fig. 7. As already concluded from the

IR data the compound is dimeric, with the monomers linked by two Al-H-Al bridges. There are two further terminal Al-H bonds at each Al atom. The structure can therefore be regarded as an Al$_2$H$_6$ dimer with one aminal molecule linked to each of the Al atoms leading to a coordination number of 5 at aluminium. While most of the crystallographically investigated alane-diamine, alane-triamine or alane-diphosphane adducts are polymeric in the solid state [20], hydride-bridged alane-amin adducts are comparatively rare [10].

The length of the dative Al-N bond is 2.078(1) Å and therefore expectedly longer than in free monomolecular H$_3$Al-NMe$_3$ [2.066(1) Å] [21] due to the higher coordination number of the Al atom. It compares reasonably well with the calculations for the model compound H$_3$N-H$_2$Al(μ-H)$_2$AlH$_2$-NH$_3$ [2.157 Å, see Fig. 3]. Also in good accordance with the calculations for the model compound are the parameters describing the coordination geometry of the aluminium atoms, which is a distorted trigonal bipyramid. Hereby the two shorter Al-H bonds to H(2) and H(3) [1.506(15) and 1.510(16) Å] and the elongated bond to the bridging H(3) [1.584(16) Å] define the trigonal plane, while the N atom and the symmetry related atom H(1') are the axial substituents. Consequently the bond to this hydrogen atom is longest at 1.992(16) Å.

As found for **1**, **2** and **3** all N-C bonds in **4** are longer than in the free TMMDA. The angle N(1)-C(1)-N(2) is 113.8(1)°. The aminal unit adopts a similar conformation as in the mono-Me$_3$Ga adduct **3**, with the N-C-N angle also becoming smaller than in free TMMDA due to the same reasons as discussed for **3**.

Experimental Section

General methods. All experiments were carried out under a dry nitrogen atmosphere with standard Schlenk and high vacuum techniques or in a glove box operated under argon. Solvents were purified and dried by standard techniques. All chemicals were commercial samples. TMMDA was purified prior to use by distillation. All NMR spectra were recorded on a Jeol JNM-LA400 spectrometer (400.05 MHz ^{1}H, 100.50 MHz ^{13}C, 104.05 MHz ^{27}Al) in C$_6$D$_6$ or toluene-d^8 as solvent dried over K/Na alloy. The infrared spectra were recorded on a MIDAC Prospect FTIR instrument. Elemental analyses were performed by the Analytical Laboratory of the Anorganisch-chemisches Institut at the Technische Universität München. The *ab initio* calculations were undertaken on the ZIV-Linux-cluster of the Universität Münster using the Gaussian 98 package of programs [22] with the methods and basis sets implemented therein.

N,N,N',N'-Tetramethylmethylendiamine-bis-trimethylaluminium (1). A solution of *N,N,N',N'-*tetramethylmethylendiamine (2.30 ml, 20.0 mmol) in pentane (20 ml) was dropped into a solution of trimethylaluminium (7.21 g, 100 mmol) in pentane (40 ml) under cooling to 0 °C. The reaction mixture was stirred overnight. All volatile components were removed under vacuum and the residue was dissolved in a few ml of toluene and crystallized at −20 °C. Yield 2.14 g (8.7 mmol, 87%) of colourless crystals (very sensitive to air and moisture). M.p. 102 – 104 °C, sublimation point 62 °C (0.01 mbar). ^{1}H NMR: $\delta = -0.58$ [s, 12H, Al(CH$_3$)$_2$], 2.01 [s, 4H, NCH$_2$N], 3.86 [s, 6H, N(CH$_3$)$_2$]. – ^{13}C NMR: $\delta = -9.32$ [q, $^1J_{CH} = 111.4$ Hz, Al(CH$_3$)$_2$], 43.84 [s, N(CH$_3$)$_2$], 76.37 [s, br., NCH$_2$N]. – ^{27}Al-NMR: $\delta = 186$ ($\nu_{1/2} = 2600$ Hz). Elemental analysis: C$_{11}$H$_{32}$N$_2$Al$_2$ (246.3 g mol^{-1}): calcd. C 53.64, H 13.09, N 11.37; found C 51.01, H 12.83, N 10.92.

N,N,N',N'-Tetramethylmethylendiamine-bis-trimethylgallium (2). A solution of *N,N,N',N'-*tetramethylmethylendiamine (1.02 ml, 8.0 mmol) in hexane (20 ml) was dropped into a solution of trimethylgallium (1.82 g, 16.0 mmol) in hexane (20 ml) under cooling to 0 °C. The reaction mixture was stirred for 5 h. The volume was reduced to 10 ml and the solution stored at −78 °C. After one week 1.72 g (5.18 mmol, 65%) of colourless crystals are obtained (very sensitive to air and moisture. M.p. 82 °C, sublimation point 52 °C (0.01 mbar). ^{1}H NMR: $\delta = -0.22$ [s, 18H, Ga(CH$_3$)$_2$], 1.92 [s, 12H, N(CH$_3$)$_2$], 3.31 [s, 2H, NCH$_2$N]. - ^{13}C\{^{1}H\} NMR: $\delta = -4.84$ [s, Ga(CH$_3$)$_2$], 43.86 [s, N(CH$_3$)$_2$], 78.77 (s, NCH$_2$N). Elemental analysis for C$_{11}$H$_{32}$N$_2$Ga$_2$ (331.8 g mol^{-1}): calcd. C 39.82, H 9.71, N 8.44; found C 39.80, H 9.70, N 8.44.)

N,N,N',N'-Tetramethylmethylendiamine-trimethylgallium (3). A solution of *N,N,N',N'-*tetramethylmethylendiamine (1.02 ml, 0.82 g, 8.0 mmol) in hexane (20 ml) was dropped into a solution of trimethylgallium (1.82 g, 16.0 mmol) in diethyl ether (5 ml) under cooling to 0 °C. The reaction mixture was stirred overnight. All volatile components were removed under reduced pressure to yield 0.89 g (4.11 mmol, 51%) of a yellowish oil (very sensitive to air and moisture), which was crystallized from pentane at −78 °C. M.p. 10 °C. ^{1}H NMR: $\delta = -0.43$ [s, 9H, Ga(CH$_3$)$_2$], 2.01 [s, 12H, N(CH$_3$)$_2$], 3.07 (s, 2H, NCH$_2$N). – ^{13}C NMR $\delta = -6.78$ [s, q $^1J_{CH} = 118.1$ Hz, Ga(CH$_3$)$_2$], 43.90 [s, q $^1J_{CH} = 132.5$ Hz N(CH$_3$)$_2$], 80.53 [s, t $^1J_{CH} = 145.4$ Hz NCH$_2$N]. – ^{15}N\{^{1}H\}-NMR $\delta = -259.87$ (s). Elemental analysis for C$_9$H$_{23}$N$_2$Ga (216.1 g mol^{-1}): calcd. C 44.42, H 10.73, N 12.96; found C 44.31, H 10.69, N 12.74.

N,N,N',N'-Tetramethylmethylendiamine-trihydroaluminium-dimer (4). Tetramethylformamidinium chloride (2.05 g, 15.0 mmol) was added in small portions to a solution of lithiumaluminiumhydride (0.57 g, 15.0 mmol) in diethyl ether (80 ml) at −78 °C. The mixture was allowed to warm to ambient temperature overnight while stirring. After filtration from the precipitated lithium chloride the filtrate was concentrated under reduced pressure to half the volume. Upon storage of this solution at −78 °C for two days, colourless and extremely pyrophoric crystals were isolated. Yield 1.45 g (10.95 mmol, 73%). M.p. 44 °C, sublimation point 35 °C (0.01 mbar). ^{1}H NMR: $\delta = 2.02$ [s, 12H, N(CH$_3$)$_2$], 3.11 (s, 2H, NCH$_2$N), 3.99 (s, 3H, AlH$_3$). – ^{13}C NMR: $\delta = 44.2$ [s, q $^1J_{CH} = 136.5$ Hz N(CH$_3$)$_2$], 80.81 (s, t $^1J_{CH} = 144.6$ Hz NCH$_2$N). – ^{27}Al NMR: $\delta = 133$ ($\nu_{1/2} = 1700$ Hz). Elemental analysis for C$_5$H$_{17}$N$_2$Al (132.12 g mol^{-1}): calcd. C 45.41, H 12.97, N 21.20; found C 45.18, H 12.87, N 21.10.

Crystal structure determinations. Crystals of **1**, **2** and **4** were prepared under argon in a matrix of perfluorinated polyether. A single crystal of **3** was grown *in situ* on the diffractometer by establishing a solid liquid equilibrium of a sample, selecting a well formed seed crystal and melting the remainder followed by cooling the sample first by 2 K over 6 h, then more rapidly to 133 K. Scattering intensities of **1**, **3** and **4** collected on a Nonius CAD4 diffractometer, those of **2** on a DIP 2020 image plate diffractometer. Intensity corrections for **2** were applied by means of the program SCALEPACK [23], the other data were used without absorption correction. Anisotropic refinement [24] of all displacement parameters was applied to non-H-atoms, isotropic to H atoms. Deposition numbers at the Cambridge Crystallo-

Compound	1	2	3	4
Formula	$C_{11}H_{32}Al_2N_2$	$C_{11}H_{32}Ga_2N_2$	$C_8H_{23}GaN_2$	$C_5H_{17}AlN_2$
Molec. mass	246.35	331.83	217.00	132.19
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	$Pbca$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	14.0376(8)	7.2212(2)	8.0138(5)	6.5984(2)
b [Å]	12.4474(11)	10.7111(3)	8.1224(4)	7.9408(2)
c [Å]	19.4707(16)	12.3185(5)	18.9807(19)	9.4451(2)
α [°]	90	104.9401(13)	90	66.9612(11)
β [°]	90	103.0444(14)	100.751(8)	79.5158(11)
γ [°]	90	106.5365(12)	90	77.8496(11)
V [Å^3]	3402.1(5)	835.24(5)	1213.79(16)	442.48(2)
$\rho_{calcd.}$ [g cm^{-3}]	0.962	1.319	1.187	0.992
Z	8	2	4	2
F (000) [e]	1104	348	464	148
μ [mm^{-1}]	0.151	3.205	2.223	0.152
T [K]	133(2)	143(2)	133(2)	148(2)
$\theta_{min} - \theta_{max}$ [°]	2.09 – 27.12	3.05 – 27.69	2.18 – 26.96	2.82 – 27.22
h Range	$0 \leq h \leq 17$	$0 \leq h \leq 9$	$-10 \leq h \leq 2$	$0 \leq h \leq 8$
k Range	$0 \leq k \leq 15$	$-13 \leq k \leq 12$	$0 \leq k \leq 10$	$-8 \leq k \leq 10$
l Range	$-24 \leq l \leq 0$	$-16 \leq l \leq 15$	$-24 \leq l \leq 24$	$-11 \leq l \leq 12$
Measd. refl.	3674	36275	3257	1814
Indep. refl.	3674	3594	2642	1814
R_{int}	–	0.0670	0.0459	–
Parameters	194	264	192	141
R_1/wR_2	0.0588 / 0.1601	0.0638 / 0.1034	0.0311 / 0.0695	0.0307 / 0.0770
$\rho_{fin, max/min}$ [eA^{-3}]	0.477 / -1.001	0.634 / -0.436	0.358 / -0.416	0.256 / -0.174
CCSD-no.	246634	246635	246636	246637

Table 4. Details of data collection and refinements for the crystal structure determinations of **1**, **2**, **3** and **4**.

graphic Structure Database (CCDC) as well as further detail on data collection and refinement are compiled in Table 4.

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