

Monomeric organoaluminium complexes $\text{RAl}(\text{OR}^*)_2$ and R_2AlOR^* with an optically active amino alkoxide ligand

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Received 2 June 1999; accepted 4 August 1999

Dedicated to Professor Dr Dirk Walther on the occasion of his 60th birthday.

Abstract

The reactions of trialkylaluminium, R_3Al , with (*S*)-(–)- α,α -diphenyl-2-pyrrolidinyl-methanol have been investigated, in which unusual bis-complexes $\text{RAl}(\text{OR}^*)_2$ were obtained [$\text{OR}^* = (\text{S})\text{-}\alpha,\alpha$ -diphenyl-2-pyrrolidinyl-methoxide (Dpm), $\text{R} = \text{Me}$ (**1**), Et (**2**), 1-Nor (**3**)]. A similar reaction carried out with $\text{R} = t\text{-Bu}$ yields, by contrast, the expected mono-alkoxide R_2AlOR^* (**4**). All compounds were characterised by X-ray crystallography and NMR spectroscopy. The molecular structures are monomeric. In **1–3**, the aluminium centres bonded to the nitrogen atoms of two chelating ligands are five-coordinate, while the metal atom contained in **4** is tetrahedrally surrounded. The absolute structures of all complexes were determined from X-ray diffraction data. The formation of the dative Al–N bonds is stereospecific in all cases. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminium; Alkoxides; Amines; X-ray diffraction; Chirality

1. Introduction

During the past several years the chemistry of organoaluminium complexes has attracted considerable attention due to possible applications of those compounds in both material science and organic synthesis. For the latter, chiral complexes with the ability to support stereospecific transformations are of special interest. Several chiral alkylaluminium alkoxides have been described as intermediates in stereospecific organic reactions [1]. Moreover, organoaluminium compounds containing a bifunctional amino alkoxide group have been considered as potential catalysts in polymerisation reactions of lactone rings yielding polyesters [2].

In general, complexes with composition $[\text{R}_2\text{AlOR}^*]_x$ can be obtained by reaction of the aluminiumorganyl

R_3Al with the respective optically active amino alcohol HOR^* [3–12]. Structurally characterised compounds show the metal centre coordinated by the nitrogen atom of the amino alkoxide ligand. Additionally, OR^* may act as a bridging ligand. Therefore, complexes are usually dimeric ($x = 2$) with two chelating rings linked by a planar Al_2O_2 unit, and a pentagonal polyhedron is observed around the metal atom. Only one monomeric species ($\text{OR}^* = (2\text{S},3\text{R})\text{-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butoxide}$) has been published up to now and little is known about those parameters which determine the degree of association [6]. Previous investigations showed that the optical activity of the amino alcohol is transferred to the resulting alkoxide in each case.

This study is part of our systematic investigations of the chemistry of organometal complexes of Group 13 elements with various types of optically active aminoalkoxides [10–12]. We report the preparation and structures of organoaluminium derivatives, which contain the (*S*)- α,α -diphenyl-2-pyrrolidinyl-methoxide (Dpm) ligand bearing two sterically demanding phenyl groups substituted to the α -carbon atom.

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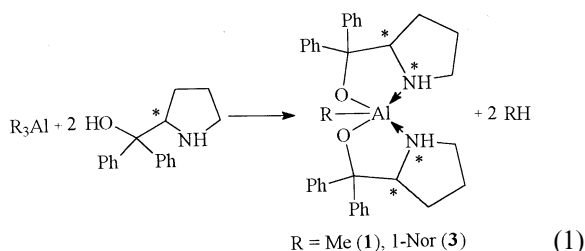
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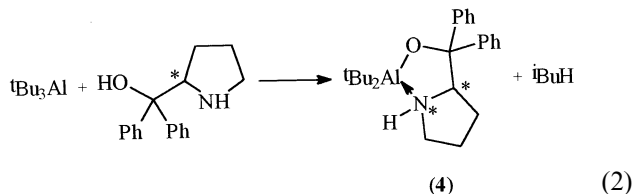
2. Results and discussion

2.1. Preparation

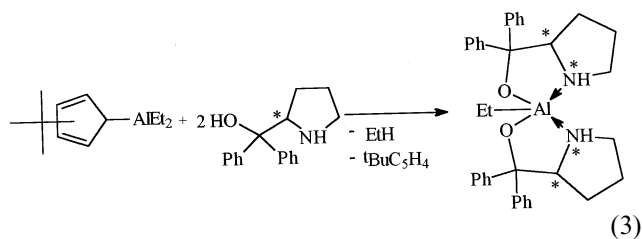
The addition in molar ratio of 1:1 R_3Al ($R = Me$, 1-Nor) to a slurry of the (*S*)- α,α -diphenyl-2-pyrrolidiny-methanol in *n*-pentane results in the formation of bis-aminoalkoxides $[MeAl(Dpm)_2]$ (**1**) and $[(1-Nor)Al(Dpm)_2]$ (**3**), respectively, rather than the expected mono-complexes $[R_2Al(Dpm)]_x$. Thus, two alkyl groups in R_3Al are substituted for two alkoxide ligands (Eq. (1)). **3** can be prepared in higher yields using a 1:2 molar ratio of the starting materials. The products could be isolated in good yields. Previously, the preparation and NMR spectroscopic characterisation of a structurally related complex $MeAl\{OC_6H_4(CH_2NMe)_2\}_2$ obtained by 1:2 reaction of $AlMe_3$ with the respective mono-*ortho*-chelating phenolate ligand has been reported [13].



A reaction similar to Eq. (1) carried out with $R = t-Bu$ led, by contrast, to the mono-complex $[(t-Bu)_2Al(Dpm)]$ (**4**). This result is consistent with the reaction pathway described in earlier studies (Eq. (2)) [3–10].



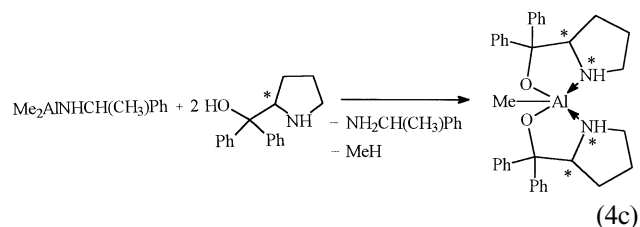
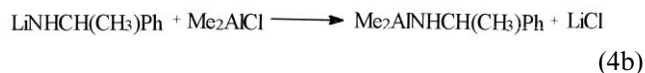
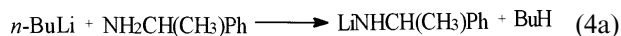
The ethyl compound, being analogous with **1** and **2**, was obtained by reaction of diethyl-*t*-butylcyclopentadienyl-aluminium with (*S*)- α,α -diphenyl-2-pyrrolidiny-methanol in *n*-pentane at room temperature (r.t.). One ethyl group and the cyclopentadienyl moiety are substituted for two aminoalkoxide ligands, e.g. the starting materials are converted in ratio 1:2 (Eq. (3)). The postulated by-products could not be detected.



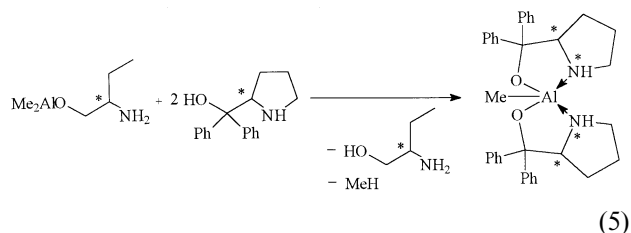
Compounds **1**, **2** and **4** are highly sensitive to both moisture and oxygen, while **3** decomposes in air after 5 min, and its reaction with water proceeds rather smoothly due to the bulkiness of the alkyl group attached to the metal atom.

Compounds **1–3** are very soluble in aromatic solvents and ethers but less soluble in aliphatic hydrocarbons, whereas **4** was found to be very soluble in both aromatic hydrocarbons and ethers. Crystals of **1–4** are colourless and transparent.

In a second reaction, compound **1** was obtained by addition of dimethylaluminium-1-diphenylamide **5** to the amino alcohol at r.t. The amide ligand and one methyl group of **5** are replaced by two Dpm moieties even if the starting materials are used in stoichiometric quantities (Eq. (4c)). Compound **5** was produced as pale yellow powder by reaction of lithium-1-diphenylamide with dimethylaluminium chloride (Eqs. (4a) and (4b)). This compound is very soluble in aromatic and less soluble aliphatic hydrocarbons.



Alternatively, high yields of **1** can be obtained by reaction of dimethylaluminium-(*R*)-2-aminobutoxide [11] with (*S*)- α,α -diphenyl-2-pyrrolidiny-methanol leading to substitution of one methyl group and the (*R*)-2-aminobutoxide moiety by two Dpm ligands (Eq. (5)). Dimethylaluminium-(*R*)-2-aminobutoxide and (*R*)-2-aminobutanol were found in the reaction mixture using 1H -NMR spectroscopy.



2.2. X-ray structures

The bis-aminoalkoxides **1**, **2** and **3** crystallise in space groups without inversion centres and mirror planes — $P2_1$, $P2_12_12_1$ and $P2_12_12_1$, respectively — with one molecule of the alkoxide in each asymmetric unit. To

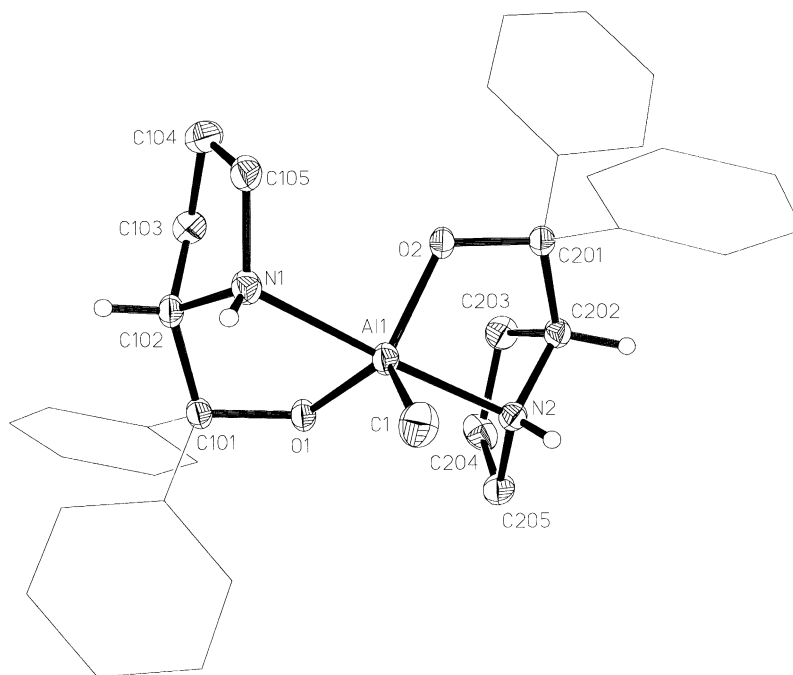


Fig. 1. Molecular structure of $[\text{MeAl}(\text{Dpm})_2]$ (**1**). Thermal ellipsoids at 40% level. Hydrogen atoms other than those attached to asymmetric coordinated atoms were omitted for clarity.

the author's knowledge, no structure of any other metalorganic bis-complex $[\text{RAl}(\text{OR}')_2]$ has been published (OR' can mean either chiral or achiral aminoalkoxide ligand). Compound **3**, the first structurally characterised norbornyl derivative of aluminium, co-crystallises with diethylether as a 1:1 adduct.

Within the series **1–3**, similar molecular structures are formed (Figs. 1–3). They show the central five-coordinate aluminium atom surrounded by the alkyl moiety and both oxygen and nitrogen atoms of two Dpm ligands. Analysing the metal coordination throughout the series, the transition from trigonal bipyramidal

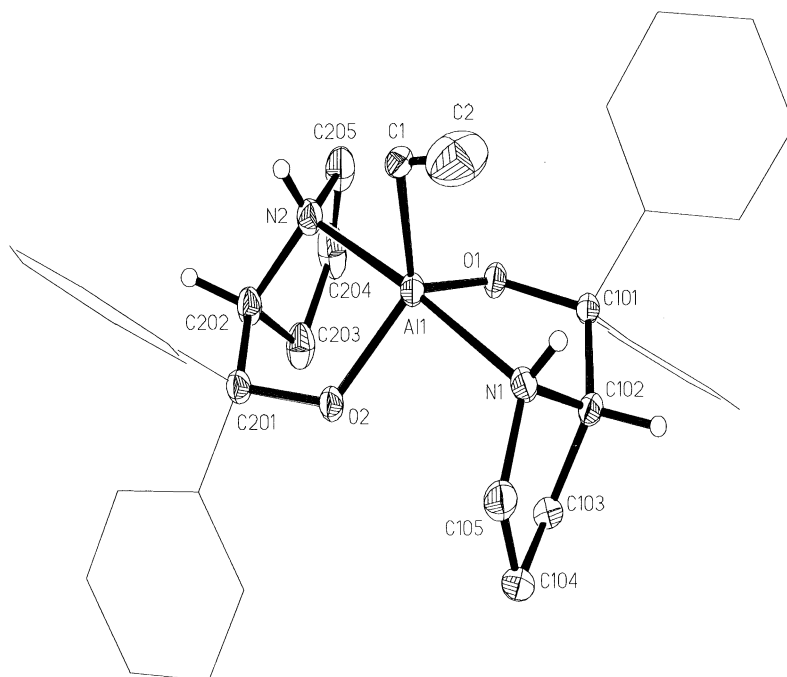


Fig. 2. Molecular structure of $[\text{EtAl}(\text{Dpm})_2]$ (**2**). Thermal ellipsoids at 40% level. Hydrogen atoms other than those attached to asymmetric coordinated atoms were omitted for clarity.

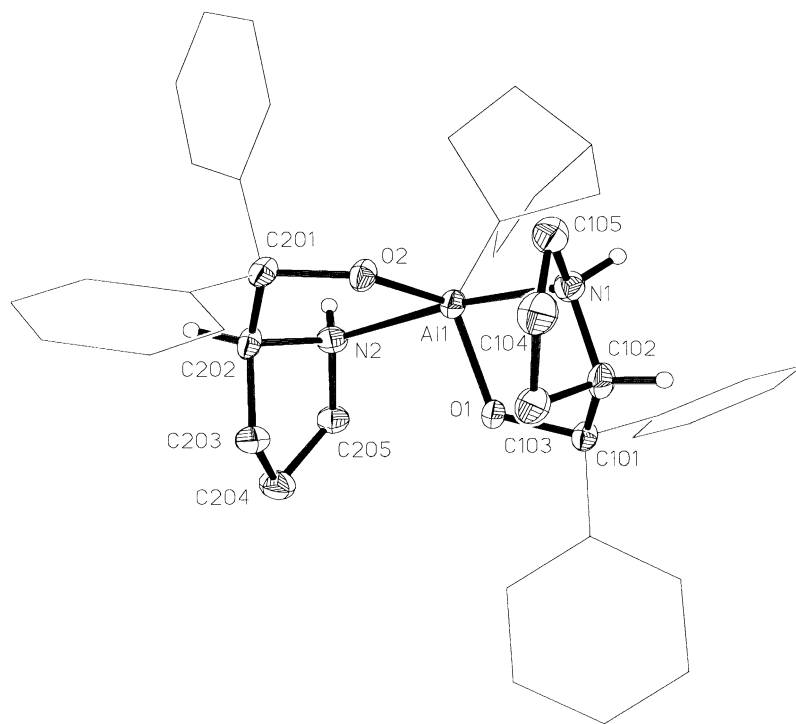


Fig. 3. Molecular structure of $[1\text{-NorAl}(\text{Dpm})_2]$ (**3**). Thermal ellipsoids at 40% level. Hydrogen atoms other than those attached to asymmetric coordinated atoms and minor disorder of the 1-Nor moiety were omitted for clarity.

(TBP) to square pyramidal (SP) geometry along the Berry coordinate was found to consistently deviate by 10% (the departure from a geometry representing a true Berry pseudo rotation was calculated to be approximately 4°) [14,15]. Thus, the respective polyhedron around aluminium is close to a perfect TBP with apical nitrogen atoms. In **1** the axial–axial angle N1–Al1–N2 is 172.1° and the equatorial plane (Al1, O1, O2, C1) adopts an almost ideal geometry. The greatest distortion from idealised TBP geometry is shown in the O–Al1–N intra-ring angles of 84.0 and 84.2° . Appropriate angles in analogous dimeric structures $[\text{R}_2\text{AlOR}]_2$ are effected by the strained Al_2O_2 unit and lie around 75° [7,10,11]. The angle between least-square planes defined by the atoms of the two chelating rings is 52.7 (**1**), 55.9 (**2**) and 60.1° (**3**). Its variation reflects the sterical demands of the respective alkyl substituents attached to aluminium. N1–Al1–N2 is simultaneously reduced from 171.2° in **1** to 167.9° in **3**. In **1**, both the Al–O and the Al–N bond lengths are nearly equalised with mean values of 1.786 and 2.120 Å, respectively, both being of the expected magnitudes. By comparison, the Al–O intra-ring and the Al–N distances are slightly shorter in $\text{Al}\{\text{OC}_6\text{H}_4(\text{CH}_2\text{NMe})\text{-2,6-Me-4}\}_3$ and average $1.759(3)$ and $2.078(3)$ Å [13]. The larger (six-membered) and less strained chelating rings causes a widening of endocyclic O–Al–N angles by 5.5° in the same complex.

Furthermore, the angle formed by Al–O ring bonds is opened by 9.4° . The distortion of the TBP geometry (28%), caused by the bulky exocyclic substituent attached to aluminium, is remarkably higher than in **1–3** (Table 1).

Table 1

Bond lengths (Å), bond angles ($^\circ$) and distortion of the geometry around Al for compounds **1**, **2** and **3**· Et_2O

	1	2	3
<i>Bond lengths</i>			
Al1–O1	1.788(1)	1.784(1)	1.781(3)
Al1–O2	1.784(1)	1.779(1)	1.786(3)
Al1–C1	1.978(2)	2.037(2)	2.022(4)
Al1–N1	2.124(2)	2.115(2)	2.141(4)
Al1–N2	2.117(1)	2.138(2)	2.145(4)
<i>Bond angles</i>			
O2–Al1–O1	120.1(1)	119.2(1)	117.0(1)
O1–Al1–N2	92.1(1)	92.3(1)	90.2(1)
O2–Al1–N2	84.0(1)	84.0(1)	83.2(1)
O2–Al1–N1	91.7(1)	90.7(1)	90.1(2)
O1–Al1–N1	84.2(1)	84.2(1)	83.9(1)
N2–Al1–N1	172.1(1)	171.2(1)	167.9(2)
O2–Al1–C1	118.5(1)	119.5(1)	122.8(2)
O1–Al1–C1	121.4(1)	121.2(1)	120.2(2)
C101–O1–Al1	118.3(1)	119.3(1)	119.2(3)
C201–O2–Al1	119.2(1)	119.0(1)	120.6(3)
C1–Al1–N1	93.1(1)	96.6(1)	97.7(2)
C1–Al1–N2	94.8(1)	92.2(1)	94.4(2)
TBP $\rightarrow$ SP (%)	10.4	9.8	10.4

According to the characteristics of the amino alcohol used for the preparation of **1–3**, the chiral centres C102 and C202 are *S*. The nitrogen atoms become four-coordinate — they are additional asymmetrically substituted atoms. The configuration of the N1 and N2 centres is *S* in each case. Thus, the forming of the dative Al–N bond proceeds stereospecifically. This is a feature observed in some related chiral mono-alkoxides of aluminium [6,9,11]. Only one exception has been found up until now, the epimeric dimethylaluminium-*cis*-(1*R*,2*S*)-2-*N*-benzylamino-1-cyclohexyl-methoxide complex. Its nitrogen centres contained in two crystallographically independent six-membered chelating rings are *R* and *S* [11]. Moreover, stereospecific formation of

Table 2
Degree of association x in dialkyl aluminium complexes $[\text{R}_2\text{AlOR}]_x$ containing chelating rings of different sizes

OR'	x	Ref.
<i>Five-membered</i>		
Me OCH ₂ CHEtNH ₂	2	[11]
Me OCHMeCH ₂ NMe ₂	2	[10]
Me OCH ₂ CH ₂ NH ₂	2	[10]
Me OCH ₂ CH(C ₄ H ₈)NH	2	[11]
Et, SiMe ₃ OCH ₂ CH(CH ₂ Ph)NH ₂	2	[9]
Me OCHPhCM ₂ H ₄ NHMe	2	[3]
<i>t</i> -Bu OCHPh ₂ CH(C ₃ H ₆)NH	1	4
<i>Six-membered</i>		
Me OCH ₂ CH ₂ CH ₂ NMe ₂	2	[16]
Me OCH ₂ CH(C ₅ H ₉)NH(CH ₂ Ph)	2	[11]
Me OCHPh(CH ₂ Ph)CHMeCH ₂ NMe ₂	1	[6]

the metal–nitrogen bond has been confirmed for two mono-derivatives of Group 13 elements with Dpm, Me₂Ga(Dpm) and [Me₂In(Dpm)]₂ [12,16].

Compound **4** is the first monomeric aminoalkoxide of aluminium $[\text{R}_2\text{AlOR}]_x$ ($x = 1$) with a five-membered chelating ring. Until now, only a six-membered species has been shown to be monomeric and the possible correlation between ring size and degree of association has been discussed in this connection [6]. Comparison of all reported structures $[\text{R}_2\text{AlOR}]_x$ however shows that the degree of association is more likely controlled by the bulkiness of the *exo*-cyclic substituents at the α -carbon atom rather than by the chain length of OR' (Table 2). Interestingly, even those complexes with only one sterically demanding substituent at α -C or N and those with two SiMe₃ groups bonded to Al are dimeric. The gallium and indium derivatives [Me₂Ga(Dpm)] and [Me₂In(Dpm)]₂ are monomeric and dimeric, respectively [12,16]. Structural differences occurring between mono-complexes of Group 13 elements with Dpm are due to the fact that the size of the atom increases but the Lewis acidity decreases with higher atomic numbers, and both effects influence the degree of association in opposite directions.

The aluminium centre in **4** is coordinated in a distorted tetrahedral fashion by two *t*-Bu groups and both the oxygen and the nitrogen atom of the Dpm moiety (Fig. 4). The intra-ring angle Al1–O1–N1 of 86.1° is remarkably reduced in comparison with the idealised tetrahedral angle, but it is by 8° greater than in dimeric complexes [9–11]. At 1.769 Å, Al1–O1 is longer than

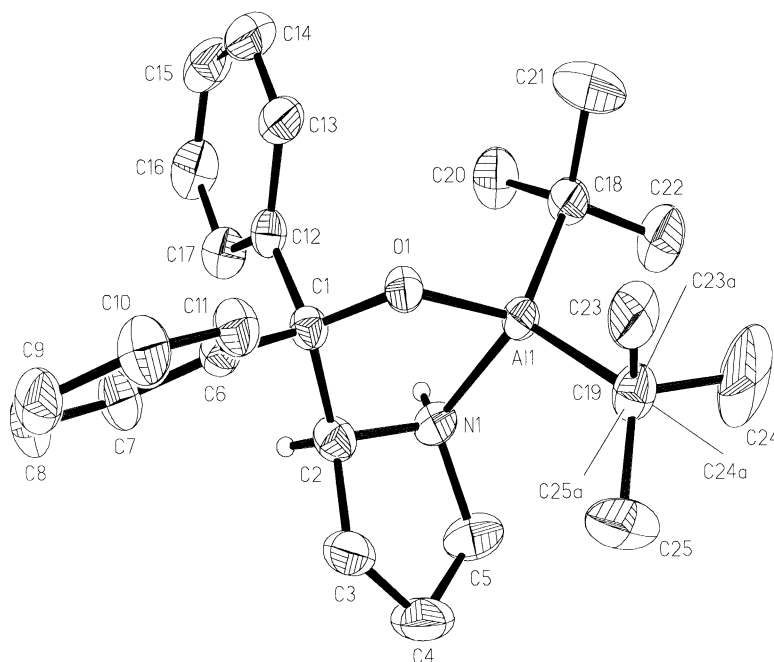


Fig. 4. Molecular structure of $[\text{t-Bu}_2\text{Al}(\text{Dpm})]$ (**4**). Thermal ellipsoids at 40% level. Hydrogen atoms other than those attached to asymmetric coordinated atoms were omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for compound **4**

Bond lengths		Bond angles	
Al1–O1	1.769(2)	O1–Al1–C18	118.3(1)
Al1–N1	2.035(3)	O1–Al1–C19	108.7(1)
Al1–C18	2.016(3)	C18–Al1–C19	116.2(1)
Al1–C19	2.031(3)	O1–Al1–N1	86.9(1)
O1–C1	1.407(4)	C18–Al1–N1	105.9(2)
N1–C2	1.501(4)	C19–Al1–N1	117.8(2)
N1–C5	1.499(5)		

expected for idealised normal Al^{IV}–O bonds (1.69 Å), whereas Al1–N1 = 2.035 Å is significantly shortened compared with the reference value for dative Al^{IV}–N distances, 2.08 Å [17]. This indicates a significant delocalisation between both bond types. In accordance with the structures of [Me₂Ga(Dpm)], [Me₂In(Dpm)]₂ and **1–3**, the configuration of the N1 centre is *S*.

In each chelating ring of **1** the two carbon atoms are displaced by almost equal amounts but in opposite directions from a plane defined by N, Al and O (C101, 0.34 Å, and C102, –0.29 Å; C201, 0.32 Å, and C202, –0.29 Å) corresponding with C–C twist conformation. Comparison with appropriate parameters calculated for other structures in this study shows that this particular ring pucker is remarkably stable. The same holds true for the pyrrolidinyl moieties adopting conformations close to the C103 and C203 envelope (C3 envelope in the case of **4**). We consider the constant ring conformations observed in **1–4** to be a direct consequence of the identical configuration of chiral centres within the Dpm moieties (Table 3).

2.3. NMR studies

The major features of the ¹H, ¹³C and ²⁷Al spectra of **1–4** are listed in Table 4. They are generally consistent with the solid-state structures discussed above. In the ¹H-NMR spectrum of **1**, the aluminium-bonded methyl group gives rise to a sharp singlet at –1.42 ppm. In comparison with dimeric complexes [R₂AlOR']₂, the coordination of aluminium by nitrogen atoms of two Dpm ligands causes an upfield shift by about 1 ppm [6,10]. This signal is followed by multiplets for the pyrrolidinyl rings. Four signals at $\delta = 7–7.62$ ppm are associated with phenyl groups. In the ¹³C-NMR spectrum a resonance of very low intensity for the aluminium-bonded methyl group is detected at $\delta = -15.05$ ppm, followed by the expected signals for the ligands.

In the ¹H-NMR spectrum of **2**, two complex multiplets are observed which are associated with the CH₂ moiety of EtAl, and the methyl group causes a triplet at 0.47 ppm. The chemical shifts for the ligands are observed in the expected ranges. Two signals of low intensity (–4.25 and 11.19 ppm) in the ¹³C-NMR spectrum can be attributed to the aluminium-bonded ethyl group.

Complex multiplets at $\delta = -0.21–0.89$ ppm in the ¹H-NMR spectrum of **3** are observed for the norbornyl moiety, followed by signals associated with the hydrogen atoms of the ligand. In the ¹³C-NMR spectrum chemical shifts at 31.43–43.62 ppm are due to the carbon atoms in the norbornyl residue.

In contrast to what would be expected for a dimeric complex [R₂AlOR']₂, the ¹H-NMR resonances for *t*-Bu bonded to aluminium in **4** are nonequivalent (0.78 and 1.35 ppm). Chemical shifts at 31.11 and 31.74 ppm in the ¹³C-NMR spectrum are due to the methyl groups of the *t*-Bu moiety. No signal could be assigned to the tertiary carbon atom.

Broad signals in the ²⁷Al-NMR spectra of **1–3** at $\delta = 124–128$ ppm indicate a five-coordinate aluminium atom. In the spectrum of **4**, by contrast, a signal associated with the four-coordinate metal centre appears at 158 ppm. These values are comparable with those of similar five- and four-coordinate aluminium compounds [10,18].

3. Experimental

3.1. General remarks

All manipulations were performed under an atmosphere of argon using normal Schlenk techniques. Commercially available trimethylaluminium and amino alcohols were used for the preparations. Amino alcohols were freshly distilled prior use. *t*-Bu₃Al was prepared according to the literature method [19,20]. Solvents were dried over LiAlH₄, purified and saturated with argon prior use.

3.2. X-ray crystallographic study

Details of the crystal data and a summary of collection and refinement parameters for **1–4** are given in Table 5. Selected bond lengths and angles are listed in Tables 1 and 3. Single crystals of compounds were obtained by crystallisation from Et₂O (at 5°C for **1**, **2**, **3**·Et₂O and –12°C for **4**). Data were collected on a SMART CCD (Siemens) using graphite monochromated Mo–K α radiation ($\lambda = 0.71073$ Å; ω scans) at –60°C. An empirical absorption correction was performed with SADABS [21]. All structures were solved by direct methods (SHELXS [22]) and refined against *F*² using SHELXL-97 [23]. All heavy atoms were refined anisotropically, hydrogen atoms were refined either independently or the riding model was used. The intermolecular atomic distances in **1**, **2**, **3**·Et₂O and **4** indicate Van der Waals type interactions. The absolute structures for **1–4** were confirmed by refinement of the Flack parameter [24].

In structure **3** the 1-norbornyl ligand is disordered. It was refined with distance restraints for chemically equivalent bonds. Both components are related by a

Table 4
 ^1H -, ^{13}C - and ^{27}Al -NMR data for compounds **1–4** (C_6D_6 , 22°C [ppm])

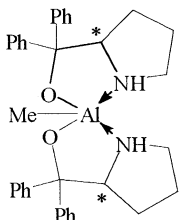
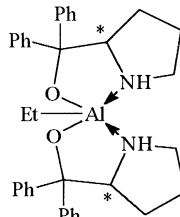
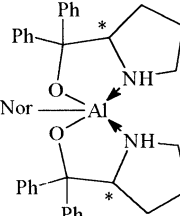
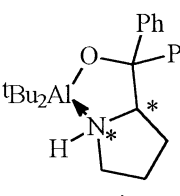
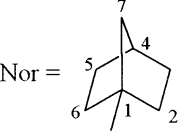
Compound	^1H		^{13}C		^{27}Al ($w_{1/2}$ [Hz])
 1	–1.42 (s, 3H)	$\text{CH}_3\text{Al}-$	–15.05 (br)	$\text{CH}_3\text{Al}-$	126
	1.27 (m, 4H)	$-\text{CH}_2-$	23.90	$-\text{CH}_2-$	(1980)
	1.52 (m, 4H)	$-\text{CHCH}_2-$	26.71	$-\text{CHCH}_2-$	
	2.05 (m, 2H)	$-\text{NHCH}_2-$	44.72	$-\text{NHCH}_2-$	
	2.26 (m, 2H)		67.47	$-\text{CHNH}-$	
	2.39 (m, 2H)	$-\text{CHNH}-$	77.13	$-\text{OC}-$	
	3.87 (m, 2H)	$-\text{CHNH}-$	125.09	Ph–	
	7.04 (m, 8H)	Ph–	126.40	Ph–	
	7.17 (m, 4H)	Ph–	150.45	Ph–	
	7.58 (m, 4H)	Ph–	150.80	Ph–	
 2	–0.94 (m, 1H)	$\text{CH}_3\text{CH}_2\text{Al}-$	–4.25 (br)	$\text{CH}_3\text{CH}_2\text{Al}-$	128
	–0.77 (m, 1H)		11.19	$\text{CH}_3\text{CH}_2\text{Al}-$	(2230)
	0.47 (t, 3H)	$\text{CH}_3\text{CH}_2\text{Al}-$	24.03	$-\text{CH}_2\text{CH}_2\text{CH}_2-$	
	1.26 (m, 4H)	$-\text{CH}_2-$	26.80	$-\text{CHCH}_2\text{CH}_2-$	
	1.51 (m, 4H)	$-\text{CH}_2-$	44.87	$-\text{NHCH}_2-$	
	2.10 (m, 2H)	$-\text{NHCH}_2-$	67.20	$-\text{CHNH}-$	
	2.27 (m, 2H)		77.06	$-\text{OC}-$	
	2.48 (m, 2H)	$-\text{CHNH}-$	125.91	Ph–	
	3.89 (m, 2H)	$-\text{CHNH}-$	126.45	Ph–	
	7.04 (m, 8H)	Ph–	150.93	Ph–	
 3	0.21 (m, 1H)	Nor	24.67	$-\text{CH}_2\text{CH}_2\text{CH}_2-$	124
	0.41 (m, 4H)	Nor	28.32	$-\text{CHCH}_2\text{CH}_2-$	(2320)
	0.71 (m, 4H)	Nor	31.34	C3	
	0.89 (m, 2H)	Nor	31.63	C5	
	1.23 (m, 4H)	$-\text{CH}_2-$	35.14	C2	
	1.97 (m, 4H)	$-\text{CH}_2-$	35.47	C6	
	2.14 (m, 2H)	$-\text{CH}_2-$	37.84	C4	
	2.35 (m, 2H)		43.62	C7	
	3.26 (m, 2H)	$-\text{CHNH}-$	45.71	$-\text{NHCH}_2\text{CH}_2-$	
	4.13 (m, 2H)	$-\text{CHNH}-$	66.42	$-\text{CHNH}-$	
 4	0.78 (s, 9H)	$(\text{CH}_3)_3\text{C}$	23.69	$-\text{CH}_2\text{CH}_2\text{CH}_2-$	158
	1.35 (s, 9H)	$(\text{CH}_3)_3\text{C}-$	27.08	$-\text{CHCH}_2\text{CH}_2-$	(1720)
	1.27 (m, 2H)	$-\text{CH}_2-$	31.11	$(\text{CH}_3)_3\text{C}-$	
	1.59 (m, 2H)	$-\text{NHCH}_2-$	31.74	$(\text{CH}_3)_3\text{C}-$	
	2.20 (m, 1H)	$-\text{CHCH}_2-$	44.91	$-\text{NHCH}_2-$	
	2.69 (m, 1H)		67.32	$-\text{CHNH}-$	
	2.86 (m, 1H)	$-\text{CHNH}-$	78.36	$-\text{OC}-$	
	3.91 (m, 1H)	$-\text{CHNH}-$	125.73	Ph–	
	7.00 (m, 4H)	Ph–	125.87	Ph–	
	7.13 (m, 2H)	Ph–	149.65	Ph–	
 1-Nor =	7.46 (m, 2H)	Ph–	150.19	Ph–	
	7.58 (m, 2H)	Ph–			

Table 5

Crystallographic data for compounds **1**, **2**, **3**·Et₂O and **4**

Compound	1	2	3 ·Et ₂ O	4
Formula	C ₃₅ H ₃₉ AlN ₂ O ₂	C ₃₆ H ₄₁ AlN ₂ O ₂	C ₄₅ H ₅₇ AlN ₂ O ₃	C ₂₅ H ₃₆ AlNO
Formula weight (g mol ^{−1})	546.66	560.69	700.90	393.53
Crystal	Pyramidal faces	Rectangular blocks	Platelet	Platelet
Colour	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.25 × 0.50 × 0.70	0.45 × 0.45 × 0.40	0.40 × 0.35 × 0.20	0.40 × 0.45 × 0.45
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁
<i>Z</i>	2	4	4	2
<i>a</i> (Å)	9.493(2)	12.0762(8)	12.278(1)	9.875(2)
<i>b</i> (Å)	13.565(3)	14.058(1)	17.605(1)	13.461(3)
<i>c</i> (Å)	12.011(2)	18.394(1)	18.219(1)	10.230(2)
β (°)	106.40(3)	90	90	118.55(3)
<i>V</i> (Å ³)	1483.8(5)	3122.7(3)	3938.1(5)	1194.5(4)
<i>D</i> _{calc.} (Mg m ^{−3})	1.224	1.193	1.182	1.094
Absorption coefficient (mm ^{−1})	0.102	0.099	0.093	0.099
θ range (°)	1.8–26.4	1.8–26.2	1.6–24.0	2.3–24.8
Reflections/ <i>R</i> _{int}	11471/0.017	23083/0.044	25442/0.079	7772/0.047
Data/parameters	5336/508	5717/529	6052/643	3530/376
GOF on <i>F</i> ²	1.063	1.106	1.012	0.997
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.028/0.066	0.039/0.083	0.071/0.125	0.048/0.124
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.030/0.067	0.052/0.090	0.088/0.136	0.053/0.132
Largest difference peak (e Å ^{−3})	−0.11/0.12	−0.17/0.21	−0.52/0.31	−0.15/0.18
Absolute structure parameter	−0.1(1)	0.02(5)	−0.02(3)	−0.1(2)

rotation of 116° about Al1–C1 (site occupation 3:2). The *t*-butyl group in structure **4** is disordered. It was refined with distance restraints for chemically equivalent bonds. The disordered moieties are related by a rotation of 40° about Al1–C19 (site occupation 3:2).

3.3. [MeAl(Dpm)₂] (**1**)

To a stirred solution of 1.8 g (0.025 mol) trimethylaluminium in *n*-pentane (50 ml) *S*-(−)-α,α-diphenyl-2-pyrrolidinyl-methanol (6.3 g, 0.025 mol) was added at r.t. After stirring the reaction mixture for 12 h the colourless precipitate was filtered off. Recrystallisation from diethyl ether yielded MeAl(Dpm)₂ (**1**). Yield: 6.2 g (46% with respect to DpmH). Anal. Found for C₃₅H₃₉O₂N₂Al; (546 g mol^{−1}): C, 76.22; H, 6.98; N, 5.98; Al, 4.53. Calc.: C, 76.92; H, 7.14; N, 5.13; Al, 4.94%.

To a solution of 1.6 g (0.01 mol) of **5** in 30 ml *n*-pentane *S*-(−)-α,α-diphenyl-2-pyrrolidinyl-methanol (2.5 g, 0.01 mol) was added at r.t. After stirring the reaction mixture for 2 h the colourless precipitate was filtered off and extracted with diethyl ether. The solution was cooled to −50°C yielding colourless crystals of **1**. Yield: 3.5 g (64% with respect to DpmH).

3.3.1. Lithium-1-phenyl-ethylamide

To a solution of 6.1 g (0.05 mol) 1-phenyl-ethylamine in *n*-pentane (100 ml) a solution of *n*-butyllithium in *n*-hexane (55.5 ml, 0.9 molar) was added. After the gas

had evolved from the reaction mixture, the solution was filtered and dried in vacuum yielding lithium-1-phenyl-ethylamide as a pale yellow, highly air- and moisture-sensitive powder. Yield: 5.6 g (89%). ¹H-NMR (THF-*d*₈): δ = −0.25 (br. s, NH, 1H); 1.26 (d, CH₃; 3H); 4.18 (m, CH, 1H); 6.99–7.32 (3m, Ph, 5H).

3.3.2. Dimethylaluminium-1-phenylethylamide (**5**)

To a stirred solution of 2.8 g (0.03 mol) dimethylaluminiumchloride in *n*-pentane lithium-1-phenylethylamide (3.81 g, 0.03 mol) was added. The reaction mixture was stirred for 2 h, then LiCl was filtered off. A pale yellow precipitate was allowed to separate from the clear solution at −50°C. The solid was dried in vacuum. Yield: 4.2 g (86%). Anal. Found for C₁₀H₁₆NAl; (163 g mol^{−1}): C, 73.41; H, 9.01; N, 8.96; Al, 16.32. Calc.: C, 73.62; H, 9.81; N, 8.59; Al, 16.56%. ¹H-NMR, (C₆D₆): δ = −0.55 (q, (CH₃)₂, 6H); 1.04 (d, NH, 1H); 1.14 (d, CH₃, 3H); 3.88 (m, CH, 1H); 6.88–7.18 (3m, Ph, 5H). ¹³C-NMR (C₆D₆): δ = −5.32 ((CH₃)₂–); 23.17 (CH₃); 48.71 (CH); 120.33–141.59 (Ph). ²⁷Al-NMR (C₆D₆): δ = 162.

To a solution of 1.5 g (0.01 mol) of dimethylaluminium-(*R*)-2-aminobutoxide [11] in 50 ml diethyl ether *S*-(−)-α,α-diphenyl-2-pyrrolidinyl-methanol (2.5 g, 0.01 mol) was added at r.t. After the reaction mixture had been stirred for 24 h the colourless precipitate was filtered off and extracted with diethyl ether. The solution was cooled to −50°C yielding colourless crystals of **1**. Yield: 4.1 g (75% with respect to DpmH).

3.4. [EtAl(Dpm)₂] (2)

To a solution of 5.2 g (0.025 mol) diethyl-*t*-butyl-cyclopentadienyl-aluminium in 50 ml *n*-pentane *S*-(–)- α,α -diphenyl-2-pyrrolidinyl-methanol (6.3 g, 0.025 mol) was added at r.t. The reaction mixture was stirred for 24 h then the colourless precipitate was filtered off and extracted with diethyl ether. Cooling the solution to –50°C yielded colourless crystals of **3**. Yield: 5.01 g (36% with respect to DpmH). Anal. Found for C₃₆H₄₁O₂N₂Al (560 g mol^{–1}): C, 77.01; H, 6.89; N, 5.23; Al, 4.57. Calc.: C, 77.14; H, 7.32; N, 5.00; Al, 4.82%.

3.4.1. Diethyl-*t*-butylcyclopentadienyl-aluminium

To a solution of 13.4 g (14.6 ml, 0.12 mol) diethyl-aluminiumchloride in 150 ml *n*-pentane 15.1 g (0.12 mol) *t*-butyl-cyclopentadienyllithium was added at r.t. The reaction was stirred for 24 h, then LiCl was filtered off. The solvent was removed and the residue distilled under vacuum. B.p.: 105°C/3 Torr. Yield: 16.2 g (65%). ¹H-NMR (C₆D₆): δ = 0.08 (m, CH₂, 4H); 0.71 (t, CH₃, 6H); 1.24 (s, (CH₃)₃, 9H); 3.39 (m, Cp; 2H); 5.92 (m, Cp, 1H); 6.13 (m, Cp, 1H).

3.5. [1-NorAl(Dpm)₂] (3)

To a stirred solution of 4.0 g (0.013 mol) tris-(1-norbornyl)-aluminium in 50 ml *n*-pentane *S*-(–)- α,α -diphenyl-2-pyrrolidinyl-methanol (6.4 g, 0.026 mol) was added at r.t. After the reaction mixture was stirred for 2 h the colourless precipitate was filtered off and extracted with diethyl ether. Cooling the solution to –50°C yielded colourless crystals of **3**. Yield: 4.5 g (58%). (If the starting materials are reacted in a molar ratio of 1:1 the yield of **3** decreases to 35% with respect to DpmH.) Anal. Found for C₄₁H₄₇O₂N₂Al; (626 g mol^{–1}): C, 78.52; H, 7.87; N, 4.10; Al, 4.12. Calc.: C, 78.59; H, 7.53; N, 4.49; Al, 4.31%.

3.5.1. 1-Nor₃Al

To a suspension of 2.6 g (0.02 mol) aluminiumtrichloride in 100 ml *n*-pentane 1-norbornyllithium (6.1 g, 0.06 mol) was added at r.t. The reaction mixture was stirred for 24 h and then filtered. The resulting solution was reduced to a volume of 20 ml. Storing the solution at –50°C for 2 days yielded 1-Nor₃Al as a colourless powder. Recrystallisation from *n*-pentane was repeated twice. Yield: 3.1 g (49%). Anal. Found for C₂₁H₃₃Al; (312 g mol^{–1}): C, 80.63; H, 10.21; Al, 8.48. Calc.: C, 80.76; H, 10.58; Al, 8.65%. ¹H-NMR: δ = 1.26–1.66 (4m; 12H). ¹³C-NMR: δ = 31.35 (C3 + C5), 36.31 (C2 + C6), 37.79 (C4), 44.41 (C7).

3.6. [t-Bu₂Al(Dpm)] (4)

To a solution of 1.8 g (0.009 mol) tri-*t*-butyl-aluminium in 50 ml *n*-pentane *S*-(–)- α,α -diphenyl-2-pyrrolidinyl-methanol (2.3 g, 0.009 mol) was added at r.t., spontaneous gas evolution (*iso*-butane) was observed. The reaction mixture was allowed to stir for 24 h. Then the solvent was removed under vacuum and the residue was extracted with diethyl ether. Cooling the solution to –50°C yielded crystals of **4**. Yield: 2.1 g (58%). Anal. Found for C₂₅H₃₆ONAl; (393 g mol^{–1}): C, 76.21; H, 10.03; N, 3.8; Al, 6.35. Calc. C, 76.33; H, 9.16; N, 3.56; Al, 6.87%.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 119269 (**1**), 119270 (**2**), 119271 (**3**), 119272 (**4**). Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

- [1] (a) F. Bigi, G. Casiraghi, G. Casnati, G. Sartori, L. Zetta, J. Chem. Soc. Chem. Commun. (1983) 1210. (b) K. Maruoka, T. Itoh, T. Shirasaka, H. Yamamoto, J. Am. Chem. Soc. 110 (1988) 310. (c) D. Seebach, A.K. Beck, R. Imwinkelried, S. Roggo, A. Wonnacott, Helv. Chim. Acta 70 (1987) 954. (d) S.-I. Hashimoto, N. Komesima, K. Koga, J. Chem. Soc. Chem. Commun. (1979) 437. (e) C.J. Northcott, Z. Valenta, Can. J. Chem. 65 (1987) 1917. (f) M. Quimpere, K. Jankowski, J. Chem. Soc. Chem. Commun. (1987) 676. (g) M.T. Reetz, S.-H. Kyung, C. Bolm, T. Tierke, Chem. Ind. (1986) 824.
- [2] (a) D. Seebach, L. Müller; Angew. Chem. 105 (1993) 483. (b) A.D. Pajerski, R.W. Lenz, Makromol. Chem. Macromol. Symp. 73 (1993) 7. (c) S. Inoue, T. Aida, Makromol. Chem. Macromol. Symp. 73 (1993) 27.
- [3] M.L. Sierra, V. Srin, J. de Mel, J.P. Oliver, Organometallics 8 (1989) 2486.
- [4] J.P. Oliver, R. Kumar, Polyhedron 9 (1990) 409.
- [5] M.L. Sierra, R. Kumar, J.P. Oliver, Organometallics 11 (1992) 206.
- [6] R. Kumar, M.L. Sierra, J.P. Oliver, Organometallics 13 (1994) 4285.

- [7] H. Schumann, M. Frick, B. Heymer, F. Girgsdies, J. Organomet. Chem. 512 (1996) 117.
- [8] D.A. Atwood, M.P. Remington, D. Rutherford, Organometallics 15 (1996) 4763.
- [9] D.A. Atwood, F.P. Gabbai, J. Lu, M.P. Remington, D. Rutherford, M.P. Sibi, Organometallics 15 (1996) 2308.
- [10] K.-H. Thiele, E. Hecht, T. Gelbrich, U. Dümichen, J. Organomet. Chem. 540 (1997) 89.
- [11] E. Hecht, T. Gelbrich, K.-H. Thiele, J. Sieler, Z. Anorg. Allg. Chem. 624 (1998) 315.
- [12] E. Hecht, T. Gelbrich, S. Wernik, R. Weimann, K.-H. Thiele, J. Sieler, H. Schumann, Z. Anorg. Allg. Chem. 624 (1998) 1061.
- [13] M.P. Hogerheide, M. Wesseling, J.T.B.H. Jastrzebski, J. Boersma, H. Kooijman, A.L. Spek, G. van Koten, Organometallics 14 (1995) 4483.
- [14] R.R. Holmes, Progr. Inorg. Chem. 32 (1984) 119 and references therein.
- [15] A.L. Spek, Acta Crystallogr. Sect. C 34 (1990) 46.
- [16] E. Hecht, T. Gelbrich, K.-H. Thiele, J. Sieler, Main Group Chem., accepted for publication.
- [17] A. Haaland, in: G.H. Robinson (Ed.), Coordination Chemistry of Aluminum, VCH, New York, 1993, p. 49.
- [18] R. Benn, Angew. Chem. Int. Ed. Engl. 22 (1983) 779.
- [19] H. Lehmkuhl, Justus Liebigs Ann. Chem. 719 (1986) 40.
- [20] W. Uhl, Z. Anorg. Allg. Chem. 570 (1989) 37.
- [21] G.M. Sheldrick, SADABS, Program for scaling and correction of area detector data, University of Göttingen, Germany, 1997.
- [22] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
- [23] G.M. Sheldrick, SHELXL-97, Program for crystal structure determination, University of Göttingen, Germany, 1997.
- [24] (a) H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876. (b) G. Bernardinelli, H.D. Flack, Acta Crystallogr. Sect. A 41 (1985) 500.