Synthesis and Structures of Aminoalkoxyalanes

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 65th birthday

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Reactions of various amino alcohols with $AlH_3{\cdot}NMe_3$ in hydrocarbons or ethers yielded the corresponding aminoalkoxyalanes $R_2N(X)_nOAlH_2$ **1–4** which are dimeric in the solid state. The structures of **1–4** show a characteristic Al_2O_2 ring system with pentacoordinated Al atoms. Pentacoordination is also observed in bis(–)-*R*-ephedrinoalane **(5)** which is, however, monomeric. Reduction of acetophenone with (–)-*R*-ephedrinoalane **(3)** proceeded without any noticeable stereoselectivity. Temperature-dependent ^{27}Al NMR studies suggest that the well-defined structures found in the solid state are not retained in solution.

Introduction

Although $LiAlH_4$ and $NaBH_4$ are amongst the most widely used hydride reducing reagents,[1] their stereoselectivity is negligible.[2] Therefore, modifications of these hydrides by suitable substituents to achieve adequate stereo- and enantioselectivity have been investigated. Amongst these reagents is lithium binaphtholato-*tert*-butoxy hydrido aluminate, Noyori's reagent, which shows very high enantioselectivity.[3] The factors which control the reaction mechanism, and consequently the stereoselectivity, are not yet fully understood. The main reason for this lies in the lack of knowledge concerning the composition of the active reducing species in solution. Recently, we have shown that the stability of alkoxyaluminum hydrides and alkali metal organyloxohydridoaluminates in solution depends on the nature of the substituents at the Al centers.[4] In principle, it should be possible to turn AlH_3 into a reagent with high stereo- and possibly enantioselectivity, for instance by introducing chiral substituents.[5] In this paper we describe new aminoalkoxoalanes, some of them with chiral centers, as well as some temperature-dependent ^{27}Al NMR studies, which provide information about their nature in solution.

Synthesis

The synthesis of aminoalkoxo alanes was performed by allowing the amino alcohols R*OH to react with $AlH_3{\cdot}NMe_3$ [see Equation (1) and (2)] particularly those leading to alanes of type R^*OAlH_2, because their hydride content is higher than that of the alanes $(R^*O)_2AlH$.

$$R^*OH + AlH_3{\cdot}NMe_3 \rightarrow R^*OAlH_2 + NMe_3 + H_2 \quad (1)$$

$$2R^*OH + AlH_3{\cdot}NMe_3 \rightarrow (R^*O)_2AlH + NMe_3 + 2\,H_2 \quad (2)$$

$$2\,R^*OAlH_2 \rightarrow (R^*O)_2AlH + AlH_3 \quad (3)$$

The reactions were performed in tetrahydrofuran or toluene with *N*,*N*-dimethylaminoethanol, *N*,*N*-dimethylaminopropanol, (−)-(*S*)-1-methylpyrrolidine-2-methanol, (*N*-methyl-L-prolinol) or (−)-*N*-methylephedrine. Common to all these amino alcohols is the tertiary amino group. Reactions in a 1:1 ratio led to the alane derivatives **1−4**, while the 2:1 reaction of the ephedrine with $AlH_3{\cdot}NMe_3$ yielded the bis(aminoalkoxo)alane **5**.

Compounds **1−4** proved to be dimeric in the solid state. Because no compounds of type $R^*OAlH_2{\cdot}NMe_3$ [$R^*O = R_2N(CH_2)_nO$] were obtained, it is evident that the amino group of the amino alcohol has displaced the Me_3N ligand from the Al center. Taking this into account, several different structural units may result, as depicted by Formulae **A−G**.

Although the dimeric nature of these compounds is ascertained in the solid state to be of type **B**, it cannot be excluded that the compounds may adopt other structures in solution.

Reduction of acetophenone with the ephedrinoalane **3** resulted in practically no stereospecific induction; these experiments will therefore not be described.

Spectroscopic Properties

^{27}Al NMR spectroscopy should allow us to distinguish between **A** and **C**, with tetracoordinated Al centers, and types **B**, **D**, and **F**, with pentacoordinate Al atoms. A structure of type **G** should result in two ^{27}Al resonances with a quintet for the AlH_4 anion in the proton-coupled spectrum. For a structure of type **E**, a single broad resonance is be expected (exchange signal). The resonances for structures

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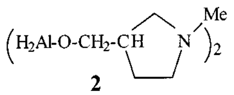
$(H_2Al\text{-}O\text{-}CH_2\text{-}CH_2\text{-}NMe_2)_2$

1



2

$(H_2Al\text{-}O\text{-}CHPh\text{-}CHMe\text{-}NMe_2)_2$

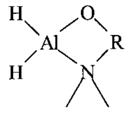
3

$(H_2Al\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NMe)_2$

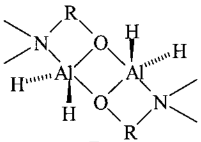
4

$HAl(O\text{-}CHPh\text{-}CHMe\text{-}NMe_2)_2$

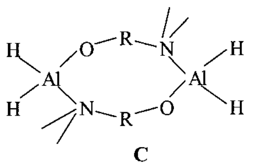
5



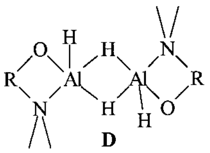
A



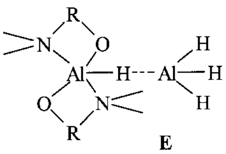
B



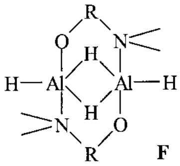
C



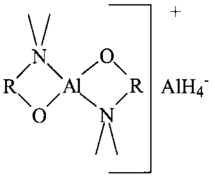
D



E



F



G

with pentacoordinate Al centers should appear further upfield, indicating electronically better shielded atoms. Table 1 lists the ^{27}Al NMR shifts and IR spectroscopic data for the Al−H stretching vibrations.

Table 1. ^{27}Al chemical shifts of compounds **1−5** (main signal) in [D$_8$]toluene at 27 °C (δ in ppm, half-height width $h_{1/2}$ in Hz) and νAlH (in cm^{-1}) in the IR spectra

	δ^{27}Al	$h_{1/2}$	νAlH$_2$/AlH
1	91	1090	1755, 1716
2	91	1880	1767, 1730
3	96	4260	1811, 1776
4	92	1970	1749, 1715
5	83	3690	1777

With the exception of compound **5**, all ^{27}Al resonances lie in the narrow range of 91−96 ppm. All signals are quite broad, and it was not possible to resolve ^{27}Al,^{1}H-coupling. This is in agreement with the rather high asymmetry about the Al center which allows for rapid relaxation. The δ^{27}Al values are by themselves not necessarily a convincing argument for tetra- or pentacoordination because the observed chemical shifts are on the border of tetra- and pentacoordination.[6] However, by comparing these data with those of $(ROAlH_2)_2$ (R = alkyl, δ^{27}Al = 115−130),[4,7] featuring tetracoordination for Al, then the δ^{27}Al values for compounds **1−5** support pentacoordination in toluene solution (*vide infra*). This is particularly evident for compound **5** with δ^{27}Al = 83. The most striking difference between alkoxyalanes with small alkyl groups and the aminoalkoxyalanes is that, in solution, the latter are not subject to ligand exchange, which would lead to AlH_3 and bis(aminoalkoxy)alanes, as shown in Equation (3).

Although the dimeric nature of compounds **1−4** were ascertained by X-ray structure analysis, there are alternatives as depicted by formulae **D−F**.

A structure of type **E**, which might even become ionic as shown in **G**, can be excluded immediately because only a single ^{27}Al NMR signal is observed in toluene solution and none for AlH_4^-. This also excludes structures with two chemically and spectroscopically different Al centers. Isomers **D** and **F** should be discernible from structure **B** by IR spectroscopy: the absorptions for terminal AlH groups and for tetracoordinated Al atoms are expected in the range of 1800−1900 cm^{-1}, and for the bridging AlH_2Al groups at about 1650 cm^{-1}.[4,7,8] The presence of two IR absorptions in the range from 1703−1777 cm^{-1} can be assigned to antisymmetric and symmetric AlH_2 vibrations for pentacoordinated Al centers, and this rules out the presence of structures **D** and **F** in solution.

However, the temperature-dependent ^{27}Al NMR spectra of compound **1** in toluene reveal that the situation in toluene is more complex (see Figure 1). Firstly, the spectra show the presence of hexacoordinated species which seem to gain in concentration at low temperature. On warming the solution, the dominant signal at δ ≈ 60 (−70 °C) moves to δ ≈ 90 at higher temperature, indicating a rapid equilibrium between penta- and tetracoordinated species. However, with increasing temperature the signal not only becomes sharper, as expected, but rather at 20 °C the $\delta = 91$ signal represents a contribution of >90% by a pentacoordinated Al species. We assume that this signal represents a situation of a rapid equilibrium [see Equation (4)] between various molecules having penta- and tetracoordinated centers. ${}^1J({}^{27}\mathrm{Al},{}^1\mathrm{H})$ could not be observed at any temperature owing to the considerable line widths (1090−4250 Hz). Similar ^{27}Al NMR spectra were observed for compounds **2−4**. Therefore, there is no single species present in solution, and this should be reflected in the reactions of these compounds. Equation (4) describes the state of these molecules in solution.

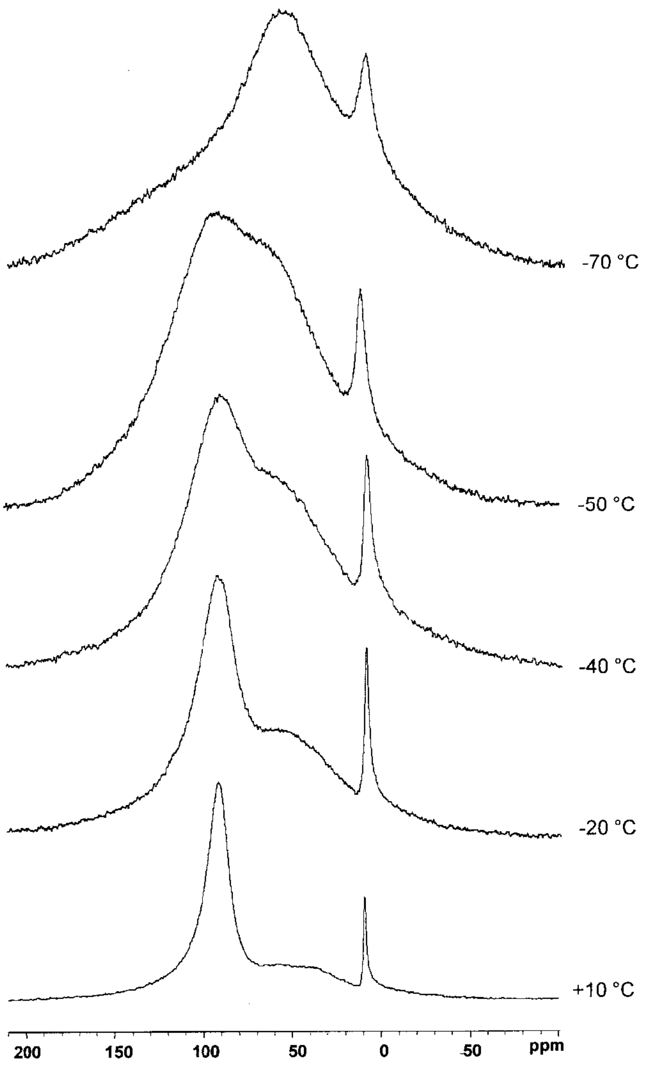


Figure 1. Temperature-dependent ^{27}Al NMR spectra of compound **1** in deuterated toluene

Evidence for the stability of the dimeric entities of compounds **1−4** comes from mass spectra. In all cases, the $[M_2 - 2\ \mathrm{H}]^+$ ion has been detected, demonstrating that the compounds are volatile, but not as monomeric units; rather, they also retain their dimeric state of aggregation in the gas phase. Compound **5**, however, is monomeric in the gas phase in agreement with its structure in the crystal.

Molecular Structures

Compounds **1−5** were obtained as single crystals, and their structures were determined by X-ray methods. Figure 2−6 represent the molecular structures. The general features of these structures are: i) all compounds are dimeric in the solid state, except **5**, even though they all have pentacoordinated Al atoms, and ii) the presence of a central, planar, or almost planar, Al_2O_2 four-membered ring. Compounds **1**, **2**, and **3** contain aminoalkoxy groups forming a five-membered ring with the Al atom. This geometry induces a considerable distortion about the Al centers from a trigonal bipyramidal arrangement. As expected, the Al−O bond in the "trigonal plane" is shorter than the Al−O bond in the axial position. Except for compound **1**, where the sum of the bond angles for this plane is only 349.2°, almost perfect "planes" are present in compounds **2−5** (359 ± 1°).

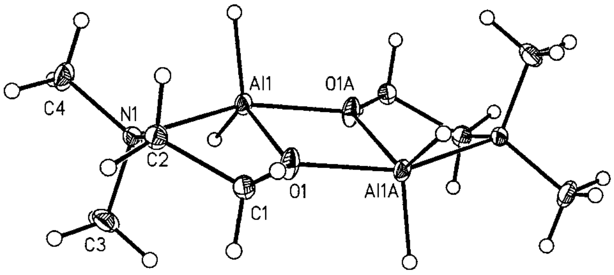
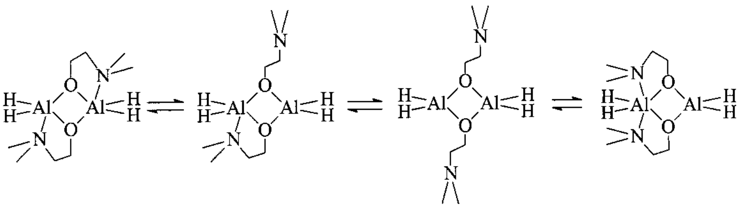


Figure 2. Molecular structure of dimeric *N,N*-dimethylaminoethoxyalane **(1)**; thermal ellipsoids are drawn on a 25% probability scale; selected bond lengths (in Å): Al1−O1 1.850(2), Al1−O1A 1.903(2), Al1−N1 2.133(2), Al1−H1 1.50(2), Al1−H2 1.54(3).; selected bond angles (in °): O1−Al−O1A 75.61(8), Al1−O1−C1 122.6(1), Al1A−O1−C1 132.4(1), Al1−O1−Al1A 104.39(8), N1−Al1−O1 79.71(7), N1−Al1−O1A 154.50(7), H1−Al1−H2 120(1), H1−Al−O1 125.4(9), H2−Al1−O1 114(1), N1−Al1−H1 92.9(9), N1−Al−H2 94(1)

The axis N1−Al1−O1A in the centrosymmetric molecule **1** is bent towards the equatorial Al1−O1 bond (see Figure 2), and the deviations from the 90° angles (axial to equatorial) result from ring strain both of the Al_2O_2 four-membered ring [O1−Al1−O1A 75.61(8)°] as well as of the five-membered Al−O−C−C−N ring [distorted envelope configuration with N1−Al1−O1 = 79.71(7)°].

In contrast to **1**, which crystallizes in the centrosymmetric monoclinic space group $P2_1/n$, compounds **2** and **3**



(4)

crystallize in the acentric monoclinic space group $P2_1$, as expected for the presence of chiral aminoalkoxy ligands. There are two independent molecules of **2** in the unit cell, both having the same configuration but a different conformation (see Figure 3). The sum of bond angles for the atoms around the "trigonal plane" is 360°, and the H−Al−H bond angle is close to 120°. The Al−N coordination generates a new chiral center at the nitrogen atom, the absolute stereoconfiguration being of the *S*-type. The two "terminal" pyrrolidine rings are oriented towards the same side with respect to the Al_2O_2 ring, resulting in a "boat conformation", and the two molecules reveal an (*S,R*) and an (*R,R*) configuration. The CH_2O moiety of the prolinato group forms a shorter Al−O distance within the five-membered $AlNC_2O$ ring than to the Al atom of the next H_2Al-OR' unit [1.833(2) vs. 1.919(2) Å].

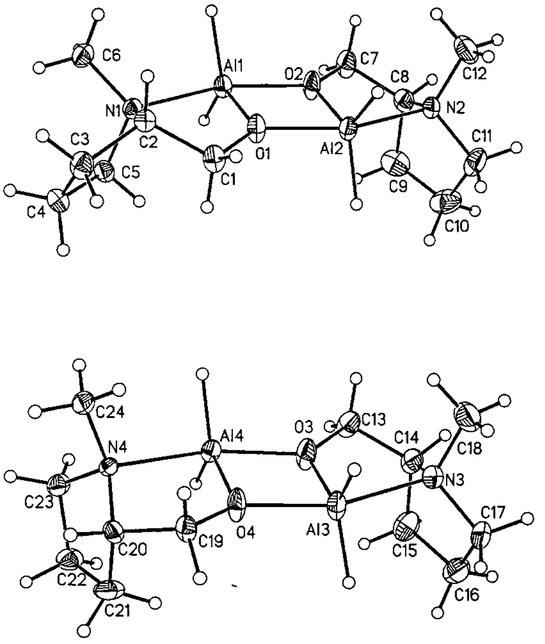


Figure 3. Molecular structure of dimeric *N*-methyl-L-prolinatoalane **(2)**; thermal ellipsoids represent a 25% probability; selected bond lengths (in Å): Al1−O1 1.833(2), Al1−O2 1.919(2), Al1−N1 2.141(2), Al2−O1 1.901(2), Al1−H1 1.51(3), Al1−H2 1.59(3), Al2−H3 1.51(3), Al2−H4 1.55(3); selected bond angles (in °): O1−Al1−O2 74.73(9), N1−Al1−O1 80.73(9), N1−Al1−O2 155.46(9), H1−Al1−H2 118(2), H1−Al1−O1 122(1), H2−Al1−O1 120(1), N1−Al1−H1 92(1), N1−Al1−H2 94(1), Al1−O1−Al2 105.4(1), Al1−O1−C1 122.0(2), Al2−O1−C1 132.5(2), O2−Al2−O1 75.20(9), O2−Al2−N2 80.33(9), O1−Al2−N2 155.5(1)

In compound **3** (Figure 4), we observe a slightly nonplanar Al_2O_2 ring [sum of bond angles = 354.98(8)°]. The geometry around the two Al atoms indicates a strongly distorted trigonal bipyramid, the axial N−Al−O bonds being 153.28(8)° and 150.57(8)°, respectively. However, there is a perfect "trigonal plane" as shown by the sum of the bond angles (360°). But we find the same sum of bond angles for atoms H1B, O1 and N2 around atom Al1. This indicates that the geometry at the Al atoms can also be considered as a distorted "tetragonal pyramid". This involves atoms H1A, O1, O2 and N2 as the base and H1B as the top of the pyramid. It is, of course, evident that the absolute stereoconfiguration at atoms C3 and C14, as well as at C2 and C13 (*R* or *S*), has not changed, as demonstrated by the analogous arrangement of the phenyl groups with respect to the Al_2O_2 ring.

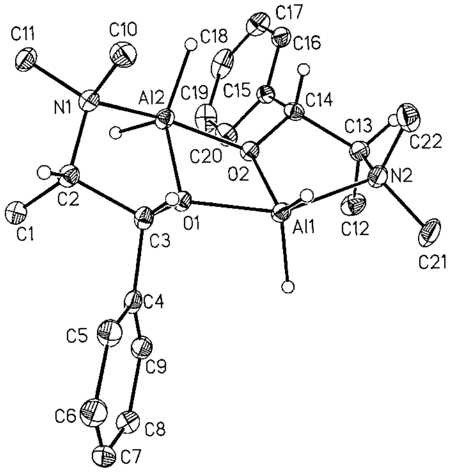


Figure 4. Molecular structure of dimeric (−)-*N*-methylephedrinatoalane **(3)**; thermal ellipsoids are depicted on a 25% probability scale; selected bond lengths (in Å): Al1−O1 1.940(2), Al1−O2 1.848(2), Al1−N2 2.145(2), Al2−O1 1.870(2), Al2−O2 1.920(2), Al2−N1 2.140(2), Al1−H1A 1.59(3), Al1−H1B 1.54(2); selected bond angles (in °): O1−Al1−O2 75.88(7), O1−Al1−N2 153.23(8), N2−Al1−O2 80.92(8), H1A−Al1−H1B 119(1), H1A−Al1−O2 127.1(9), H1B−Al1−O2 114.2(9), O1−Al1−H1A 92.7(9), O1−Al1−H1B 105.5(9), N2−Al1−H1A 90.7(9), N2−Al1−H1B 97(1), O1−Al2−O2 75.85(7), O1−Al2−N1 80.61(8), Al2−O1−C3 121.1(1), Al2−N1−C2 105.7(1)

Compound **4**, a derivative of *N,N*-dimethylaminopropanol, differs from the other dimeric aminoalkoxyalanes as the trigonal bipyramid is less distorted owing to the formation of a six-membered $AlOC_3N$ ring, which exerts less ring strain (Figure 5). Consequently, the axial N−Al−O bond is now 164.43(6)°, approximately 10° wider than in compounds **1**−**3**. Like compound **1**, compound **4** is also centrosymmetric. Nevertheless, due to the different Al−O bond lengths and the sharp bond angles O1−Al1−O1A [77.96(5)°] and Al1−O1−Al1A [102.04(6)°], the H−Al−O bond angles are quite different [128.6 and 113.1(7)°]. The six-membered rings are present in a chair conformation.

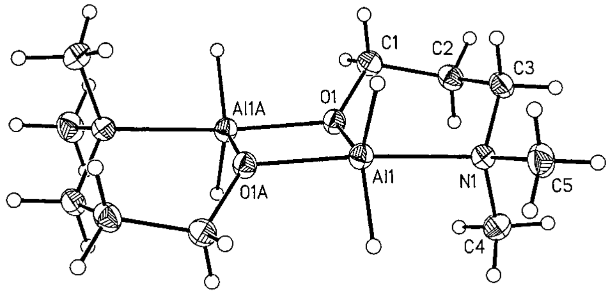


Figure 5. Molecular structure of dimeric (dimethylamino)propanolatoalane **(4)**; thermal ellipsoids depict a 25% probability; selected bond lengths (in Å): Al1−O1 1.834(1), Al1−O1A 1.930(1), Al1−N1 2.127(1), Al1−H1 1.53(2), Al1−H2 1.55(1); selected bond angles (in °): O1−Al1−O1A 77.96(5), Al1−O1−Al1A 102.04(5), Al1−O1−C1 125.8(1), Al1A−O1−C1 125.8(1), H1−Al1−H2 118(1), H1−Al1−O1 128.6(7), H2−Al1−O1 113.1(7), N1−Al1−O1A 164.43(6), N1−Al1−H1 87.3(6), N1−Al1−H2 91.7(7)

In contrast to the mono(aminoalkoxy)alane compound **5**, the bis(ephedrino)alane is monomeric but also features a pentacoordinated Al center (Figure 6). The molecule shows a twofold axis lying in the Al−H vector. While the axial positions of the slightly distorted pentagonal bipyramid are occupied by the nitrogen atoms [N−Al−N(0A) 174.3°] the trigonal plane is formed by the hydride hydrogen atom and two oxygen atoms, all bond angles for this plane being 120°. The Al−O bond lengths are shorter (1.760 Å) than in compounds **1−4**, while the Al−N bond lengths are almost the same as in the other compounds reported here.

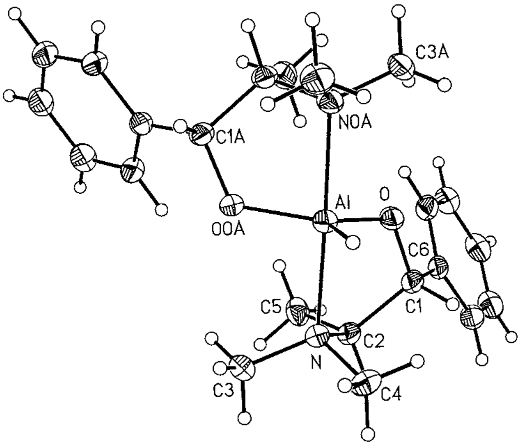


Figure 6. ORTEP plot of the molecular structure of bis(ephedrino)alane **(5)**; thermal ellipsoids represent a 25% probability; aromatic and methyl hydrogen atoms are omitted for clarity; selected bond lengths (in Å): Al−O 1.7603(2), Al−N 2.138(2), Al−H 1.83(2), O−C1 1.398(2), N−C3 1.478(3), N−C4 1.478(3); selected bond angles (in °): O−Al−O(0A) 119.9(1), O−Al−N 92.54(7), O−Al−N(0A) 84.61(7), O−Al−N 174.3(1), O−Al−H 120.0(1)N−Al−H 92.9(1). C1−O−Al 119.4(1), C3−N−C4 107.4(2), C2−N−Al 103.0(1)

Discussion

Amino alcohols react smoothly in a 1:1 molar ratio with $AlH_3 \cdot NMe_3$, providing aminoalkoxyalanes $R_2N(CH_2)_nOAlH_2$ quantitatively. During the reaction, not only is H_2 formed but also the Me_3N coordinated to AlH_3 is displaced by the amino group of the amino alcohol, a displacement that is most likely entropy-driven owing to the formation of five- or six-membered rings in which the amino group coordinates to the Al center. It is typical for compounds **1−4** that the Al atoms are pentacoordinated, two monomeric $R_2N(CH_2)_nOAlH_2$ units form dimers by Al−O coordination which leads to a central Al_2O_4 four-membered ring with two significantly different Al−O bond lengths. The O−Al−O bond angles are rather acute (about 75°) while the Al−O−Al bond angles are quite wide (about 105°), with the oxygen atoms residing in a planar Al_2C environment. Similar structures have been found for aminoalkoxy-diorganylalanes $[R_2N(CH_2)_nOAlR_2']_2$-gallanes and $[R_2N(CH_2)_nOGaR_2]$.[9] These classes of compounds are also dimeric. However, they may become monomeric by increasing the size of the ligand. Thus, the Me_2Al and the Me_2Ga derivatives of the darvon alcohol [(+)-(2*S*,3*R*)-4-dimethylamino-1,2-diphenyl-2-butanol] are monomeric in the solid state.[10] Interestingly, reactions of R_2AlCl (R = Me, Et) with amino alcohols not only gives access to dimeric aminoalkoxy alkyl chloroalanes $[R^*OAl(R)Cl]_2$ but, in the case of Me_2AlCl and (*S*)-α,α-diphenyl-2-pyrrolidinyl methanol, an ionic complex $\{MeAl(R^*O)_2AlMe\}^+[MeAlCl_3]^-$ is formed.[12] Although compounds **1−5** are the first structurally characterized aminoalkoxyalanes, one gallium homologue has been reported previously: *N,N''*-dimethylaminoethoxydihydridogallane.[11] The bond lengths in the gallium compound are slightly longer than in the comparable aluminium compounds, and this holds also for the alane and gallane (E = Al, Ga) pairs of $[tBuOEH_2]_2$.[7b] Table 2 shows a comparison of the structural parameters of the dimeric compounds **1−4** with similar aminoalkoxydiorganylalanes.

First of all, it can be noted that the $Al-O_{ax}$ bond lengths are approximately up to 0.09 Å longer than the $Al-O_{eq}$ bonds. In general, the Al−O and particularly the Al−N bond lengths of the diorganylamine derivatives are longer than those of the alane derivatives, while the $N-Al-O_{ax}$ bond angles do not vary by more than 3.5°. Furthermore, a comparison of the only two closely related pairs of alane and gallane derivatives is also included in Table 2.

Bond lengths are generally somewhat longer for the gallium compounds,[6b] while the bond angles are almost identical.[7b] Although pentacoordination at Al is the structural feature for all aminoalkoxydihydridoalanes described here,

Table 2. Comparison of bond lengths (in Å) and bond angles (in °) in structurally related dimeric aminoalkoxyalanes and dimeric alkoxydialkylalanes; (−)MEP = (−)-*N*-methylephedrine, (−)NMP = *N*-methyl-L-proline

	d(Al−N)	*d*(Al-$_{ax}$)	*d*(Al-$_{eq}$)	N−Al−O	ref.
$[Me_2NCH_2CH_2OAlH_2]_2$, **1**	2.133(3)	1.903(2)	1.850(2)	154.50(7)	-
$[Me_2NCH_2CHMeOAlMe_2]_2$	2.246(2)	1.927(1)	1.852(1)	151.0(1)	[8]
$[2\text{-}C_5H_4NCH_2OAl\textit{i}Bu]_2$	2.130(5)	1.935(5)	1.853(5)	151.7(2)	[12]
[(−)MEP−$AlH_2]_2$, **3**	2.143(2)	1.940(2)	1.848(2)	153.23(8)	-
[(−)MEP−$AlMe_2]_2$	2.193(8)	1.946(7)	1.864(6)	151.6(3)	[11]
[(−)NMP−$AlH_2]_2$, **2**	2.141(2)	1.919(2)	1.833(2)	155.4(9)	-
$[Me_2N(CH_2)_3O-AlH_2]_2$, **4**	2.127(1)	1.930(1)	1.834(1)	164.43(6)	-
	d(Al−H) or *d*(Ga−H)		*d*(Al−O) or *d*(Ga−O)		ref.
$[Me_2NCH_2CH_2OAlH_2]_2$, **1**	1.50(2), 1.54(2)		1.850(2), 1.903(2)		-
$[Me_2NCH_2CH_2O-GaH_2]_2$	1.50(7), 1.73(5)		1.911(3), 2.053(3)		[10]
$[Me_3CO-AlH_2]_2$	1.55(4), 1.55(5)		1.810(3), 1.815(3)		[6b]
$[Me_3CO-GaH_2]_2$	1.61(10), 1.69(12)		1.908(9), 1.902(9)		[6b]

the situation in solution is different. At ambient temperature, the ^{27}Al NMR spectra demonstrate the dominating presence of a dimer. However, a temperature-dependent series of ^{27}Al NMR as well as ^{1}H and ^{13}C NMR spectra clearly show that the room-temperature spectrum represents an averaged dynamic situation. The line width is also indicative of this assumption. Furthermore, at low temperature a significant amount of hexacoordinated Al centers is present besides the pentacoordinated Al and possibly the tetracoordinated species. Therefore, a comparatively complex situation exists in solution. A more detailed study will be needed to evaluate the kinetics and energetics of the species involved in the equilibrium (4). Taking these equilibria into account, the practical absence of any stereoselective reduction of acetophenone with prolinolatodihydridoalane or (+)-*N*-methylephedrinodihydridoalane can be understood.

Experimental Section

All manipulations were carried out using Schlenk techniques under an N_2 atmosphere, using flame-dried glassware. $AlH_3{\cdot}NMe_3$ was prepared from $[Me_3NH]Cl$ and $LiAlH_4$.[15] The amino alcohols are commercially available and were used as supplied. NMR: Jeol GSX 270 and Jeol EX 400:TMS C_6D_6, $AlCl_3$ in H_2O, LiCl in D_2O as standards. Routine spectra were recorded at 24.5 °C. − IR: Nicolet FT, range 4000−400 cm^{-1}. − X-ray: Siemens P4 diffractometer, Mo-K_α-radiation, graphite monochromator, CCD area detector. − C,H,N analysis was performed with an automated analyzer. Al was determined by TEDA titration.

Dimeric *N,N*-Dimethylaminoethoxyalane (1): $AlH_3{\cdot}NMe_3$ (0.71 g, 7.9 mmol) was dissolved in toluene (25 mL). At −25 °C a solution of $Me_2NCH_2CH_2OH$ (0.71 g, 8 mmol) in toluene (10 mL) was added slowly with stirring. After the gas evolution had ceased, the solution was reduced in vacuo to about half of its volume. The crystals that separated at −20 °C were isolated. Toluene was then removed partially from the filtrate. Compound **1** (810 mg, 86.9%) was isolated; m.p. 184−186 °C (dec.). − ^{1}H NMR (C_6D_6): δ = 1.95 (s, 12 H, N*Me*$_2$), 1.96 [t,^{3}J(H,H) = 5.6 Hz, 4 H, NC*H*$_2$], 3.57 [t,^{3}J(H,H) = 5.6 Hz, 4 H, OC*H*$_2$], ca. 4 (broad, 4 H, Al*H*$_2$). − ^{13}C NMR (C_6D_6): δ = 44.3 (N*Me*$_2$), 55.4 (NCH$_2$), 58.4 (OCH$_2$). − ^{27}Al NMR (C_6D_6): δ = 91 ($h_{1/2}$ = 1090 Hz), 94 ($h_{1/2}$ = 900 Hz). − IR (Nujol, Hostaflon): $\tilde{\nu}$: 3000 vs, 2978 vs, 2921 vs, 2885 vs, 2841 vs, 2808 sh, m, 2800 sh, m, 2794 m, 1755 vs/1719 vs [νAlH$_2$], 1496 m, 1459 vs, 1438 s, 1429 s, 1403 m, 1378 m, 1354 m, 1277 vs, 1254 vs, 1185 vs, 1089 vs, 1073 vs, 955 vs, 908 vs, 825 vs, 779 vs, 748 vs, 718 vs, 684 m, 556 vs, 550 vs cm^{-1}. − MS (70 eV): *m/z* = 233 [(**1**)$_2$ − H]$^+$, 203 [(**1**)$_2$ − 2 Me − H]$^+$. − $C_8H_{24}Al_2O_2N_2$ (234.3): calcd. C 41.02, H 10.33, Al 23.04, N 11.96; found C 40.58, H 9.85, Al 23.11, N 11.34.

Dimeric *N*-Methylprolinatoalane (2): To a stirred solution of $AlH_3{\cdot}NMe_3$ (0.84 g, 9.5 mmol) in toluene (10 mL) was added dropwise a solution of *N*-methylprolinol [(*S*)-2-hydroxymethyl-1-methylpyroline, 1.06 g, 9.5 mmol] in toluene (10 mL). After gas evolution had ceased, stirring was continued for one hour. Repeated crystallisations at −78 °C gave colorless needles (2.45 g, 90.4%), m.p. 134−151 °C (dec.). − ^{1}H NMR (C_6D_6): δ = 1.18−1.27 (m, 1 H), 1.34−1.42 (m, 1 H), 1.78−1.94 (m, 3 H), 1.99−2.03 (m, 1 H), 2.04 (s, 3, NC*H*$_3$), 3.18−3.24 (m, 1 H), 3.51 [dd, *J*(H,H) = 2.1 Hz, 11 Hz, 1 H], 3.63 [dd, *J*(H,H) = 4.7 Hz, 11 Hz, 1 H). − ^{13}C NMR: δ = 21.3 (*C*H$_2$), 27.6 (*C*H$_2$), 43.7 (N*C*H$_3$), 56.1 (N*C*H$_2$), 57.9 (N*C*H), 67.6 (O*C*H$_2$). − ^{27}Al NMR: δ = 91 ($h_{1/2}$ = 1880 Hz). − IR (Nujol, Hostaflon): $\tilde{\nu}$: 2971 vs, 2939 vs, 2907 s, 2873 vs, 2813 w, 1767 vs/1730 vs, [νAlH$_2$], 1486 w, 1477 w, 1460 s, 1451 w, 1422 m, 1381 m, 1365 m, 1351 m, 1340 m, 1319 m, 1298 m, 1281 m, 1253 m, 1241 m, 1215 m, 1193 m, 1141 s, 1097 vs, 1060 s, 1043 s, 1029 vs, 996 vs, 920 vs, 897 m, 886 m, 831 vs, 810 vs, 773 vs, 737 vs,br, 633 vs, 577 vs, 560 vs, 537 vs cm^{-1}. − MS (70 eV): *m/z* = 286 [M$^+$], 285 [M$^+$ − H], 284 [M$^+$ − 2 H], 269 [M$^+$ − 2 H − CH$_3$], 256 [M$^+$ − 2 CH$_3$], 255 [M$^+$ − H − 2 CH$_3$]. − $C_{12}H_{28}Al_2N_2O_2$ (286.32): calcd. C 50.34, H 9.86, Al 9.42, N 9.78; found C 49.29, H 9.99, Al 9.15, N 9.35.

Dimeric (−)-Ephedrinoalane (3)$_2$: As described for **2**, $AlH_3{\cdot}NMe_3$ (1.73 g, 19.4 mmol) in toluene (17.1 mL) was treated with (−)-(1*R*,2*S*)-2-dimethylamino-1-phenyl-propanol (2.68 g, 15.0 mmol) dissolved in toluene (27.3 mL). Crystallisation at −20 °C yielded **3** (2.75 g, 88.8%) as colorless crystals, m.p. 166 °C (dec.), softening at ≈139 °C. − ^{1}H NMR (C_6D_6): δ = 0.69 [d, ^{3}J(H,H) = 7.2 Hz, 6 H, 3-*H*], 1.89 (s, 6 H, NC*H*$_3$), 2.15 (s, 6 H, NC*H*$_3$), 2.47 [dq, ^{3}J(H,H) = 5.4 Hz, 2 H, 2-*H*], 4.1 (s, br., 4 H, Al*H*$_2$), 5.41 [d, ^{3}J(H,H) = 5.4 Hz, 2 H, 1-*H*], 7.06 [dd, ^{3}J(H,H) = 7.5 Hz, 2 H, *p-H*(Ar)], 7.22 [dd, ^{3}J(H,H) = 7.5 Hz, 4 H, *m-H*(Ar)], 7.55 [d,^{3}J(H,H) = 7.5 Hz, 4 H, *o-H*(Ar)]. − ^{13}C NMR (C_6D_6): δ = 10.5 (*C*H$_3$), 40.6 (N*C*H$_3$), 46.2 (N*C*H$_3$), 65.5 (N*C*H), 72.9 (O*C*H), 127.3, 127.7, 127.9 (*C*−Ar), 140.9 [*i-C*(Ar)]. − ^{27}Al NMR (C_6D_6): δ = 96 ($h_{1/2}$ = 4260 Hz) − IR (Nujol, Hostaflon): $\tilde{\nu}$: 3082 m, 3060 m, 3024 s, 3007 s, 2989 vs, 2925 s, 2901 vs, 2890 vs, 2869 vs, 2847 s, 2798 m, 1811 vs/1776 vs/1703 vs, br.(ν AlH$_2$), 1604 m, 1492 m, 1463 vs, 1449 vs, 1432 vs, 1406 vs, 1386 vs, 1364 m, 1349 m, 1302 m, 1243 m, 1217 m, 1196 m, 1177 m, 1129 m, 1109 vs, 1101 vs, 1070 vs, 1010 vs, 961 vs, 899 vs, 865 vs, 850 vs,sh, 824 s, 789 vs, 758 vs, 742 vs, 726 vs,sh, 716 vs, 703 vs, 661 vs, 591 vs, 574 vs; (toluene): $\tilde{\nu}$ = 1805 vs,sh, 1784 vs,br, 1748 vs,br cm^{-1}. − $C_{22}H_{36}Al_2N_2O_2$ (414.49): calcd. C 63.75, H 8.75, Al 13.02, N 6.76; found C 63.01, H 8.62, Al 12.85, N 6.40.

Dimeric *N,N*-Dimethylaminopropanolatoalane (4)$_2$:To $AlH_3{\cdot}NMe_3$ (0.84 g, 9.5 mmol) in toluene (10 mL) was added a solution of $Me_2N(CH_2)_3OH$ (0.97 g, 9.45 mmol) in toluene (10 mL) at −10 °C, while stirring. Stirring was continued for 30 minutes after gas evolution had ceased. Crystallisation at −20 °C gave **4** (1.09 g, 87.9%) as colorless prisms, melting in the range of 118−133 °C. − ^{1}H NMR (C_6D_6): δ = 1.19 [tt, ^{3}J(H,H) = 5.5 Hz, 4 H, 2-*H*], 2.00 (s, 12 H, N*Me*$_2$), 2.15 [t, ^{3}J(H,H) = 5.5 Hz, 4 H, NC*H*$_2$], 3.90 [t, ^{3}J(H,H) = 5.5 Hz, 4 H, OC*H*$_2$]. − ^{13}C NMR (C_6D_6): δ = 26.3 (C2), 45.6 (N*Me*$_2$), 59.4 (NCH$_2$), 64.0 (OCH$_2$). − ^{27}Al NMR (C_6D_6): δ = 92 ($h_{1/2}$ = 1970 Hz) − IR (Nujol, Hostaflon): $\tilde{\nu}$ = 3009 s, 3004 s, 2993 s, 2960 vs, 2926 vs, 2904 vs, 2876 vs, 2866 vs, 2840 s, 2806 m, 1749 vs/1715 vs (νAlH$_2$), 1475 vs, 1455 s, 1429 vs, 1398 w, 1385 w, 1377 w, 1356 w, 1301 m, 1269 s, 1252 m, 1234 s, 1184 s, 1170 s, 1098 vs, 1087 vs, 1049 vs, 1016 vs, 967 s, 900 vs, 862 vs, 772 vs, 748 vs, 721 vs, 598 vs, 558 vs, 545 vs cm^{-1}. − $C_{10}H_{28}O_2N_2Al_2$ (262.30): calcd. C 45.79, H 10.76, Al 20.57, N 10.68; found C 44.95, H 10.99, Al 20.43, N 10.09.

Bis(ephedrino)alane (5): To a stirred solution of $AlH_3{\cdot}NMe_3$ (0.49 g, 5.5 mmol) in diethyl ether (10 mL) was added a solution of (−)-(1*R*,2*S*)-2-dimethylamino-1-phenylpropanol (1.97 g, 11.0 mmol) in tetrahydrofuran (10 mL). After addition, stirring was continued for 1 hour. All volatile material was then removed from the solution in vacuo. Crystallisation of the solid residue at −20 °C from toluene/hexane (2:1, 15 mL) gave clear crystals (1.78 g, 84%), m.p. 86 °C, softening ≈70 °C. − ^{1}H NMR (C_6D_6): δ = 0.97 [d,^{3}J(H,H) = 7.2 Hz, 6 H, 3-*H*], 2.30 (s, 6 H, NC*H*$_3$), 2.38 (s, 6 H, NC*H*$_3$), 2.31−2.36 [m,^{3}J(H,H) ≈ 5 Hz, 2 H, 2-*H*], 5.34 [d,

Table 3. Crystallographic data and data referring to data collection and structure solution of compounds **1−5**

Compound	1	**2**	**3**	**4**	**5**
Empirical formula	$C_8H_{24}Al_2N_2O_2$	$C_{12}H_{28}Al_2N_2O_2$	$C_{22}H_{36}Al_2N_2O_2$	$C_{10}H_{28}Al_2N_2O_2$	$C_{29}H_{41}AlN_2O_2$
Formula mass	234.25	286.32	414.49	262.30	476.62
Cryst. size [mm]	0.3×0.3×0.35	0.22 ×0.25 ×0.35	0.20 ×0.20 ×0.30	0.30 ×0.35 ×0.40	0.35×0.3×0.27
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	hexagonal
Space group	*P*2(1)/*n*	*P*2(1)	*P*2(1)	*P*2(1)/*c*	*P*3(1)21
a [Å]	6.073(3)	6.7904(1)	8.343(3)	6.8829(3)	12.2199(9)
b [Å]	10.645(4)	14.2260(2)	12.223(3)	10.6099(5)	12.2199(9)
c [Å]	10.721(4)	17.2732(3)	11.789(3)	11.1632(4)	15.865(1)
α [°]	90	90	90	90	90
β [°]	95.25(2)	93.632(1)	91.48(1)	102.477(1)	90
γ [°]	90	90	90	90	120
V [Å^3]	690.2(5)	1665.24(4)	1201.7(6)	795.96(6)	2051.7(3)
Z	2	4	2	2	3
ρ(calcd.), [Mg/m^3]	1.127	1.142	1.145	1.094	1.157
μ [mm^{-1}]	0.194	0.172	0.139	0.175	0.101
F(000)	256	624	448	288	774
Index range	$-1 \leq h \leq 7$ $-13 \leq k \leq 12$ $-12 \leq l \leq 7$	$-8 \leq h \leq 8$ $-18 \leq k \leq 18$ $-20 \leq l \leq 20$	$-9 \leq h \leq 9$ $-13 \leq k \leq 13$ $-13 \leq l \leq 13$	$-8 \leq h \leq 8$ $-3 \leq k \leq 13$ $-15 \leq l \leq 9$	$-14 < h < 14$ $-13 < k < 14$ $-19 < l < 19$
2 θ [°]	53.86	58.62	49.42	58.72	51.52
Temp. [K]	173(2)	193(2)	193	183(2)	200
Refl. collected	1420	9644	5920	4462	15 703
Refl. unique	1004	6368	3826	1452	2618
Refl. observed (4σ)	976	5513	3202	1295	1904
R (int.)	0.1326	0.0196	0.0239	0.0142	0.0591
No. variables	75	361	275	83	161
Weighting scheme[a] x/y	0.0906/0.1991	0.03020/0.61670	0.04300/0.000	0.0567/0.1557	0.06520/0.000
GOOF	1.122	1.074	1.014	1.094	0.923
Final R (4σ)	0.0526	0.0419	0.0379	0.0316	0.0409
Final $wR2$	0.1444	0.0850	0.0775	0.0949	0.1029
Larg. res. peak [e/Å^3]	0.416	0.168	0.141	0.159	0.280

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

^3J(H,H) = 4 Hz, 2 H, 1-*H*], {7.10−7.18 (m), 7.30 [dd, ^3J(H,H) = 7.8 Hz], 7.44 [d, ^3J(H,H) = 7.8 Hz], 20 H}. − ^{13}C NMR (C_6D_6): δ = 11.15 (*C*H$_3$), 43.5 (N*C*H$_3$), 46.5 (N*C*H$_3$), 68.2 (N*C*H), 73.0 (O*C*H), 126.2, 126.3, 128.2 (*C*−Ar), 146.5 [*i*-*C*(Ar)]. − ^{27}Al NMR (C_6D_6): δ = 83 ($h_{1/2}$ = 3690 Hz); in diethyl ether: 81 ($h_{1/2}$ = 2370 Hz). − IR (Nujol, Hostaflon): ṽ = 3081 m, 3066 m, 3023 s, 3000 vs, 2993 vs, 2980 vs, 2925 vs, 2908 vs, 2879 vs, 2865 vs, 2845 vs, 2823 vs, 2797 vs, 1777 vs,br, ν AlH_2, 1601 m, 1491 vs, 1461 vs, 1453 vs, 1447 vs, 1434 vs, 1406 m, 1386 vs, 1347 s, 1300 m, 1289 m, 1243 m, 1216 vs, 1196 m, 1167 m, 1127 vs, 1102 s, 1087 m, 1066 vs, 1017 vs, 955 vs, 921 m, 893 vs, 864 s, 855 s,sh, 826 m, 790 vs, 762 vs, 742 vs, 734 s, 710 vs, 690 vs, 675 s, 626 s, 608 vs cm^{-1}. − MS (70 eV): *m*/*z* = 384, 383 [M$^+$ − 2 H], 312, 311 [M$^+$ − $CH_3CHN(CH_3)_2$ − 2 H]. − $C_{22}H_{34}AlN_2O_2$ (385.51): calcd. C 68.54, H 8.89, N 7.27, Al 6.99; found C 67.80, H 9.25, N 6.55, Al 6.54.

X-ray Structure Determinations: Single crystals were transferred from the toluene suspensions onto precooled polyfluoroether oil (−30 °C) and the selected specimen was mounted on the tip of a glass fiber. This was transferred to the goniometer head which was cooled by a stream of N_2 gas to 193 K (LT2 device). After optically aligning the crystal, five different sets in χ of 15 frames each were collected (Δ = 0.3°), and the data were used to calculate the cell dimensions (SMART program).[16] Data collection was performed by using the hemisphere mode of the SMART program. Data for a total of 1290 frames were collected at two different χ-settings with Δ = 0.3°. The data was reduced with the program SAINT[17] and an empirical adsorption correction was applied (SADABS). The structures were solved (SHELXTL)[18] by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the H atoms bonded to Al were taken from the difference Fourier map; all others were either taken from the Fourier map or placed in calculated positions and included in the final refinement cycles. Compound **5** crystallized as **5**·0.5C_7H_8. The toluene molecule is disordered. Refinement was performed with SOF = 0.5 for two orientations. No hydrogen atoms were included for the toluene molecules. Relevant data referring to crystallography, data collection and refinement are summarized in Table 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication no. CCDC-148492−148496 (**1**−**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge C32.1 EZ, UK [Fax: (internat.) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

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