# The decomposition reaction of the dialane radical anion $[R_2Al\dot{-}AlR_2]^-$ in DME(II): crystal structures of the aluminium glycolates $[R_2Al(OCH_2)_2]K(DME)$ and $R_2Al(OCH_2)_2Al(R)(OCH_2)_2AlR_2$ $(R = CH(SiMe_3)_2)$

## Werner Uhl *, Rolf Gerding, Annegret Vester

*Fachbereich Chemie der Carl von Ossietzky Universität, Postfach 2503, D-26111 Oldenburg, Germany*

## Abstract

Tetrakis[bis(trimethylsilyl)methyl]dialane(4) (**1**) reacts with potassium in 1,2-dimethoxyethane (DME) to yield the dark blue, surprisingly stable radical anion $[R_2Al\dot{-}AlR_2]^-[K(DME)_3]^+$ (**2**) $(R = CH(SiMe_3)_2)$. An excess of potassium, however, and a longer reaction time leads to decomposition with the formation of three new compounds, which are identified now as: $[R_2Al(Me)(OC_2H_4OMe)][K(DME)]$ (**3**), $[R_2AlMe_2][K(DME)_6]$ (**4**), and the glycolato alanate $[R_2Al(OCH_2)_2][K(DME)]$ (**7**). These compounds verify that a dialkyl alanate(I) $R_2Al^-$ with aluminium in a formal oxidation state of +I is an intermediate in the course of the decomposition reaction. **7** was synthesized by the reaction of the chloro compound $Cl-AlR_2$ with $KOCH_2CH_2OK$. Its crystal structure exhibits a dialkyl aluminium fragment bound to both oxygen atoms of a chelating glycolate unit; a one-dimensional coordination polymer is formed by bridging potassium cations. As a byproduct the compound $RAl(OCH_2CH_2O)_2(AlR_2)_2$ (**8**) is isolated and characterized by a crystal structure determination showing a diglycolatomonoalkyl aluminium centre coordinated by two $AlR_2$ fragments. The central Al atom in **8** has a coordination number of five in a slightly distorted square pyramidal environment.

*Keywords:* Aluminium–aluminium bond; Radical; Potassium; Glycolate

## 1. Introduction

Tetrakis[bis(trimethylsilyl)methyl]dialane(4) (**1**) with an aluminium–aluminium bond [1] reacts with elemental potassium in 1,2-dimethoxyethane (DME) to yield the dark blue radical anion **2** [2], which from EPR measurements [2] and a crystal structure determination of the related Li(TMEDA)₂ salt [3] contains a 1e–Al–Al π-bond. Similar compounds are known with the tri(iso-propyl)phenyl substituent [4] and in two examples with central gallium atoms [5]. **2** is remarkably stable after purification by recrystallization, and solutions of **2** in DME remain unchanged at room temperature and daylight for more than four weeks. But we observe complete decomposition on the attempt to transfer a second electron to the dialuminium derivative by stirring a solution of **2** in DME with an excess of potassium over a period of three days. Three compounds are formed

without further spectroscopically detectable impurities, which we cannot separate by recrystallization or distillation.

(Me₃Si)₂HC—Al—Al—CH(SiMe₃)₂
(Me₃Si)₂HC ⟍Al—Al⟋ CH(SiMe₃)₂

**1**

$(Me_3Si)_2HC$ ⟍ $Al\dot{-}Al$ ⟋ $CH(SiMe_3)_2$ $]^-$ $[K(DME)_3]^+$
$(Me_3Si)_2HC$ ⟋ ⟍ $CH(SiMe_3)_2$
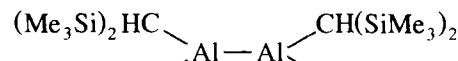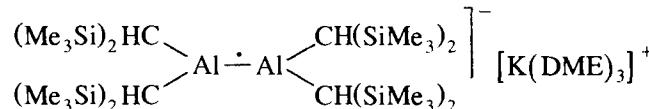
**2**

In the first part of this publication [6] we reported on the identification and synthesis by specific reactions of two components of that mixture: $[R_2Al(Me)OC_2H_4OMe][K(DME)]$ **3** and $[R_2AlMe_2][K(DME)_6]$ **4**. **3** was characterized by a crystal structure determination [6] and is a one-dimensional coordination polymer in the solid state with intermolecular interactions between potassium ions and methyl groups bound to aluminium.

* Corresponding author.

One component of the reaction mixture remained unknown until recently; as a particular characteristic it shows a $^1$H resonance in the $OCH_2$ and $OCH_3$ region with an unusual chemical shift of $\delta = 3.80$ ppm. We wish to report here the complete elucidation of the decomposition mechanism of the radical anion and the synthesis of further products, which were of interest in the course of the understanding of this mechanism and which are important due to the large interest in aluminium oxygen derivatives in recent literature [7].

$$(Me_3Si)_2HC\diagdown$$

**3**

$$(Me_3Si)_2HC\diagdown Al\diagup CH_3 \quad [K(DME)_6]^+$$

**4**
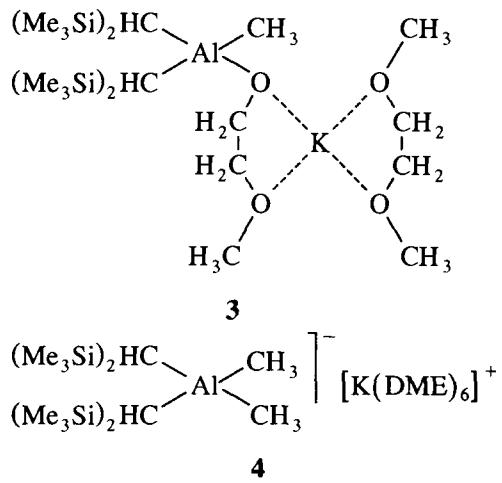
## 2. {[(Me₃Si)₂CH]₂Al(OMe)₂}⁻ (5) and [(Me₃Si)₂-CH]₂Al-OC₂H₄OMe (6)

Compounds **5** and **6** seemed to be potential candidates for the missing decomposition product, because both might be formed by an ether cleavage reaction from the radical anion and both contain a methoxy group directly bound to aluminium. **5** was synthesized by the reaction of potassium methanolate KOMe with the corresponding chloro dialkyl aluminium compound in DME according to Eq. (1). It crystallizes with two molecules DME and is readily soluble in benzene or toluene. The cryoscopically in benzene solution determined molar mass reveals half the theoretical value according to an ionic dissociation or in agreement with the high solubility to the release of one DME molecule in solution. As expected, the methoxy groups show a down-field shift in the $^1$H NMR spectrum in comparison with, for example, DME to 3.56 ppm, but not as far as in the third decomposition product.

$$(Me_3Si)_2HC\diagdown Al-Cl + 2\ KOMe$$

$$\xrightarrow{DME} \left[(Me_3Si)_2HC\diagdown Al\diagup O-CH_3 \right]^- [K(DME)_2]^+$$

**5**

$$+\ KCl \qquad\qquad\qquad (1)$$
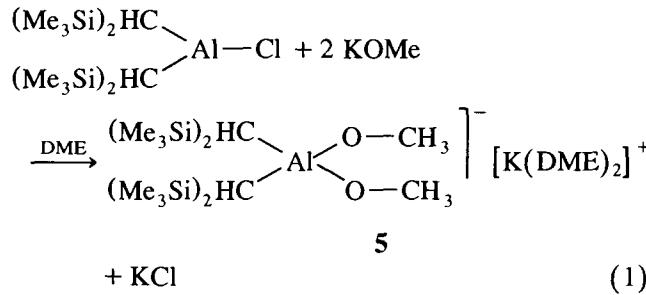
Compound **6** was synthesized by the reaction of $K-OCH_2CH_2OCH_3$ with the chloro aluminium derivative according to Eq. (2). **6** is very soluble in non-coordinating solvents, and the purification has to be carried out by sublimation under reduced pressure. The methine protons in $\alpha$-position to Al show a significant high-field shift in the $^1$H NMR spectrum up to $-1.2$ ppm, which is characteristic for bis(trimethylsilyl)methyl aluminium compounds with four-coordinated aluminium atoms [8]. The cryoscopically in benzene determined molar mass shows, however, a monomeric formula weight, so that the enhancement of the coordination number is not caused by a dimerization via Al–O–Al bridges, but probably by the intramolecular coordination of the ether oxygen atom of the 2-methoxy-1-ethanolate substituent to aluminium as shown in Eq. (2). The chemical shift of the trimethylsilyl protons and the triplett structure of the $OCH_2$ resonance at 3.7 ppm exclude that **6** is a component of the mixture obtained from the radical anion. Similar alcoholates, amides or thiolates with an additional donor atom and the formation of heterocycles by the intramolecular coordination of aluminium are known in the literature [9].

$$(Me_3Si)_2HC\diagdown Al-Cl + K-OCH_2CH_2OMe$$

$$\longrightarrow (Me_3Si)_2HC\diagdown Al \cdots + KCl \qquad (2)$$

**6**
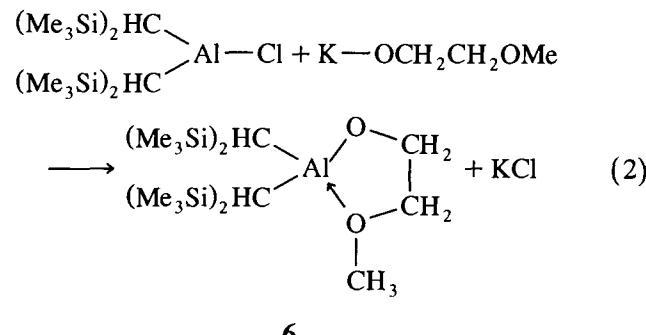
## 3. Aluminium glycolates

From the constitution of the compounds **3** and **4** [6] we supposed that a glycolate aluminium compound could have been formed. We succeeded in the synthesis of the hitherto unknown aluminium glycolates by reaction of the corresponding chloro aluminium derivative with dipotassium glycolate (Eq. (3)), which was synthesized from glycol and potassium in liquid $NH_3$ [10] and always includes small amounts of the only partially deprotonated monopotassium salt. Two compounds are isolated: the pentane insoluble potassium-{bis[bis(trimethylsilyl)methyl]-glycolatoalanate} **7** with a chelating glycolato substituent, which was characterized by NMR and IR spectra, elemental analysis and a crystal structure determination (see below) and crystallizes with different amounts of DME between a half and one molecule per formula unit. It exhibits a singulet in the proton NMR spectrum at $\delta = 3.8$ ppm and is indeed identical with the missing product of the radical anion

decomposition as shown by a comparison of all resonances in the $^1$H and $^{13}$C NMR spectra and by mixing **7** with the decomposition products.

$$(Me_3Si)_2HC \diagdown \atop (Me_3Si)_2HC \diagup Al-Cl + K-OCH_2CH_2O-K$$

$$\xrightarrow{DME} \quad \left[ {(Me_3Si)_2HC \diagdown \atop (Me_3Si)_2HC \diagup} Al {\diagup O-CH_2 \atop \diagdown O-CH_2} \right]^- [K(DME)]^+$$

**7**

$$+ \; KCl \; (+8) \qquad\qquad (3)$$
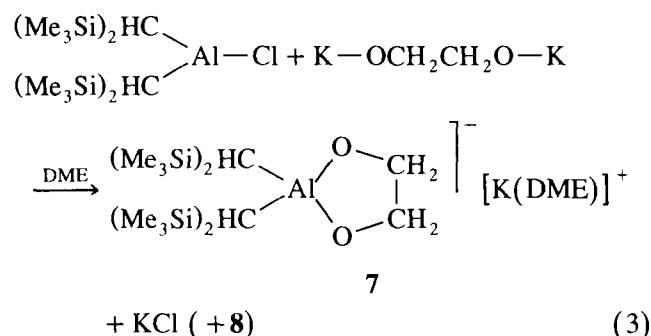
The synthesis of **7** according to Eq. (3) yields another, pentane soluble product (**8**) showing five $^1$H resonances for the trimethylsilyl groups, a complicated pattern of resonances in the OCH$_2$ region and in the $^{13}$C NMR spectrum two resonances for the OCH$_2$ groups. **8** was identified by a crystal structure determination showing a trialuminium compound with a central five-coordinated Al atom, which is bound to two chelating glycolate substituents and one bis(trimethylsilyl)methyl group. Each oxygen atom is additionally coordinated by a terminal AlR$_2$ fragment. As shown by a molar mass determination **8** dissociates in benzene solution into two fragments, which might be responsible for the complicated NMR results. Probably, the formation of **8** is caused by a KOCH$_2$CH$_2$OH impurity in the dipotassium glycolate, and the hydroxo group leads to a side reaction under formation of CH$_2$(SiMe$_3$)$_2$.

$$(Me_3Si)_2HC \diagdown \atop (Me_3Si)_2HC \diagup Al {\diagdown O \atop \diagdown O} {CH_2CH_2 \atop } Al {\diagdown R \atop } {O \diagup \atop O \diagdown} Al {\diagup CH(SiMe_3)_2 \atop \diagdown CH(SiMe_3)_2} \quad {CH_2CH_2 \atop }$$

**8** (R = CH(SiMe$_3$)$_2$)
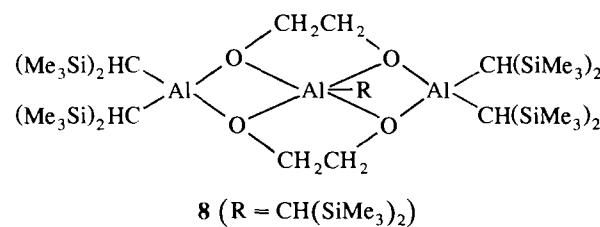
## 4. The mechanism of the reaction of 2 with potassium

As previously described, the reaction of the dialuminium radical anion **2** with an excess of potassium in DME does not give the desired dialkyl aluminium(I) species by the transfer of a second electron, but yields a mixture of three unknown decomposition products. Two of them (**3** and **4**) have already been published in the first part of this work [6]. The third is now identified as aluminium glycolate **7**. The mechanism of the decomposition reaction seems to be clear from the constitution of these three products. The first compound formed is the methyl alkoxy alanate **3**, which is the product of an insertion of a dialkyl aluminium(I) fragment into a C–O

bond of a DME molecule, or in other words of an oxidative addition of a C–O bond to Al(I) yielding the normal oxidation state of +3. The two further compounds, dimethyl alanate **4** and glycolato alanate **7**, are always detected in equimolar amounts, they are formed by a second insertion of Al(I) into the remaining O–Me bond of the DME fragment in **3**, yielding an intermediate with two Al–Me units bridged by a glycolato dianion. A following dismutation reaction leads to the more symmetrical products **4** and **7**. So, as originally intended, a dialkyl aluminate(I) with aluminium in a formal oxidation state of +1 is formed by the treatment of **2** with an excess of potassium, but only as a reactive intermediate which is unstable under the conditions needed to facilitate the electron transfer and decomposes under insertion into DME molecules.

## 5. Crystal structure of 7

**7** crystallizes in the space group $P2_1/n$ with four dimers in the unit cell (Fig. 1). Relevant crystal, data collection and structure refinement parameters are given in Table 1, atomic coordinates and isotropic displacement parameters in Table 2. The aluminium atoms are coordinated by two carbon atoms of the CH(SiMe$_3$)$_2$ substituents and two oxygen atoms of the chelating glycolate group in a distorted tetrahedral environment with the smallest angle between the oxygen atoms (93.4; 93.9°; Table 3) and the largest angle between the carbon atoms (114.9; 115.8°). Five-membered heterocycles are formed, which show nearly a twist conformation. The Al–C distances (201.7; 202.2 pm) are smaller than usually observed in compounds with tetra-coordinated Al atoms and the voluminous bis(trimethylsilyl)methyl group (~ 205 pm [8]); the Al–O bond lengths (179.7; 178.9 pm) lie within the region expected for a coordinatively saturated Al atom [13]. The Al–O and Al–C distances observed for **7** are in excellent agreement with that found in the compound R$_2$Al(OCH$_2$CH$_2$OMe)$_2$K (R = CH(SiMe$_3$)$_2$) [6] containing two terminal bonded glycolato monomethylether substituents instead of the chelating glycolate group.

**7** polymerizes, as shown in Fig. 1, via O–K–O bridges to give a one-dimensional coordination polymer along [1 0 0]. Each potassium ion is additionally coordinated by one DME molecule, so a coordination number of four is reached towards oxygen atoms. The substituents bound to the polymer are arranged in an isotactic manner, so that the alkyl groups point to one, the DME ligands to the other side of the chain. The K–O distances vary unsystematically between 268 and 283 pm and lie within the normally observed region [14]. The potassium ions are not tetrahedrally surrounded by the four oxygen atoms, but the glycolate oxygens show an approximately linear arrangement (O–K–O 160.8°
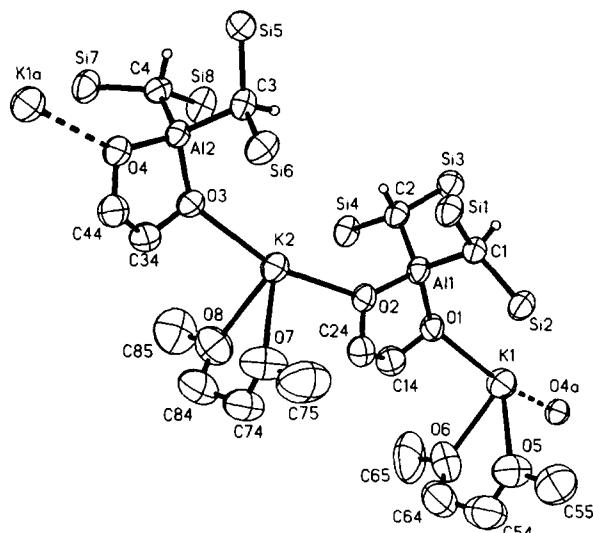
Fig. 1. Molecular structure of **7**. The thermal ellipsoids are drawn at the 40% probability level. The methylgroups of the SiMe$_3$ substituents are omitted for clarity. K1a is calculated by the symmetry operation $x - 1$, $y$, $z$ and O4a by $x + 1$, $y$, $z$.

and 160.0°). Free coordination sites result, which are occupied by methyl groups of the CH(SiMe$_3$)$_2$ substituents with the shortest contacts K1 $\cdots$ C21 and

K2 $\cdots$ C62 each with 347.6 pm. That is longer than the standard value for K–C interactions (320 pm [15]) and was also observed within our group in other potassium alanate complexes [16].

## 6. Crystal structure of 8

**8** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Relevant crystal, data collection and structure refinement parameters are given in Table 1, atomic coordinates and isotropic displacement parameters in Table 4. The crystal structure of **8** (Fig. 2) exhibits two different types of Al atom with coordination numbers five (Al1) and four (Al2 and Al3). Al1 is coordinated in a nearly ideal square pyramidal form by four oxygen atoms of two chelating glycolate anions in the base and a carbon atom in the apical position. Five-coordinated Al atoms are quite common and some recent results are cited in Ref. [17]. The Al1–C1 distance (199.0 pm; Table 5), as well as the distances of Al2 and Al3 to the $\alpha$-carbon atoms (198.8 pm), are shortened in comparison with compound **7** or other aluminium derivatives with four-coor-

Table 1
Crystal data and data collection parameters for **7** and **8**

| | 7 | 8 |
|---|---|---|
| Formula | C$_{20}$H$_{52}$AlKO$_4$Si$_4$ | C$_{39}$H$_{103}$Al$_3$O$_4$Si$_{10}$ · 0.5C$_5$H$_{14}$ |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$; Nr. 14 [11] | $P2_1/c$; Nr. 14 [11] |
| Z | 8 | 4 |
| Temperature (K) | 293 | 293 |
| $d_{calc.}$ (g cm$^{-3}$) | 1.073 | 1.038 |
| $a$ (pm) | 1588.46(8) | 2134.2(2) |
| $b$ (pm) | 1962.9(1) | 1330.5(1) |
| $c$ (pm) | 2126.6(1) | 2426.9(2) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 92.45(2) | 107.30(1) |
| $\gamma$ (°) | 90 | 90 |
| $V$ (10$^{-30}$ m$^3$) | 6624.7(6) | 6580(1) |
| $\mu$ (10$^2$ m$^{-1}$) | 3.52 | 2.71 |
| Crystal size (mm) | 0.7 × 0.7 × 0.4 | 0.5 × 0.7 × 0.9 |
| Four-cycle diffractometer | A ED 2 | A ED 2 |
| Radiation: Mo K$_\alpha$, graphitemonochromator | | |
| 2$\Theta$ range | 3.0° ≤ 2$\Theta$ ≤ 48° | 3.4° ≤ 2$\Theta$ ≤ 52° |
| Reciprocal space | 0 ≤ $h$ ≤ 18 | 0 ≤ $h$ ≤ 26 |
| | 0 ≤ $k$ ≤ 22 | 0 ≤ $k$ ≤ 16 |
| | −24 ≤ $l$ ≤ 24 | −29 ≤ $l$ ≤ 28 |
| Scan mode | $\omega - 2\Theta$ | $\omega - 2\Theta$ |
| Independent reflections | 10396 | 12918 |
| Reflections ($F > 4\sigma(F)$) | 5062 | 8022 |
| Program: SHELXTL PLUS, SHELXL-93 [12] | | |
| Refined parameters | 567 | 548 |
| $R_1 = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$ ($F > 4\sigma(F)$) | 0.0655 | 0.0614 |
| $wR^2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ | 0.1941 | 0.176 |
| Maximum largest residual (10$^{30}$ e m$^{-3}$) | 0.291 | 0.684 |

Further details of the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-404073 (**7**) and CSD-404072 (**8**).

Table 2

Atomic coordinates and equivalent isotropic displacement parameters ($10^{-22}$ m$^2$) for the atoms of the asymmetric unit in **7**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|------|------|------|------|------|
| Al(1) | 0.2102(1) | 0.79202(8) | 0.14884(8) | 4.46(4) |
| O(1) | 0.3017(2) | 0.7660(2) | 0.1953(2) | 5.3(1) |
| C(14) | 0.2741(4) | 0.7321(4) | 0.2498(3) | 7.8(2) |
| O(2) | 0.1398(2) | 0.7755(2) | 0.2110(2) | 5.2(1) |
| C(24) | 0.1869(4) | 0.7569(4) | 0.2662(3) | 7.1(2) |
| C(1) | 0.2111(3) | 0.8923(3) | 0.1286(3) | 4.2(1) |
| Si(1) | 0.1033(1) | 0.92802(9) | 0.12003(9) | 5.48(5) |
| C(11) | 0.0649(4) | 0.9534(3) | 0.1989(3) | 7.8(2) |
| C(12) | 0.0976(4) | 1.0026(3) | 0.0646(3) | 7.5(2) |
| C(13) | 0.0239(4) | 0.8665(3) | 0.0857(4) | 8.2(2) |
| Si(2) | 0.2865(1) | 0.94337(9) | 0.17869(9) | 5.48(5) |
| C(21) | 0.3968(4) | 0.9263(3) | 0.1544(3) | 7.5(2) |
| C(22) | 0.2746(4) | 1.0381(3) | 0.1704(3) | 7.7(2) |
| C(23) | 0.2813(5) | 0.9256(4) | 0.2649(3) | 8.3(2) |
| C(2) | 0.1840(3) | 0.7305(3) | 0.0745(3) | 4.9(2) |
| Si(3) | 0.2500(1) | 0.7514(1) | 0.00683(8) | 6.01(5) |
| C(31) | 0.2051(5) | 0.8239(4) | −0.0409(3) | 9.3(2) |
| C(32) | 0.2664(5) | 0.6826(4) | −0.0529(3) | 9.8(3) |
| C(33) | 0.3578(4) | 0.7758(4) | 0.0362(3) | 8.9(2) |
| Si(4) | 0.1754(1) | 0.63819(9) | 0.0934(1) | 6.00(5) |
| C(41) | 0.2814(4) | 0.5999(4) | 0.1135(4) | 10.0(3) |
| C(42) | 0.1057(4) | 0.6212(3) | 0.1614(3) | 7.8(2) |
| C(43) | 0.1230(5) | 0.5870(3) | 0.0281(3) | 8.8(2) |
| Al(2) | −0.2708(1) | 0.75024(8) | 0.14575(8) | 4.28(4) |
| O(3) | −0.1899(2) | 0.7278(2) | 0.2031(2) | 5.2(1) |
| C(34) | −0.2280(4) | 0.7087(4) | 0.2596(3) | 6.9(2) |
| O(4) | −0.3523(2) | 0.7503(2) | 0.2013(2) | 5.3(1) |
| C(44) | −0.3147(4) | 0.7420(4) | 0.2624(3) | 7.1(2) |
| C(3) | −0.2485(3) | 0.8448(3) | 0.1114(3) | 4.7(2) |
| Si(5) | −0.3178(1) | 0.86580(9) | 0.04174(8) | 5.55(5) |
| C(51) | −0.4268(4) | 0.8352(4) | 0.0553(3) | 7.6(2) |
| C(52) | −0.2770(5) | 0.8266(4) | −0.0312(3) | 8.0(2) |
| C(53) | −0.3321(5) | 0.9581(3) | 0.0213(3) | 8.8(2) |
| Si(6) | −0.2393(1) | 0.91218(9) | 0.17233(9) | 5.76(5) |
| C(61) | −0.3437(4) | 0.9309(4) | 0.2050(3) | 8.4(2) |
| C(62) | −0.1655(5) | 0.8891(3) | 0.2400(3) | 8.1(2) |
| C(63) | −0.1940(5) | 0.9948(3) | 0.1433(3) | 9.2(3) |
| C(4) | −0.2871(3) | 0.6761(3) | 0.0812(3) | 4.7(2) |
| Si(7) | −0.3644(1) | 0.60858(9) | 0.0982(1) | 6.41(5) |
| C(71) | −0.3475(6) | 0.5694(4) | 0.1770(4) | 11.6(3) |
| C(72) | −0.3695(5) | 0.5360(4) | 0.0401(4) | 11.5(3) |
| C(73) | −0.4730(4) | 0.6438(4) | 0.0966(4) | 11.0(3) |
| Si(8) | −0.1851(1) | 0.64358(9) | 0.0535(1) | 6.58(6) |
| C(81) | −0.1936(5) | 0.6139(4) | −0.0312(4) | 11.5(3) |
| C(82) | −0.1420(5) | 0.5722(4) | 0.1041(4) | 10.5(3) |
| C(83) | −0.1008(4) | 0.7106(3) | 0.0557(3) | 7.5(2) |
| K(1) | 0.47704(9) | 0.77424(8) | 0.21554(7) | 6.83(4) |
| O(5) | 0.4850(4) | 0.8420(3) | 0.3331(3) | 9.9(2) |
| C(54) | 0.5048(6) | 0.7998(6) | 0.3842(4) | 11.9(3) |
| C(55) | 0.5097(6) | 0.9103(5) | 0.3422(4) | 12.3(3) |
| O(6) | 0.4882(3) | 0.7022(3) | 0.3226(3) | 10.0(2) |
| C(64) | 0.4695(6) | 0.7325(6) | 0.3790(4) | 11.4(3) |
| C(65) | 0.4772(7) | 0.6315(5) | 0.3207(6) | 15.9(5) |
| K(2) | −0.02462(8) | 0.75472(8) | 0.22799(6) | 6.15(4) |
| O(7) | −0.0167(4) | 0.8008(3) | 0.3519(2) | 10.5(2) |
| C(74) | 0.0147(6) | 0.7517(5) | 0.3936(4) | 9.8(3) |
| C(75) | 0.0088(7) | 0.8671(5) | 0.3684(4) | 13.7(4) |
| O(8) | −0.0087(4) | 0.6618(3) | 0.3216(3) | 9.6(2) |
| C(84) | −0.0236(6) | 0.6842(5) | 0.3816(4) | 10.5(3) |
| C(85) | −0.0378(6) | 0.5948(4) | 0.3097(5) | 12.5(3) |

dinated Al atoms [8] and fall into the region usually observed for trialkyl alanes with voluminous substituents [1,8,18]. The glycolate oxygen atoms bridge the Al atoms, so that Al2 and Al3 are bonded to both glycolato substituents and four-membered $Al_2O_2$ heterocycles are formed. Owing to the higher coordination number of the oxygen atoms ($2 \times Al$; $1 \times C$) in comparison with **7**, the Al–O bonds are significantly lengthened to 187.9 pm on average. The four heterocycles in **8** are non-planar. The $Al_2O_2$ groups are folded across the $O \cdots O$ axes by 15° and 4.7°, and the five-membered $AlO_2C_2$ heterocycles reveal nearly an envelope conformation. Compounds like **8** are, to our knowledge, up to now unknown, but a similar nitrogen derivative with Me–N–$C_2H_4$–N–Me dianions and methyl aluminium groups has been published [19].

# 7. Experimental

All procedures were carried out under an atmosphere of purified argon in dried solvents (n-pentane and cyclopentane over $LiAlH_4$; DME, diisopropylether, diethylether, toluene and benzene over Na/benzophenone). Methanol, ethylene glycol and ethylene glycol monomethyl ether were treated with sodium and dis-

tilled. Cl–Al[CH(SiMe$_3$)$_2$]$_2$ was prepared according to Ref. [1].

## 7.1. [Bis(1,2-dimethoxyethane)kalium]-{dimethanolato-bis[bis(trimethylsilyl)methyl]alanate (5)

0.11 g (3.4 mmol) methanol in 10 ml DME were treated with 0.13 g (3.4 mmol) potassium in small pieces at reflux. A solution of 0.64 g (1.7 mmol) Cl–Al[CH(SiMe$_3$)$_2$]$_2$ in 10 ml DME is added to the so-produced suspension of potassium methanolate after cooling to $-30°C$. The reaction mixture is warmed to room temperature, stirred for 1 h, filtered and dried in vacuo. The residue is recrystallized from mixtures of n-pentane and DME ($20/ - 30°C$). Yield: 0.68 g (64%), colourless crystals. D.p. (under Ar; closed capillary): 54°C. Molar mass (cryoscopically in benzene): obs. 323; Calc. 627.2 g mol$^{-1}$. $^1$H NMR ($C_6D_6$; 250 MHz): $\delta = 3.56$ (6H; AlOCH$_3$); 3.05 (8H; OCH$_2$); 3.01 (12H; OCH$_3$–DME); 0.26 (36H; SiMe$_3$); $-1.20$ ppm (2H; AlCH). $^{13}$C NMR ($C_6D_6$; 62.896 MHz): $\delta = 71.2$ (OCH$_2$); 58.6 (OCH$_3$–DME); 51.3 (AlOCH$_3$); 5.2 (SiMe$_3$); 0.3 (br.; AlC). IR (paraffine; CsBr plates; cm$^{-1}$): 1285 w, 1250 sh, 1242 s $\delta$CH$_3$; 1209 w, 1194 m, 1185 sh, 1105 sh, 1095 vs $\nu$CC, $\nu$CO; 1020 s $\delta$CH; 896 s, 844 vs, 790 m, 775 m, 748 s, 735 m $\rho$CH$_3$(Si);

Table 3
Important bond lengths (pm) and angles (°) for 7

| | | | |
|---|---|---|---|
| Al(1)–O(1) | 179.6(4) | Al(1)–C(1) | 201.5(5) |
| Al(1)–O(2) | 179.7(4) | Al(1)–C(2) | 201.8(6) |
| Al(2)–O(3) | 178.9(4) | Al(2)–C(3) | 203.2(5) |
| Al(2)–O(4) | 178.9(4) | Al(2)–C(4) | 201.1(6) |
| O(1)–K(1) | 280.4(4) | O(2)–K(2) | 268.3(4) |
| K(1)–O(6) | 268.0(6) | K(2)–O(8) | 270.4(5) |
| K(1)–O(4)' | 278.1(4) | K(2)–O(7) | 278.3(5) |
| K(1)–O(5) | 283.0(6) | | |
| O(3)–K(2) | 270.8(4) | O(4)–K(1)' | 278.1(4) |
| O(1)–C(14) | 142.3(7) | O(2)–C(24) | 141.3(7) |
| O(3)–C(34) | 141.9(7) | O(4)–C(44) | 141.5(7) |
| O(5)–C(54) | 139.0(9) | O(6)–C(64) | 138 (1) |
| O(5)–C(55) | 140.9(9) | O(6)–C(65) | 139.8(9) |
| O(7)–C(74) | 138.8(8) | O(8)–C(84) | 138.0(9) |
| O(7)–C(75) | 140.3(9) | O(8)–C(85) | 141.4(9) |
| C(14)–C(24) | 152.3(9) | C(34)–C(44) | 152.8(8) |
| C(54)–C(64) | 143 (1) | C(74)–C(84) | 147 (1) |
| C(1)–Si(1) | 185.2(5) | C(2)–Si(3) | 186.3(6) |
| C(1)–Si(2) | 186.1(5) | C(2)–Si(4) | 186.3(5) |
| C(3)–Si(5) | 185.4(6) | C(4)–Si(7) | 185.4(6) |
| C(3)–Si(6) | 185.3(6) | C(4)–Si(8) | 186.0(6) |
| O(1)–Al(1)–O(2) | 93.4(2) | O(1)–Al(1)–C(2) | 113.3(2) |
| O(1)–Al(1)–C(1) | 112.4(2) | O(2)–Al(1)–C(2) | 110.7(2) |
| O(2)–Al(1)–C(1) | 110.1(2) | C(1)–Al(1)–C(2) | 114.9(2) |
| O(4)–Al(2)–O(3) | 93.9(2) | O(4)–Al(2)–C(3) | 112.3(2) |
| O(4)–Al(2)–C(4) | 112.1(2) | O(3)–Al(2)–C(3) | 109.8(2) |
| O(3)–Al(2)–C(4) | 110.8(2) | C(4)–Al(2)–C(3) | 115.8(2) |
| O(2)–K(2)–O(3) | 160.8(1) | O(4)'–K(1)–O(1) | 160.0(1) |

O(4)' calculated by $x - 1$, $y$, $z$; K(1)' calculated by $x + 1$, $y$, $z$.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters ($10^{-22}$ m$^2$) for the atoms of the asymmetric unit in **8**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Al(1) | 0.25894(4) | 0.56739(7) | 0.28662(4) | 3.33(2) |
| C(1) | 0.2509(2) | 0.5077(2) | 0.3593(1) | 4.32(8) |
| Si(1) | 0.19092(5) | 0.56795(8) | 0.39230(4) | 4.99(3) |
| C(11) | 0.1057(2) | 0.5690(3) | 0.3405(2) | 6.2(1) |
| C(12) | 0.1805(2) | 0.5010(4) | 0.4572(2) | 7.8(1) |
| C(13) | 0.2157(2) | 0.6990(3) | 0.4167(2) | 7.5(1) |
| Si(2) | 0.32598(5) | 0.45848(9) | 0.41486(4) | 5.93(3) |
| C(21) | 0.3911(2) | 0.4098(4) | 0.3843(2) | 7.8(1) |
| C(22) | 0.3664(2) | 0.5575(4) | 0.4687(2) | 8.1(1) |
| C(23) | 0.3063(2) | 0.3470(4) | 0.4548(2) | 9.6(2) |
| Al(2) | 0.17544(5) | 0.45281(7) | 0.19167(4) | 3.77(2) |
| C(2) | 0.1587(2) | 0.4471(2) | 0.1065(1) | 4.83(8) |
| Si(3) | 0.15171(6) | 0.56194(8) | 0.06116(4) | 5.99(3) |
| C(31) | 0.1424(3) | 0.5382(4) | −0.0170(2) | 9.7(2) |
| C(32) | 0.2264(3) | 0.6421(4) | 0.0885(2) | 9.4(2) |
| C(33) | 0.0769(3) | 0.6360(4) | 0.0587(2) | 10.1(2) |
| Si(4) | 0.19923(7) | 0.34058(9) | 0.07949(5) | 6.69(3) |
| C(41) | 0.2226(3) | 0.2349(4) | 0.1326(3) | 11.5(2) |
| C(42) | 0.1407(3) | 0.2835(4) | 0.0128(2) | 10.6(2) |
| C(43) | 0.2758(3) | 0.3780(4) | 0.0633(2) | 10.2(2) |
| C(3) | 0.1220(2) | 0.3680(2) | 0.2277(1) | 4.43(8) |
| Si(5) | 0.03246(5) | 0.37097(9) | 0.18773(5) | 6.05(3) |
| C(51) | −0.0211(2) | 0.3248(4) | 0.2318(2) | 9.5(2) |
| C(52) | 0.0108(2) | 0.2955(4) | 0.1191(2) | 8.5(1) |
| C(53) | 0.0055(2) | 0.5039(3) | 0.1687(2) | 8.2(1) |
| Si(6) | 0.15069(6) | 0.24701(8) | 0.26762(5) | 6.15(3) |
| C(61) | 0.1133(3) | 0.1315(3) | 0.2274(2) | 9.2(2) |
| C(62) | 0.2415(2) | 0.2306(3) | 0.2895(2) | 7.8(1) |
| C(63) | 0.1288(3) | 0.2461(4) | 0.3372(2) | 9.2(2) |
| Al(3) | 0.34106(4) | 0.74149(7) | 0.28436(4) | 3.42(2) |
| C(4) | 0.3494(2) | 0.7926(2) | 0.2099(1) | 3.77(7) |
| Si(7) | 0.31194(5) | 0.91632(7) | 0.17964(4) | 5.00(3) |
| C(71) | 0.3517(2) | 1.0255(3) | 0.2246(2) | 7.6(1) |
| C(72) | 0.2219(2) | 0.9239(3) | 0.1707(2) | 7.8(1) |
| C(73) | 0.3153(3) | 0.9391(4) | 0.1042(2) | 8.5(1) |
| Si(8) | 0.42806(5) | 0.77230(8) | 0.19047(5) | 5.37(3) |
| C(81) | 0.4895(2) | 0.6834(4) | 0.2367(2) | 7.8(1) |
| C(82) | 0.4100(3) | 0.7169(4) | 0.1162(2) | 9.8(2) |
| C(83) | 0.4762(2) | 0.8909(4) | 0.1930(3) | 9.3(2) |
| C(5) | 0.3856(2) | 0.7916(3) | 0.3636(1) | 4.73(8) |
| Si(9) | 0.47689(6) | 0.7759(1) | 0.39520(5) | 7.26(4) |
| C(91) | 0.5027(2) | 0.6426(4) | 0.3918(2) | 9.0(2) |
| C(92) | 0.5067(3) | 0.8065(5) | 0.4748(2) | 12.7(2) |
| C(93) | 0.5237(3) | 0.8585(5) | 0.3589(3) | 11.5(2) |
| Si(10) | 0.35604(6) | 0.91138(8) | 0.38873(4) | 6.02(3) |
| C(101) | 0.2704(2) | 0.9448(3) | 0.3461(2) | 7.5(1) |
| C(102) | 0.4083(3) | 1.0240(4) | 0.3870(2) | 9.7(2) |
| C(103) | 0.3516(3) | 0.8990(4) | 0.4649(2) | 9.0(2) |
| O(1) | 0.1765(1) | 0.5760(2) | 0.22894(9) | 3.88(5) |
| C(14) | 0.1524(2) | 0.6761(2) | 0.2154(1) | 4.69(8) |
| O(2) | 0.25589(9) | 0.7090(2) | 0.28418(9) | 3.69(5) |
| C(24) | 0.1891(2) | 0.7434(2) | 0.2643(2) | 4.47(8) |
| O(3) | 0.2615(1) | 0.4584(2) | 0.23690(9) | 3.88(5) |
| C(34) | 0.3253(2) | 0.4391(3) | 0.2324(2) | 5.04(9) |
| O(4) | 0.34268(9) | 0.5987(2) | 0.28157(8) | 3.60(5) |
| C(44) | 0.3647(2) | 0.5348(2) | 0.2434(2) | 4.64(8) |
| CP1 | 0.0000 | 0.5000 | 0.5000 | 25.1(9) |
| CP2A * | −0.008(1) | 0.430(2) | 0.470(1) | 20.0(8) |
| CP2B * | −0.033(1) | 0.495(2) | 0.437(1) | 19.4(8) |
| CP3 * | −0.0306(6) | 0.4146(9) | 0.4035(5) | 21.8(5) |

* From the disordered *n*-pentane molecule.
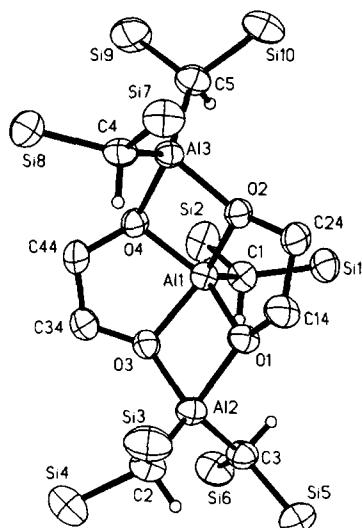
Fig. 2. Molecular structure of **8**. The thermal ellipsoids are drawn at the 40% probability level. The methylgroups of the $SiMe_3$ substituents are omitted for clarity.

680 sh, 665 s $\nu_{as}SiC$; 626 m, 608 w $\nu_s SiC$; 578 m $\nu_{as}AlO_2$; 500 w $\nu_{as}AlC_2$; 482 w $\nu_s AlC_2$; 400 $\nu_s AlO_2$; 327 w $\delta SiC$.

## 7.2. (2-methoxy-1-ethanolato)-bis[bis(trimethylsilyl)-methyl]alane (6)

0.44 g (5.8 mmol) ethylene glycol monomethyl ether are treated with 0.23 g (5.8 mmol) finely dispersed potassium in 10 ml boiling toluene. After 2 h the reaction mixture is cooled to 0°C and a solution of 2.21 g (5.8 mmol) $Cl-Al[CH(SiMe_3)_2]_2$ in 20 ml toluene is added. After warming to room temperature and further stirring for 1 h the solvent is removed in vacuo, the residue treated with 5 ml cyclopentane and filtered. The solvent is removed again and the residue sublimed in vacuo at 120°C. Yield: 1.87 g (77%); colourless, air-sensitive crystals. M.p. (under Ar; closed capillary): 61–64°C. Molar mass (cryoscopically in benzene): obs. 408; Calc. 420.9 g mol$^{-1}$. MS (310 K; 70 eV): 405.1 (9.2%; $M^+-CH_3$); 261.1 (100%; $M^+-CH(SiMe_2)_2$). $^1$H NMR ($C_6D_6$; 250 MHz): $\delta = 3.69$ (2H; t, $^3J(HH) = 6.1$ Hz; $AlOCH_2CH_2OCH_3$); 3.06 (2H; t, $^3J(HH) = 6.1$ Hz; $AlOCH_2CH_2OCH_3$); 2.93 (3H; s; $AlOCH_2CH_2OCH_3$); 0.28 (36H; s; $SiMe_3$); $-1.17$ ppm (2H; s; AlCH). $^{13}$C NMR ($C_6D_6$; 62.896 MHz): $\delta = 76.9$ and 59.7 ($OCH_2$); 58.5 ($OCH_3$); 4.7 ppm ($SiMe_3$); AlC not detected. IR (paraffine; CsBr plates; cm$^{-1}$): 1279 sh,

Table 5
Important bond lengths (pm) and angles (°) for **8**

| Al(1)–O(1) | 189.7(2) | Al(1)–O(2) | 188.6(2) |
|---|---|---|---|
| Al(1)–O(3) | 189.8(2) | Al(1)–O(4) | 187.4(2) |
| Al(1)–C(1) | 199.0(3) | | |
| Al(2)–O(1) | 187.0(2) | Al(2)–O(3) | 184.1(2) |
| Al(2)–C(2) | 199.1(3) | Al(2)–C(3) | 198.3(3) |
| Al(3)–O(2) | 186.7(2) | Al(3)–O(4) | 190.1(2) |
| Al(3)–C(4) | 198.6(3) | Al(3)–C(5) | 199.0(3) |
| O(1)–C(14) | 143.0(4) | O(2)–C(24) | 143.6(3) |
| O(3)–C(34) | 142.0(4) | O(4)–C(44) | 143.5(4) |
| C(14)–C(24) | 150.7(4) | C(34)–C(44) | 150.6(5) |
| C(1)–Si(1) | 187.8(3) | C(1)–Si(2) | 187.8(3) |
| C(2)–Si(3) | 186.3(4) | C(2)–Si(4) | 187.7(4) |
| C(3)–Si(5) | 187.0(3) | C(3)–Si(6) | 188.4(3) |
| C(4)–Si(7) | 188.2(3) | C(4)–Si(8) | 189.4(3) |
| C(5)–Si(9) | 188.0(3) | C(5)–Si(10) | 188.1(4) |
| O(4)–Al(1)–O(2) | 78.48(9) | O(3)–Al(1)–O(1) | 76.92(9) |
| O(4)–Al(1)–O(3) | 85.37(9) | O(4)–Al(1)–C(1) | 118.8(1) |
| O(2)–Al(1)–O(3) | 138.6(1) | O(2)–Al(1)–C(1) | 114.5(1) |
| O(4)–Al(1)–O(1) | 129.0(1) | O(3)–Al(1)–C(1) | 106.6(1) |
| O(2)–Al(1)–O(1) | 84.27(9) | O(1)–Al(1)–C(1) | 111.9(1) |
| O(3)–Al(2)–O(1) | 78.99(9) | O(3)–Al(2)–C(2) | 117.3(1) |
| O(3)–Al(2)–C(3) | 111.2(1) | O(1)–Al(2)–C(2) | 120.5(1) |
| O(1)–Al(2)–C(3) | 102.2(1) | C(3)–Al(2)–C(2) | 119.2(2) |
| O(2)–Al(3)–O(4) | 78.27(9) | O(2)–Al(3)–C(4) | 115.3(1) |
| O(2)–Al(3)–C(5) | 105.3(1) | O(4)–Al(3)–C(4) | 107.5(1) |
| O(4)–Al(3)–C(5) | 111.1(1) | C(5)–Al(3)–C(4) | 128.1(1) |
| C(14)–O(1)–Al(2) | 139.0(2) | C(24)–O(2)–Al(3) | 142.7(2) |
| C(14)–O(1)–Al(1) | 114.6(2) | C(24)–O(2)–Al(1) | 110.5(2) |
| Al(2)–O(1)–Al(1) | 100.3(1) | Al(3)–O(2)–Al(1) | 101.9(1) |
| C(34)–O(3)–Al(2) | 139.1(2) | C(44)–O(4)–Al(1) | 114.3(2) |
| C(34)–O(3)–Al(1) | 113.4(2) | C(44)–O(4)–Al(3) | 128.9(2) |
| Al(2)–O(3)–Al(1) | 101.3(1) | Al(1)–O(4)–Al(3) | 101.0(1) |

1249 vs $\delta CH_3$; 1190 w, 1118 s, 1055 s $\nu CC$, $\nu CO$; 1012 s $\delta CH$; 925 s, 845 vs, 780 s, 755 s, 710 w $\rho CH_3(Si)$; 672 s $\nu_{as}SiC$; 620 m $\nu_s SiC$; 582 w, 520 m, 489 m, 412 m $\nu AlC$, $\nu AlO$; 370 m, 343 vw, 325 w $\delta SiC_3$.

### 7.3. Dipotassium-glycolate

(Partly similar to Ref. [10]): $NH_3$ is condensed to 1,4 g (37.9 mmol) potassium. 1.17 g (18.93 mmol) glycol are slowly added at $-78°C$ to the resulting dark blue solution. The mixture is stirred for 2.5 h under warming to room temperature and evaporation of $NH_3$. The remaining violet powder is suspended in 60 ml DME and refluxed for 8 h, until a colourless precipitate has formed, which is separated by filtration and dried in vacuo. $K_2O_2C_2H_4$ is insoluble in hydrocarbons and ethers.

### 7.4. [(Dimethoxyethane)potassium]-{glycolato-bis[bis-(trimethylsilyl)methyl]alanate} (7) and bis(μ-glycolato)-bis{bis[bis(trimethylsilyl)methyl]alane}-[bis(trimethylsilyl)methyl]alane (8)

Solid $K_2O_2C_2H_4$ (1.45 g, 10.5 mmol) is added to a solution of 4.0 g (10.5 mmol) $Cl-Al[CH(SiMe_3)_2]_2$ in 50 ml n-pentane, and the reaction mixture stirred for 24 h at room temperature. The filtrate gives compound 8 after evaporation of the solvent and recrystallization from pentane $(20/-50°C)$. The pentane insoluble residue is treated with DME. The suspension is filtered, evaporated and the oily residue recrystallized from a mixture of diisopropylether and diethylether yielding compound 7. Yields: 1.58 g 7 (28%), colourless, slightly air-sensitive crystals; 0.377 g 8 (11%); colourless, air-sensitive crystals.

### 7.5. Characterization of 7

D.p. (under Ar; closed capillary): 246°C. $^1$H NMR $(D_8$-THF; 300 MHz): $\delta = 3.69$ (4H; $AlOCH_2$); 3.44 (4H; $OCH_2$–DME); 3.27 (6H; $OCH_3$–DME); 0.03 (36H; $SiMe_3$); $-1.51$ ppm (AlCH). $^{13}$C NMR $(D_8$-THF; 75 MHz): $\delta = 63.1$ (CO; the other CO resonances are covered by THF); 3.7 $(SiMe_3)$; 0.0 ppm (AlCH). IR (paraffine; CsBr plates; $cm^{-1}$): 1302 w, 1282 w, 1248 s $\delta CH_3$; 1169 vw, 1153 vw, 1117 vw, 1065 s, 1030 sh $\nu CC$, $\nu CO$; 1015 s $\delta CH$; 903 s, 887 sh, 843 vs, 787 sh, 775 s, 745 s, 728 sh $\rho CH_3(Si)$; 693 sh, 681 sh, 669 sh, 660 s $\nu_{as}SiC$; 631 m, 625 sh, 609 m $\nu_s SiC$; 554 m, 523 m, 504 w, 465 vw, 403 s $\nu AlO$, $\nu AlC$; 322 w $\delta SiC$.

### 7.6. Characterization of 8

D.p. (under Ar; closed capillary): 267°C. Molar mass (cryoscopically in benzene): obs. 515; calc. 998.0

g $mol^{-1}$. $^1$H NMR $(C_6D_6$; 300 MHz): $\delta = 3.79$ (2H; multiplet; $OCH_2$); 3.64 (2H; multiplet; $OCH_2$); 3.51 (4H; multiplet; $OCH_2$); 0.39, 0.341, 0.336, 0.32 and 0.26 (each 18H; $SiMe_3$); $-0.84$ (1H; AlCH); $-0.87$ (3H; AlCH); $-1.04$ ppm (1H; AlCH). $^{13}$C NMR $(C_6D_6$; 75.469 MHz): $\delta = 62.92$ and 61.70 $(OCH_2)$; 6.32, 5.90, 5.72, 5.68 and 4.98 ppm $(SiMe_3)$; AlC not detected. IR (paraffine; CsBr plates; $cm^{-1}$): 1304 m, 1260 m, 1248 s $\delta CH_3$; 1167 w, 1157 m, 1129 w, 1109 w, 1078 s, 1044 m $\nu CC$, $\nu CO$; 1020 m, 1003 m $\delta CH$; 957 m, 934 m, 847 vs, 774 m, 751 m, 721 s $\rho CH_3(Si)$; 669 m, 664 sh $\nu_{as}SiC$; 645 vw, 629 vw $\nu_s SiC$; 602 w, 530 m, 482 m, 436 w, 420 w $\nu AlC$, $\nu AlO$; 387 vw, 343 vw $\delta SiC$.

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