

## Reactions of trimethylaluminium with aliphatic diols

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Received 28 June 1995

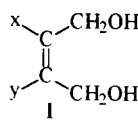
### Abstract

The reactions of trimethylaluminium with aliphatic diols, derivatives of 1,4-butandiol and 1,3-propandiol were studied. A mixture of linear and cyclic organoaluminium compounds were the products of these reactions carried out for  $\text{AlMe}_3$ :diol molar ratios of 3:2 or greater. One of the products isolated in all the studied reactions was a complex of a formula  $\text{Me}_5\text{Al}_3[\text{diol}(-2\text{H})]_2$  possessing one central five-coordinated aluminium atom and two terminal four-coordinated aluminium atoms. All the complexes were characterized by means of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{27}\text{Al}$  NMR spectra, elemental analysis and molecular weight determination.

**Keywords:** Aluminium; Aliphatic diols; Complexes; Spectroscopy; Isomers

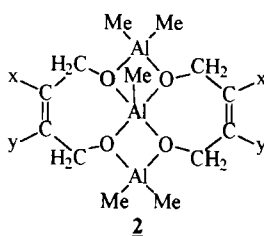
### 1. Introduction

We have previously studied reactions of trimethylaluminium with *cis*-1,4-but-2-en-diol derivatives of a general formula **1** [1–3]:



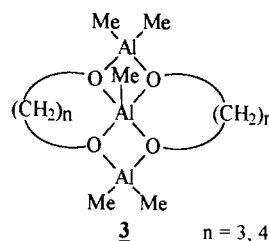
where  $x = y = \text{H}$ ;  $x = \text{SiMe}(\text{OSiMe}_3)_2$ ,  $y = \text{H}$ ;  $x, y = -\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ .

Complexes of the general formula **2** were one of the reaction products isolated and characterized by means of spectroscopic methods. These complexes possess one central five-coordinated aluminium and two terminal



four-coordinated aluminium atoms.

In this paper we present the results of our studies on the reactions of trimethylaluminium with saturated diols, derivatives of 1,4-butandiol and 1,3-propandiol. These diols do not possess a rigid  $\text{C}=\text{C}$  structure and can react with trimethylaluminium to form a mixture of linear and cyclic organoaluminium compounds. One of the products isolated in all of the studied reactions was a complex **3** of a structure analogous to the complex **2**.

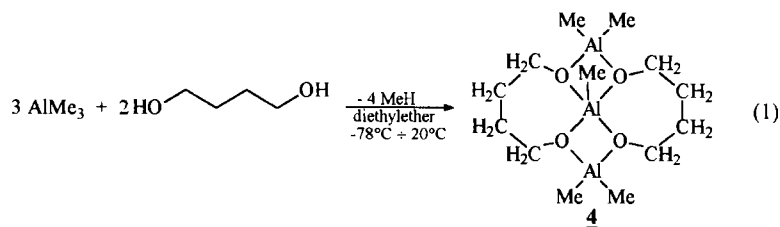


### 2. Results

The reactions of trimethylaluminium with saturated diols were carried out at an  $\text{AlMe}_3$ :diol molar ratio of 3:2, similarly to the previously studied reactions of trimethylaluminium with *cis*-1,4-but-2-en-diol derivatives.

Trimethylaluminium reacts with 1,4-butandiol to form a mixture of organoaluminium compound. The solid complex **4** was sublimed off from this mixture ( $T = 100^\circ\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr; yield, 47%):

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The  $^1\text{H}$  NMR spectrum of **4** (Fig. 1) revealed two multiplets of  $\text{CH}_2\text{O}$  and  $\text{CH}_2$  protons and three singlets of the protons of methyl groups bonded to aluminium with a  $-\text{CH}_2\text{O}-:-\text{CH}_2:\text{CH}_3\text{Al}$  integration ratio of 8:8:15 which was fully consistent with the structure **4**. The integration ratio of three singlets of methyl groups at  $-0.50$ ,  $-0.56$  and  $-0.57$  ppm was 2:2:1. The first two of these signals were assigned to four methyl groups bonded to two four-coordinated aluminium atoms and a signal at  $-0.57$  ppm corresponded to one methyl group bonded to the central five-coordinated aluminium atom.

The following signals were present in  $^{13}\text{C}$  NMR spectrum: 62.42 ppm ( $-\text{CH}_2\text{O}$ ), 30.61 ( $-\text{CH}_2-$ ) and two broad signals at  $-10.83$  ppm and  $-11.66$  ppm  $\text{CH}_3$  groups bonded to four- and five-coordinated aluminium atoms respectively. The presence of only one

signal of  $\text{CH}_2\text{O}$  carbon atoms and one signal of  $\text{CH}_2$  carbon atoms is consistent with the proposed structure of **4**.

Two broad signals at 159.7 ppm and 74.0 ppm were present in the  $^{27}\text{Al}$  NMR spectrum of **4**. The signal at 159.7 ppm appeared in the region characteristic for four-coordinated aluminium and the signal at 74.0 ppm in the region characteristic for five-coordinated aluminium.

The molecular weight of **4** determined cryoscopically was 335 (calculated, 332) which indicated an association degree equal to 1.0. Percentages of aluminium and methyl groups bonded to aluminium were very close to their theoretical values (see Section 4) which further confirmed the proposed structure of **4**.

Trimethylaluminium reacts with 1,3-propanediol to form **5** with a relatively low yield (8.5%):

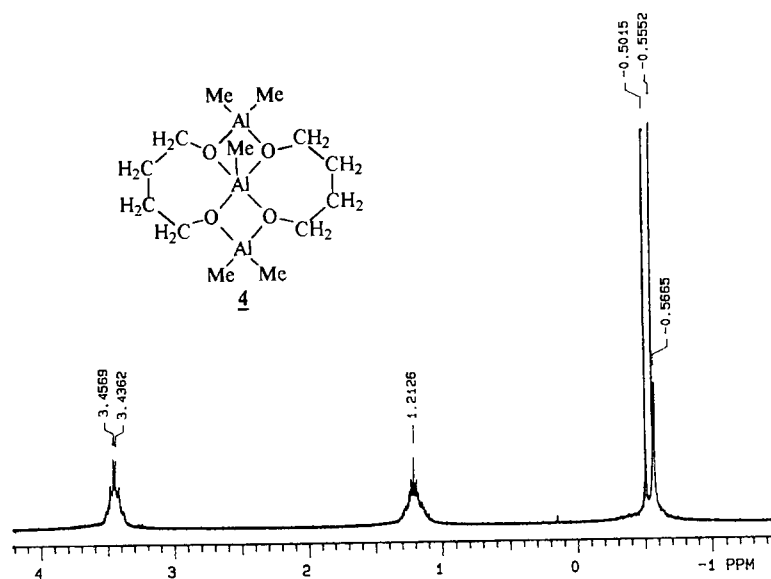
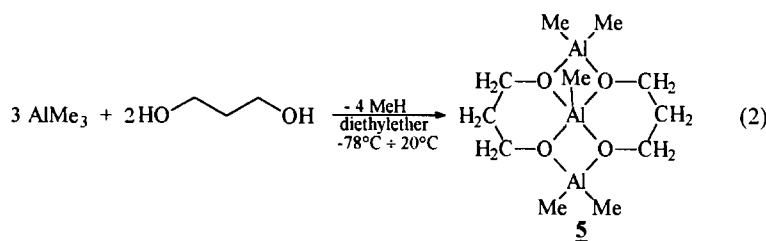
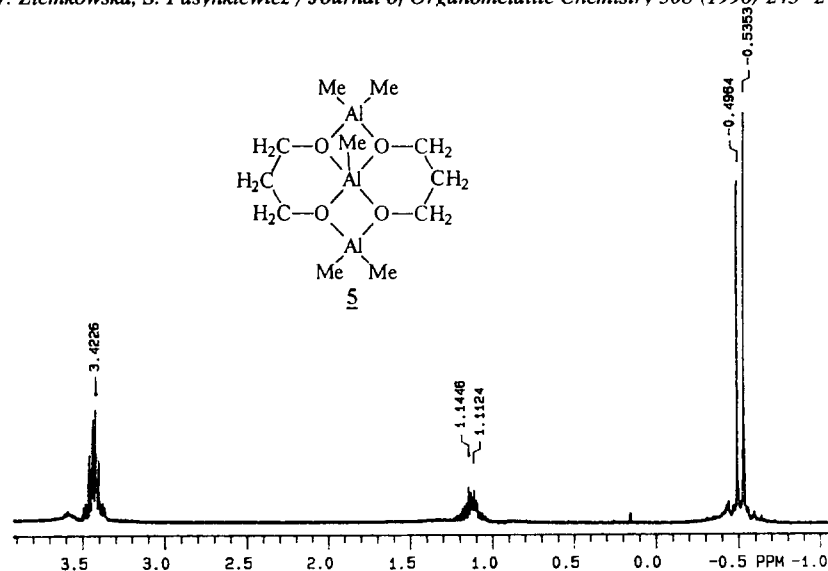


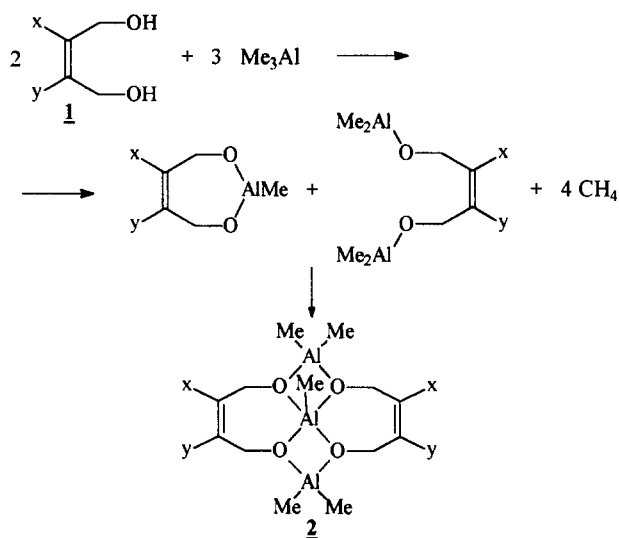
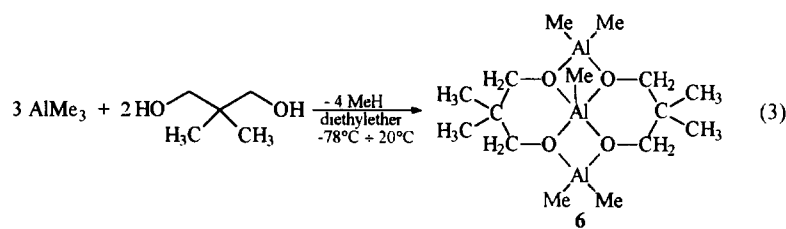
Fig. 1.  $^1\text{H}$  NMR spectrum of **4**.

Fig. 2.  $^1\text{H}$  NMR spectrum of **5**.

The  $^1\text{H}$  NMR spectrum of **5** showed two multiplets of  $\text{CH}_2\text{O}$  and  $\text{CH}_2$  protons and two singlets ( $-0.50$  and  $-0.54$  ppm) of the protons of methyl groups bonded to aluminium with a  $-\text{CH}_2\text{O}- : -\text{CH}_2- : \text{CH}_3\text{Al}$  integration ratio of 8 : 4 : 15 (Fig. 2) which was consistent with the proposed structure of **5**. The integration ratio of two singlets assigned to the protons of methyl groups was 2 : 3. The first signal at  $-0.50$  ppm was assigned to the protons of two methyl groups bonded to the terminal four-coordinated aluminium and the second signal at  $-0.54$  ppm was the result of overlapping of

the signals of two methyl groups bonded to four-coordinated aluminium and of one methyl group bonded to five-coordinated aluminium. Two signals at 153.6 and 67.0 ppm were present in the  $^{27}\text{Al}$  NMR spectrum of **5** which confirmed the existence of two kinds of aluminium atoms (four- and five-coordinated). The association degree of **5** calculated on the basis of molecular weight measurements was 1.1.

The reaction of 2,2-dimethyl-1,3-propanediol with trimethylaluminium proceeds with the formation of a solid complex **6** with 7.2% yield:



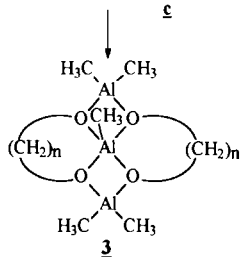
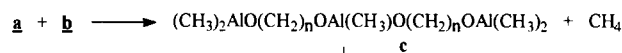
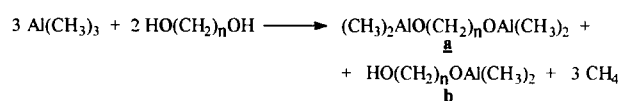
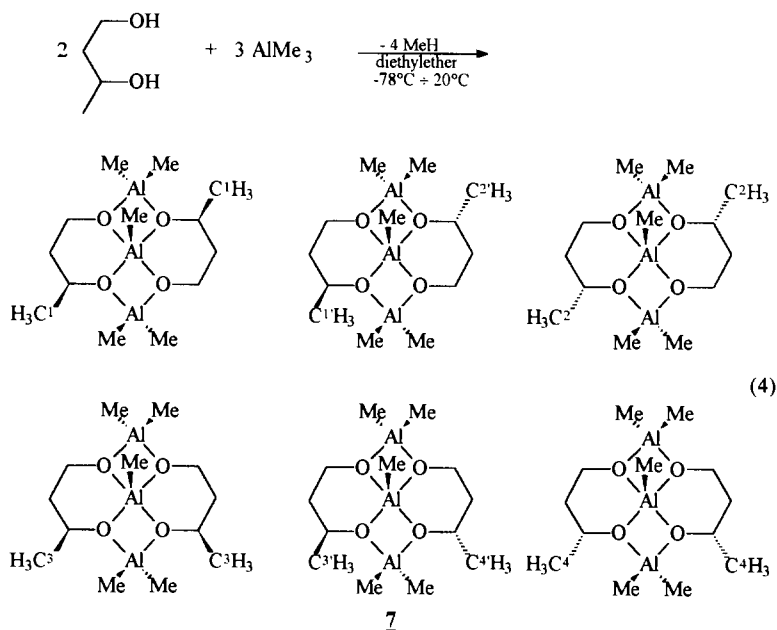
Scheme 1.

The complex **6** was isolated from the reaction mixture by sublimation ( $T = 100^\circ\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr) and was characterized by spectroscopic methods. The following signals were present in the  $^1\text{H}$  NMR spectrum of **6**: 3.34, 2.99 ppm (two doublets;  $\text{CH}_2\text{O}$ ;  $J = 10.4$  Hz), 0.91 ppm and 0.14 ppm (singlets,  $\text{CH}_3$ ),  $-0.46$ ,  $-0.52$ ,  $-0.57$  ppm (singlets,  $\text{CH}_3\text{Al}$ ). The  $-\text{CH}_2\text{O}- : \text{CH}_3 : \text{CH}_3\text{Al}$  integration ratio was 8 : 12 : 15 which was fully consistent with the proposed structure of **6**. The signals of the protons of methyl groups bonded to aluminium were in the 2 : 2 : 1 ratio. The first two of them ( $-0.46$  and  $-0.52$  ppm) were assigned to four methyl groups bonded to four-coordinated terminal aluminium atoms and the third signal at  $-0.57$  ppm was assigned to the methyl group bonded to the five-coordinated central aluminium atom.

Four sharp signals at 72.37 ppm ( $\text{CH}_2\text{O}$ ), 34.43 ppm ( $\text{C}(\text{CH}_3)_2$ ), 21.53 and 21.51 ppm ( $\text{CH}_3$ ) and a very broad signal at  $-11.08$  ppm ( $\text{AlCH}_3$ ) were observed in the  $^{13}\text{C}$  NMR spectrum of **6**. Similarly as for compounds **4** and **5** there were two broad signals at 156.0 and 68.6 ppm in the  $^{27}\text{Al}$  NMR spectrum of **6**. They were assigned to four- and five-coordinated aluminium

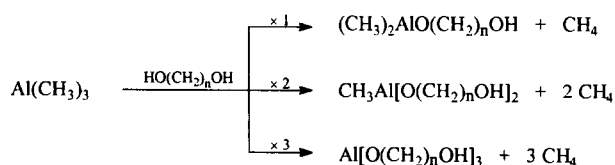
respectively. The compound **6** is monomeric in benzene as determined on the basis of molecular weight measurements.

1-Methyl-1,3-propanediol possesses a methyl group as a side chain and in the reaction with trimethylaluminium forms a mixture of six isomers of **7** with a total yield of 17.5%:

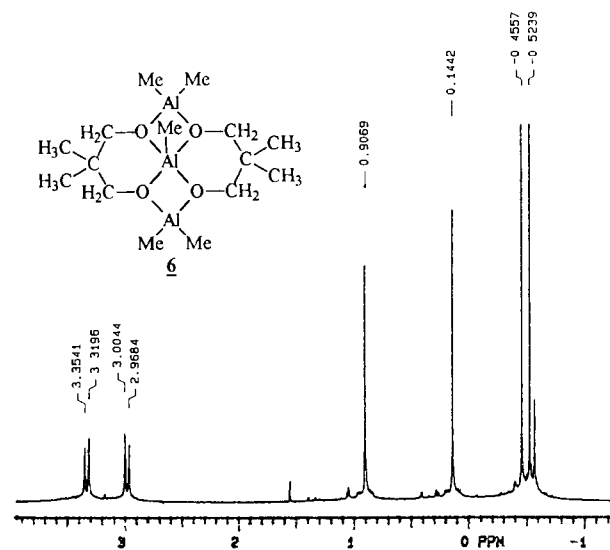


Scheme 2.

The mixture of isomers was isolated by distillation ( $T = 100^\circ\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr) as a colourless viscous liquid. An analysis of NMR spectra allowed us to propose the structure of the isomers. Most of the signals



Scheme 3.

Fig. 3.  $^1\text{H}$  NMR spectrum of **6**.

in the  $^1\text{H}$  NMR spectrum appeared as complex multiplets because of the number of isomers present in the mixture. Only protons of methyl groups  $\text{CH}_3\text{CH}$  appeared as four doublets. The analysis of the structure of isomers indicated that they were eight different kinds of methyl group proton in the six isomers. It is very probable that chemical shifts of the protons of methyl groups numbered  $\text{C}^1\text{H}_3$  and  $\text{C}^{1'}\text{H}_3$ ,  $\text{C}^2\text{H}_3$  and  $\text{C}^{2'}\text{H}_3$ ,  $\text{C}^3\text{H}_3$  and  $\text{C}^{3'}\text{H}_3$ ,  $\text{C}^4\text{H}_3$  and  $\text{C}^{4'}\text{H}_3$  (Eq. (4)) are the same or very close to each other which causes overlapping of the signals and results in an appearance of only four doublets in the  $^1\text{H}$  NMR spectrum.

These methyl groups appear in the  $^{13}\text{C}$  NMR spectra as four signals at 38.39, 38.31, 36.92 and 36.76 ppm. The other carbon atoms in  $\text{CH}_2$ ,  $\text{HCO}$  and  $\text{H}_2\text{CO}$  show in  $^{13}\text{C}$  NMR four signals each. The carbon atoms of methyl groups bonded to aluminium appear as several overlapping signals which confirms the presence of the mixture of isomers of **7**.

There were two signals at 153.0 ppm and 67.2 ppm present in the  $^{27}\text{Al}$  NMR spectrum of **7** which indicated the presence of four- and five-coordinated aluminium in the molecule. Molecular weight determined cryoscopically in benzene indicated the monomeric structure of **7**.

### 3. Discussion

It appears from our previous studies [1–3] that trimethylaluminium reacts with *cis*-2-buten-1,4-diol derivatives of the general structure **1**, with an  $\text{AlMe}_3$ :diol molar ratio of 3:2 or higher, to form complexes of the structure **2** with a high yield. All those diols possessed a double bond  $\text{C}=\text{C}$  with *cis* configuration of  $\text{CH}_2\text{OH}$  groups, indicating a facile reaction with an excess of  $\text{AlMe}_3$  according to Scheme 1.

In this work we have studied the reactions of trimethylaluminium with aliphatic diols possessing three and four carbon atoms. It was found that, besides oligomeric products, compounds of structure **3**, similar to structure **2**, were formed in these reactions. These compounds could be isolated by sublimation under reduced pressure. The results obtained suggest that aliphatic diols react with trimethylaluminium similarly as unsaturated diols to form analogues products (Scheme 2). The OH group of **b** reacts with **a** to form a linear compound **c** which stabilizes as **3** by the formation of acceptor–donor  $\text{Al}-\text{O}$  bonds.

The reactions of trimethylaluminium with aliphatic diols lead not only to the formation of **3** but also to the formation of oligomeric products, probably linear and cyclic. Trimethylaluminium can react with one, two or three molecules of aliphatic diols (Scheme 3). Products of these reactions can react further between themselves or with trimethylaluminium and diol, which leads to the formation of a mixture of oligomers.

### 4. Experimental details

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere.

$^1\text{H}$  NMR spectra were recorded with a Varian VXR 300 spectrometer, at 299.9 MHz. Chemical shifts were referenced to the residual proton signal of  $\text{C}_6\text{D}_6$  (7.15 ppm).  $^{13}\text{C}$  NMR spectra were run on the same instrument at 75.4 MHz (standard, benzene  $^{13}\text{CC}_5\text{D}_6$ , 128 ppm).  $^{27}\text{Al}$  spectra were run at 78.2 MHz (standard,  $\text{Al}(\text{acac})_3$ , 0.0 ppm). The molecular weight of the complexes was determined by the cryoscopy in benzene.

#### 4.1. Reaction of 1,4-butandiol with $\text{AlMe}_3$ (2 : 3)

1.260 g (14 mmol) of diol in 25  $\text{cm}^3$  of diethyl ether was placed in 250  $\text{cm}^3$  two-necked flask and cooled to  $-78^\circ\text{C}$ . The solution of 1.548 g (21.5 mmol) of  $\text{AlMe}_3$  in 20  $\text{cm}^3$  of diethyl ether was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm to room temperature within 2 h. Evolution of gases was observed during the course of the reaction. The solvent was distilled off and the remaining white solid was sublimed ( $T = 100^\circ\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr) yielding 1.092 g (47%) of **4**.

$^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  3.45 (m, 8H,  $\text{CH}_2\text{O}$ ), 1.21 (m, 8H,  $\text{CH}_2$ ),  $-0.50$  (s, 6H,  $\text{CH}_3\text{Al}$ ),  $-0.56$  (s, 6H,  $\text{CH}_3\text{Al}$ ),  $-0.57$  (s, 3H,  $\text{CH}_3\text{Al}$ ) ppm.  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  62.42( $\text{CH}_2\text{O}$ ), 30.61 ( $-\text{CH}_2-$ ),  $-10.83$  ( $\text{CH}_3\text{Al}$ ),  $-11.69$  ( $\text{CH}_3\text{Al}$ ) ppm.  $^{27}\text{Al}$  NMR (benzene- $d_6$ ):  $\delta$  159.7 (4-coord. Al), 74.0 (5-coord. Al) ppm. Molecular weight. Found: 335. Calc.: 332. Elemental anal. Found: Al, 24.50; hydrolysable methyl groups, 22.47. Calc.: Al, 24.40; Me, 22.59 wt.%. )

#### 4.2. Reaction of 1,3-propanediol with $\text{AlMe}_3$ (2 : 3)

The reaction was carried out as described above using 1.216 g (16 mmol) of 1,3-propanediol and 1.764 g (24.5 mmol) of trimethylaluminium. 0.207 g (8.5%) of crystalline compound **3** was obtained by sublimation ( $T = 95^\circ\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr) from the post-reaction mixture.

$^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  3.43 (m, 8H,  $\text{CH}_2\text{O}$ ), 1.13 (m, 4H,  $\text{CH}_2$ ),  $-0.50$  (s, 6H,  $\text{CH}_3\text{Al}$ ),  $-0.54$  (s, 9H,  $\text{CH}_3\text{Al}$ ) ppm.  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  63.08 ( $-\text{CH}_2-\text{O}$ ), 31.24 ( $-\text{CH}_2-$ ),  $-11.47$  ( $\text{Al}-\text{CH}_3$ ) ppm.  $^{27}\text{Al}$  NMR (benzene- $d_6$ ):  $\delta$  153.6 (4-coord. Al), 67.0 (5-coord. Al) ppm. Molecular weight. Found: 329. Calc.: 304. Elemental anal. Found: Al, 26.44; hydrolysable methyl groups, 25.20. Calc.: Al, 26.64; Me, 24.67 wt.%. )

#### 4.3. Reaction of 2,2-dimethyl-1,3-propanediol with $\text{AlMe}_3$ (2 : 3)

1.332 g (18.5 mmol) of trimethylaluminium in 25  $\text{cm}^3$  of diethyl ether was placed in 250  $\text{cm}^3$  two-necked

flask and cooled to  $-78^{\circ}\text{C}$ . The solution of 1.248 g (12 mmol) of diol in 20 cm<sup>3</sup> of diethyl ether was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm to room temperature within 2 h. Evolution of gases was observed during the course of the reaction. The solvent was distilled off and the remaining white solid was sublimed ( $T = 100^{\circ}\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr) to give 0.156 g (7.2%) of a solid compound **6**.

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  3.34 (d, <sup>2</sup>*J* = 10.4 Hz, 4H, CH<sub>2</sub>O), 2.99 (d, <sup>2</sup>*J* = 10.4 Hz, 4H, CH<sub>2</sub>O), 0.91 (s, 6H, CH<sub>3</sub>), 0.14 (s, 6H, CH<sub>3</sub>C),  $-0.46$  (s, 6H, CH<sub>3</sub>Al),  $-0.52$  (s, 6H, CH<sub>3</sub>Al),  $-0.57$  (s, 3H, CH<sub>3</sub>Al) ppm. <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>):  $\delta$  72.37(CH<sub>2</sub>O), 34.43 (C(CH<sub>3</sub>)<sub>2</sub>), 21.53, 20.51 (CH<sub>3</sub>),  $-11.08$  (CH<sub>3</sub>Al) ppm. <sup>27</sup>Al NMR (benzene-*d*<sub>6</sub>):  $\delta$  156.0 (4-coord. Al), 68.6 (5-coord. Al) ppm. Molecular weight. Found: 358. Calc.: 362.

#### 4.4. Reaction of 1-methyl-1,3-propandiol with AlMe<sub>3</sub> (2:3)

The reaction was carried out as described in 4.1 using 1.080 g (12 mmol) of 1-methyl-1,3-propandiol and 1.332 g (18.5 mmol) of trimethylaluminium. 0.349 g (17.5%) of product **7** was distilled off ( $T = 110^{\circ}\text{C}$ ;  $p = 1 \times 10^{-3}$  Torr) from the reaction mixture as a viscous colourless liquid.

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  3.75, (m, 2H, HCO), 3.44, (m, 4H, CH<sub>2</sub>O), 1.39, 1.24, 0.95, 0.80 (four multiplets, 4H, CH<sub>2</sub>), 1.002, 0.980, 0.965, 0.946 (four doublets, <sup>3</sup>*J*  $\approx$  1.5 Hz, 6H, CH<sub>3</sub>), from  $-0.448$  to  $-0.537$  (several singlets, 15H, CH<sub>3</sub>Al) ppm. <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>):  $\delta$  70.67, 70.57, 70.38, 70.27 (HCO), 61.68, 61.50, 61.44, 61.22 (H<sub>2</sub>CO), 30.39, 38.31, 36.92, 36.76(CH<sub>3</sub>), 24.17, 24.14, 23.72, 23.64 (CH<sub>2</sub>) from  $-9.33$  to  $-11.63$  (several signals CH<sub>3</sub>Al) ppm. <sup>27</sup>Al NMR (benzene-*d*<sub>6</sub>):  $\delta$  153.0 (4-coord. Al), 67.2 (5-coord. Al) ppm. Molecular weight. Found: 332. Calc.: 332. Elemental anal. Found: Al, 24.2; hydrolysable methyl groups, 22.1. Calc.: Al, 24.4; Me, 22.6 wt. %.

#### Acknowledgement

The authors thank the State Committee for Scientific Research for financial support of this work (Grant 3 3413 92 03).

#### References

- [1] S. Pasynkiewicz and W. Ziemkowska, *J. Organomet. Chem.*, 423 (1992) 1.
- [2] S. Pasynkiewicz and W. Ziemkowska, *J. Organomet. Chem.*, 437 (1992) 99.
- [3] W. Ziemkowska, S. Pasynkiewicz and E. Kalbarczyk, *J. Organomet. Chem.*, 465 (1994) 93.