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Reactions of trimethylaluminium with 2-[methylbis(trimethylsiloxy)silyl]but-2-ene-1,4-diol: synthesis and structure of $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$ *

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Abstract

The reaction of trimethylaluminium with 2-[methyl-bis(trimethylsiloxy)silyl]but-2-ene-1,4-diol was studied. A viscous liquid identified as complex **1**, $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$, was formed for molar ratios $Me_3Al/diol > 3:2$. The structure of complex **1** was determined by means of ^1H, ^{13}C NMR, elemental analysis and molecular weight determination. The central, five-coordinated aluminium atom is bonded to four oxygen atoms and for the methyl group, terminal aluminium atoms are four-coordinated. At molar ratios $Me_3Al/diol = 1:1$ and $2:3$, dimers or/and higher associates insoluble or sparingly soluble in organic solvents are formed.

Introduction

Although reactions of trialkylaluminium compounds with electron donors have been extensively studied, organoaluminium chemistry of multidentate ligands remains largely unexplored. Simple products of the reactions of trialkylaluminium compounds with monodentate ligands become complicated aggregates when multidentate ligands are used in these reactions.

The syntheses and characterization of the first examples of polyhedral aluminosilsesquioxanes were reported as a result of the reaction of Me_3Al and $(^iPrO)_3Al$ with trisilanol, a tridentate ligand [1].

The reactions of the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazocyclotetradecane with organoaluminium compounds yield products of which the most striking feature is an Al_2N_2 four-membered ring occupying the central cavity of the macrocycle [2].

The reaction of bidentate phosphine ligand bis(diphenylthiophosphinoyl) methane with diisobutylaluminium hydride affords the crystalline complex

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* Dedicated to Professor Alwyn S. Davies in recognition of his outstanding contributions to organometallic chemistry.

$[Al(C_4H_9)]_2[(C_6H_5)_2P(S)CP(C_6H_5)_2(S)_2][Al(C_4H_9)_2]_2$ [3]. The central core of the complex contains an unusual S_2Al_4 fragment. All four aluminium atoms are four-coordinated. The central methylene carbon of the bidentate phosphine ligand, initially bonded to two hydrogen atoms, is bonded to two aluminium atoms (in addition to the two phosphorus atoms) and thus is the central atom of an Al_2P_2 distorted tetrahedron.

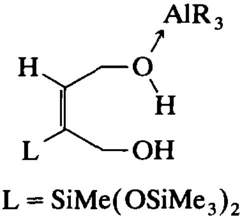
The unusual organoaluminium compound $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$ was isolated from the reaction of the bidentate ligand bis(diphenylphosphinoyl)methane with trimethylaluminium [4]. A particularly significant point about the ligand is the fact that it contains hydrogen atoms of the central methylene carbon sufficiently acidic to undergo Al–R/C–H bond cleavage. The molecule of $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$ contains two bis(diphenylphosphinoyl)methanide units bridged by three organoaluminium moieties, two dimethylaluminium fragments and one methylaluminium fragment. The central five-coordinated aluminium atom is bonded to one methyl group, to two oxygen atoms of the ligands and also to the methylene carbon atom of each ligand.

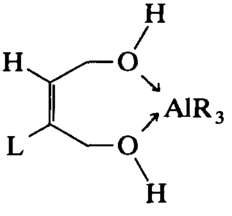
We have reported recently [5], that the product of the reaction of trimethylaluminium with 1,2-dihydroxymethylbenzene possesses a central five-coordinated aluminium atom bonded to four oxygen atoms and to one methyl group.

Complexes obtained by Robinson [4] and by us [5] have similar structures — a five-coordinated central aluminium atom and two terminal, four-coordinated aluminium atoms each bonded to two carbon and two oxygen atoms. The purpose of this work was to study the reaction of trimethylaluminium with diol {2-[methylbis(trimethylsiloxy)silyl]but-2-ene-1,4-diol}, having a bulky silyl group and to determine the structure of the product formed.

Results

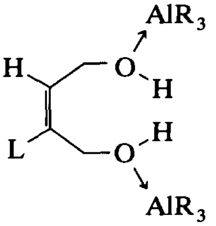
Trimethylaluminium reacts with diol at −76°C to form complexes where an aluminium atom can be bonded to one or to two oxygen atoms.



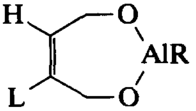


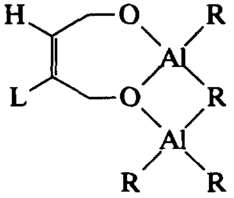
$L = SiMe(OSiMe_3)_2$
$R = Me$

The formation of a complex of one diol molecule with two Me_3Al molecules also cannot be excluded.



Methane begins to evolve at about −60°C and this process lasts until room temperature is reached. Alkoxyaluminium compounds of the following possible structures are formed during this reaction:





The further course of this reaction depends on the molar ratios of the reactants.

At molar ratios Me_3Al/diol = 3 : 2 or higher, a viscous liquid of a thermodynamically stable complex **1**, $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$, is formed in high yield. Free trimethylaluminium is present together with complex **1** in the reaction products at Me_3Al/diol = 4 : 2. It can be distilled off without changing the composition and structure of complex **1**.

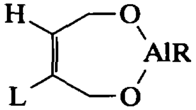
The following signals are present in the ^1H NMR spectrum of complex **1** (Fig. 1a): (a) multiplet at 6.020 ppm (H–C=C); (b) groups of signals assigned to $-CH_2-$ protons; (c) two singlets at 0.174 and 0.149 ppm (CH_3–Si) and four singlets at 0.142, 0.132, 0.130 and 0.122 ppm $[OSi(CH_3)_3]$; (d) eight singlets of CH_3–Al protons. Integration of signals is in good agreement with the calculated values for complex **1**.

Signals of $-CH_2-$ groups (Fig. 1b) are in four groups of $b_1/b_2/b_3/b_4$ = 1 : 1 : 1 : 1. Signals b_1 and b_2 are assigned to $-CH_2-$ groups situated close to $SiMe(OSiMe_3)_2$ groups. Signals b_3 and b_4 are additionally split by H–C=C protons.

CH_3 groups bonded to aluminium (Fig. 1c) give eight signals with the following chemical shifts: $d_1 = -0.433$, $d_2 = -0.446$, $d_5 = -0.472$, $d_6 = -0.489$, $d_3 = -0.510$, $d_4 = -0.545$, $d_7 = -0.681$, $d_8 = -0.705$; $d_1/d_2/d_5/d_6/d_3/d_4/d_7/d_8$ = 1 : 1 : 2 : 2 : 1 : 1 : 1 : 1.

The ^{13}C NMR spectrum (Fig. 2) comprises four signals of C=C carbons at 143.18, 141.80, 141.09 and 140.00 ppm, four signals of $-CH_2-$ groups at 61.37, 60.47, 60.29 and 59.50 ppm. Groups $OSi(CH_3)_3$ and $SiCH_3$ give two signals at 1.92 and −0.16 ppm, respectively. CH_3 groups bonded to aluminium give two signals, one (sharp) at −11.22 ppm and the second (wider) of low intensity at −13.50 ppm.

The product of the reaction at Me_3Al/diol = 1 : 1 obtained after evaporation of the solvent, is a viscous, colourless liquid. Elemental analysis shows that 94% of methyl groups reacted to give methane and the percentage of aluminium is close to that of the monomeric compound.



Very broad signals of CH_3–Al, CH_2, C=CH, CH_3–Si and CH_3–OSi groups are present in the ^1H and ^{13}C NMR spectra of the product. This indicates that it is a mixture of various associates. The physical state of the product (very viscous liquid) and its good solubility in toluene indicate a low degree of association.

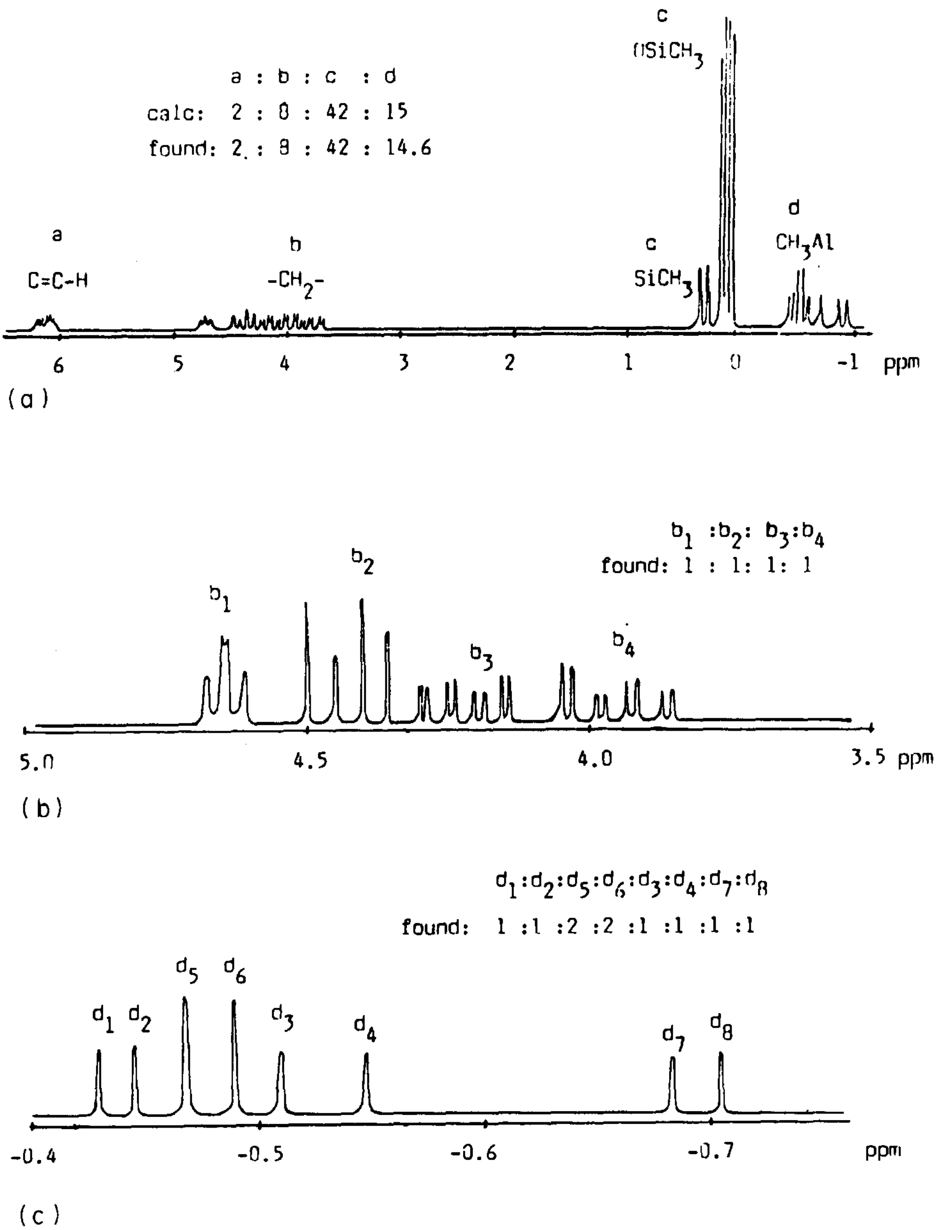


Fig. 1. ^{1}H NMR spectrum of $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$. (a) The whole spectrum; (b) the signals of the $-CH_2-$ groups; (c) the signals of the CH_3Al groups; solvent C_6D_6, standard C_6D_5H = 7.15 ppm, room temperature.

The product of the reaction carried out at molar ratios $Me_3Al/diol < 1$ is a solid, insoluble in organic solvents, forming gel in toluene. Elemental analysis shows that about 20% of the methyl groups bonded to aluminium do not react with the OH groups of diol. This means that cyclic oligomers, expanded sterically, are present in the reaction products. Difficult access to methyl groups bonded to

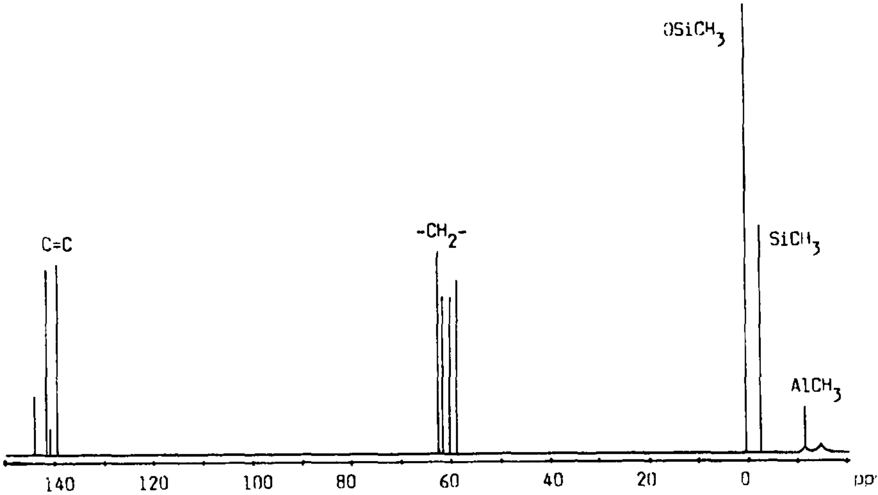


Fig. 2. ^{13}C NMR spectrum of $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$, solvent C_6D_6, standard $^{13}C_6D_6$, room temperature.

aluminium means that they do not react with OH groups. Cavities present in oligomer molecules adsorb toluene to form gels.

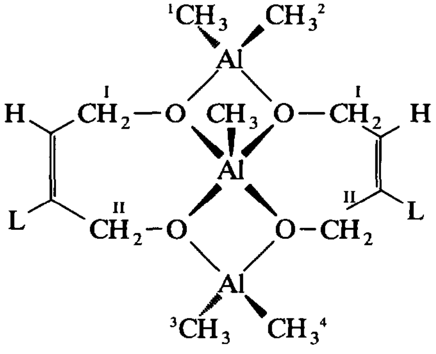
Discussion

The structure of complex **1** was established based on its ^{1}H NMR and ^{13}C NMR spectra (Figs. 1 and 2). Complex **1** is an equimolar mixture of two isomers *c* and *t* (Fig. 3). The central aluminium atom is five-coordinated and is situated above the plane formed by four oxygen atoms. These oxygen atoms together with a methyl group form a tetragonal pyramid. The remaining two aluminium atoms are four-coordinated. They are situated below a plane formed by four oxygen atoms and they are in tetrahedral coordination with two CH_3 groups and two oxygen atoms. Because of steric hindrances, both seven-membered rings are not planar and are directed above the plane formed by four oxygen atoms.

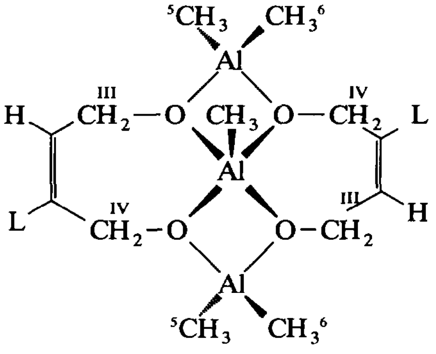
The ^{1}H NMR spectrum shows that integration of the signals assigned to protons of CH, CH_2, $SiCH_3$ and $AlCH_3$ groups (Fig. 1a) corresponds to the proposed structure of complex **1**.

A complex multiplet of C=CH protons is a result of its coupling with CH_2 protons and of different environment C=CH protons in the two isomers. CH_2 protons appear as four groups of signals (Fig. 1b). This corresponds to the isomer *c* (Fig. 3), possessing two different CH_2^{I} and CH_2^{II} groups and the isomer *t* also with two different CH_2^{III} and CH_2^{IV} groups. The signals of groups CH_2^{I} and CH_2^{III} are additionally split into doublets due to the coupling with the C=CH protons. The ratio of all four signals of CH_2 groups is 1 : 1 : 1 : 1. The protons of the methyl groups bonded to the central aluminium atoms appear as two signals d_7 and d_8 (Fig. 1c) due to their different environment in isomers *c* and *t*.

Methyl groups bonded to terminal aluminium atoms in isomer *c* give four different signals d_1, d_2, d_3 and d_4. In isomer *t*, only groups CH_3^5 and CH_3^6 have a



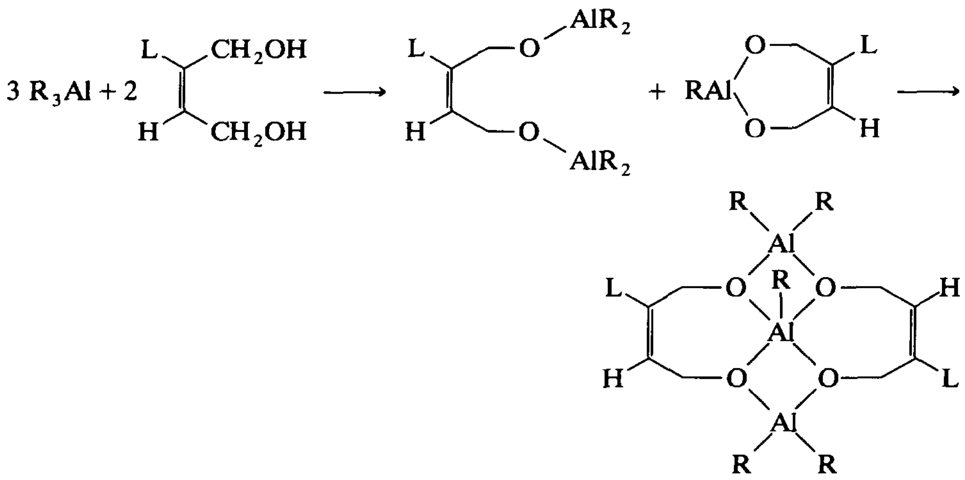
(isomer "*c*")



(isomer "*t*")

($L = SiMe(OSiMe_3)_2$)

Fig. 3. The structure of complex 1.



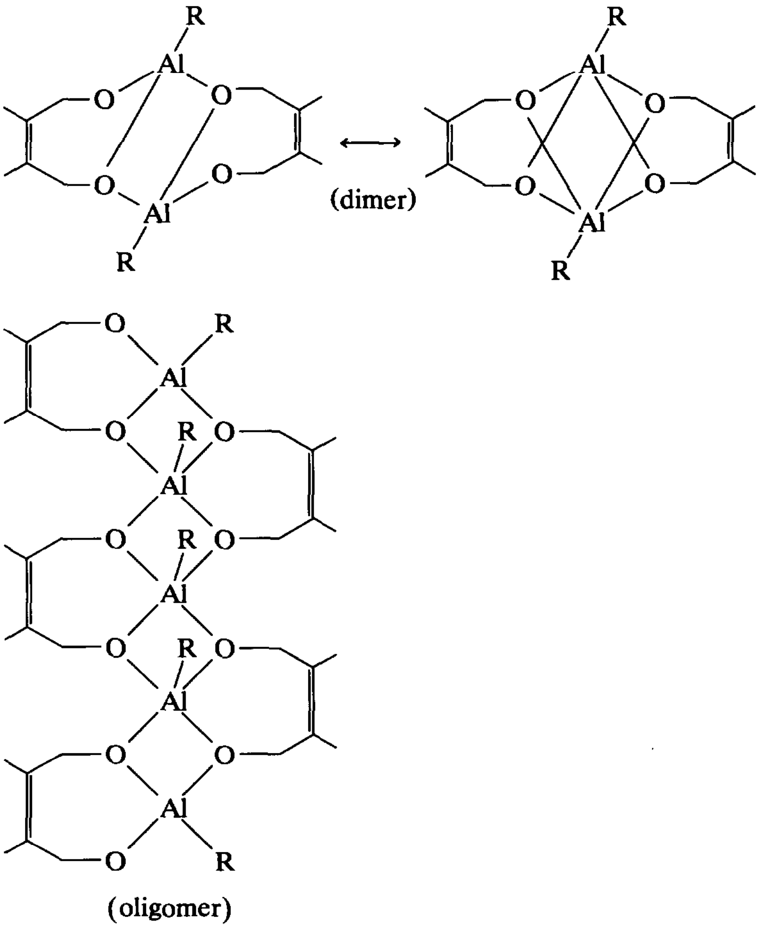
Scheme 1. Molar ratio 3:2.

different environment so their intensities (d_5 and d_6) are twice as high as the other methyl groups.

In the ^{13}C NMR spectrum, CH_2 groups appear as four different signals (Fig. 2). Methyl groups bonded to aluminium atoms give only two signals of a methyl group bonded to the central atom and of methyl groups bonded to terminal aluminium atoms.

In our previous work we have described the synthesis and structure of a complex obtained from the reaction of trimethylaluminium with 1,2-dihydroxymethylbenzene. The structure of that complex is analogous to that of complex **1** in the present work. Well defined complexes were obtained in both cases only at molar ratios Me_3Al/diol = 3:2 or higher.

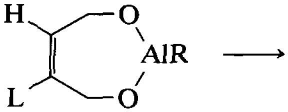
Many products can be formed in reactions of organoaluminium compounds with diol. In spite of this, only one complex is almost exclusively formed in those reactions at a molar ratio 3:2 or higher. Such a course of many reactions leading to a sole product can be explained by the highest thermodynamic and kinetic stability of complex **1**. If two different alkoxyaluminium compounds are formed in



Scheme 2. Possible structures of the associates of 1:1 reaction products.

the reaction of R_3Al with diol (Scheme 1), the coordinated saturation of all three aluminium atoms leads to the formation of complex **1**.

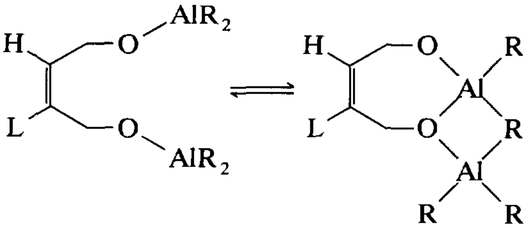
The alkoxyaluminium compounds formed can exist as dimers or higher oligomers (eq. 1).



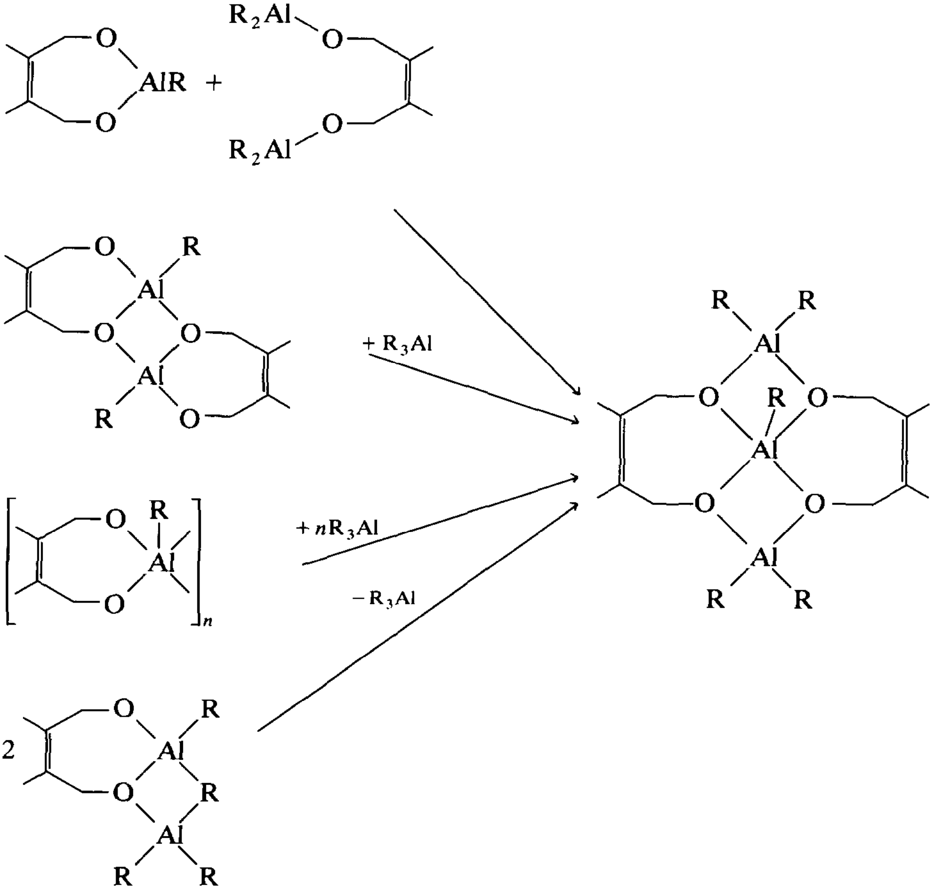
dimerization or/and association (1)

Possible structures of those associates are presented in Scheme 2.

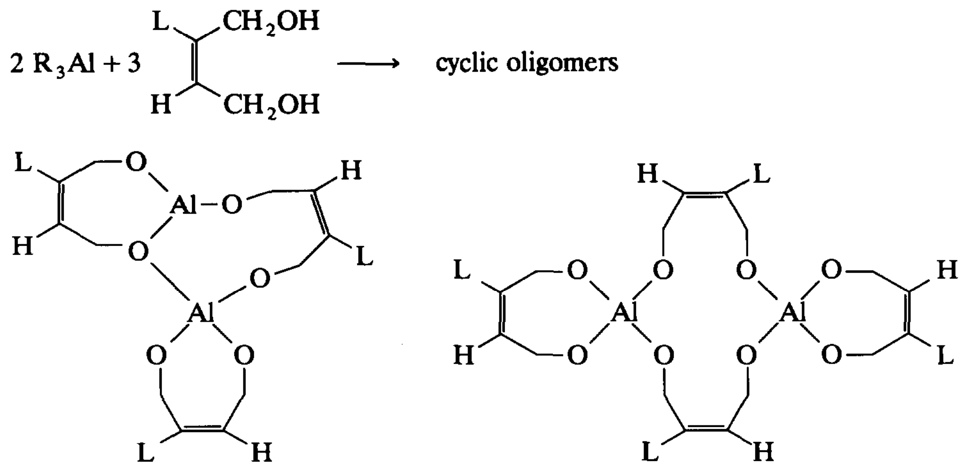
Alkoxyaluminium compound with two aluminium atoms can also have various structures (eq. 2).



(2)



Scheme 3.



Scheme 4. Molar ratio 2:3 or lower.

Regardless of the structure of the monomeric alkoxyaluminium compound or of its associates, they can react further with an excess of R_3Al to finally give a stable complex **1** (Scheme 3).

Complex **1** is the main product of the reaction carried out at a molar ratio of $Me_3Al/diol = 3:2$. For $Me_3Al/diol > 3:2$, complex **1** is also formed and an excess of Me_3Al remains unreacted.

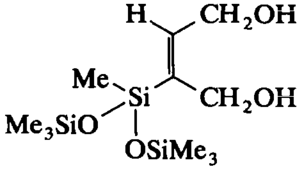
The product of the reaction carried out at $Me_3Al/diol \leq 2:3$ (an excess of diol) is a solid, insoluble in organic solvents, that forms a gel with toluene. It can be assumed that these properties are due to the structure of the reaction products being cyclic oligomers with various ring sizes (Scheme 4).

Experimental

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer.

Preparation of 2-[methyl-bis(trimethylsiloxy)silyl]but-2-ene-1,4-diol [6]*

$$Me(Me_3SiO)_2SiH + HO{-}CH_2{-}C{\equiv}C{-}CH_2OH \xrightarrow[^tBuOH]{H_2PtCl_6}$$



(A)

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* Reference number with asterisk indicates a note in the list of references.

1,4-But-3-in-diol (8.6 g, 0.1 mol), methyl-bis(trimethylsiloxy)silane (30.9 g, 0.09 mol) and t-butanol (43.0 g) were placed in a two-necked flask equipped with a magnetic stirrer and a dropping-funnel. The mixture was brought to reflux within 1 min and 2.2 g (0.01 mol) of methylbis(trimethylsiloxy)silane with a catalyst (three drops of a 0.1 *M* solution of H_2PtCl_6 in isopropanol) was added dropwise. The mixture was refluxed for 2 h, then cooled down to room temperature and the solvent was evaporated. Pure butendiol **A** was isolated from the remaining viscous liquid by distillation under reduced pressure (1×10^{-3} Torr; 70–80°C).

^1H NMR (C_6D_6): δ 6.295 (H–C=C, 1H, t); 4.308 ($-CH_2-$, 2H, s); 4.189 ($-CH_2-$, 2H, d); 3.55 (OH, 2H, s); 0.256 (CH_3–Si, 3H, s); 0.155 (CH_3–Si–O, 18H, s). ^{13}C NMR (C_6D_6): 142.33, 141.60 (C=C), 59.98, 59.56 ($-CH_2-$), 2.01 (CH_3SiO), 0.43 (CH_3Si).

Reaction of Me_3Al with 2-[methyl-bis(trimethylsiloxy)silyl]but-2-ene-1,4-diol (A) (3:2)

A solution of 1.848 g (6 mmol) of butendiol **A** in 15 ml of diethyl ether was placed in a two-necked flask equipped with a magnetic stirrer, dropping funnel and thermometer. The flask was cooled down to −76°C. A solution of 0.648 g (9 mmol) of $AlMe_3$ in 15 ml of diethyl ether was added dropwise over 1 h. The reaction mixture was then gradually warmed up to room temperature over 3 h. Gases evolved within the temperature range −60°C until room temperature; 10.7 mmol methane evolved (89.2% of the OH groups present in butendiol **A**). The solvent was distilled off from the reaction mixture (1×10^{-3} Torr, room temperature, 2 h). Traces of Me_3Al were present in the distillate. The residue was a colourless oil.

Anal. Found: Me, 10.17 wt%; Al, 9.68 wt%. $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$ calc.: Me, 9.47 wt%; Al, 10.55 wt%. ^1H NMR (Fig. 1) (C_6D_6): δ 6.020 (H–C=C, 2H, m); 4.731, 4.687, 4.682, 4.640 (b_1, $-CH_2-$, 2H, dd); 4.494, 4.448, 4.402, 4.358 (b_2, $-CH_2-$, 2H, dd); 4.298, 4.282, 4.250, 4.234, 4.209, 4.197, 4.154, 4.145 (b_3, $-CH_2-$, 2H); 4.029, 4.014, 3.977, 3.962, 3.918, 3.898, 3.869, 3.850 (b_4, $-CH_2-$, 2H); 0.174, 0.149 ($SiCH_3$, 6H, s); 0.142, 0.132, 0.130, 0.122 ($OSiCH_3$, 42H, s); −0.433, −0.446, −0.472, −0.489, −0.510, −0.545, −0.681, −0.705 (CH_3Al, 15H, s). ^{13}C NMR (Fig. 2) (C_6D_6): 143.18, 141.80, 141.09, 140.00 (C=C); 61.27, 60.47, 60.29, 59.50 ($-CH_2-$); 1.92 ($OSiCH_3$); −0.16 ($SiCH_3$); −11.22, −13.50 (CH_3Al).

Reaction of Me_3Al with butendiol A (4:2)

(a) A solution of 2.464 g (8 mmol) of butendiol **A** in 40 ml of diethyl ether was placed in a flask as above. A solution of 1.152 g (16 mmol) of $AlMe_3$ in 15 ml of diethyl ether was placed in a dropping funnel. The reaction was carried out as described above; 15.3 mmol of methane evolved (95.6% of the OH of butendiol **A**). A product **1** was obtained as a colourless oil after evaporating the solvent and volatile products (10^{-3} Torr, room temperature, 2 h).

Anal. Found: Me, 10.20 wt%; Al, 10.00 wt%. $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$ calc.: Me, 9.77 wt%; Al, 10.55 wt%. Molecular weight of **1** measured cryometrically in benzene was 846 (association degree $n = 1.1$); $[Al(CH_3)][OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2[Al(CH_3)_2]_2$ calc. MW = 768.

(b) The reaction of Me_3Al with butendiol A (4:2) was carried out again as above. Diethyl ether was distilled off from the reaction mixture under reduced pressure of an oil pump; 1.070 g of oily liquid was obtained. This was distilled at room temperature 1×10^{-3} Torr, for 7 h; 0.115 g (1.1 mmol) of $Me_3Al \cdot Et_2O$ complex was obtained as a distillate.

^1H NMR of complex $Me_3Al \cdot Et_2O$ (C_6D_6): δ 3.30 ($CH_3\mathit{CH}_2O$, 4H, q); 0.74 (CH_3CH_2O, 6H, t), −0.48 (CH_3Al, 9H, s). ^{13}C NMR of complex $Me_3Al \cdot Et_2O$ (C_6D_6): 66.25 ($CH_3\mathit{CH}_2O$); 13.61 (CH_3CH_2O); −7.80 (CH_3Al).

A distillation residue (0.951 g, 1.2 mmol) was product **1**. ^1H NMR (C_6D_6): δ 6.040 (H–C=C, 2H, m); 4.749, 4.708, 4.703, 4.659 ($-CH_2-$, 2H, dd); 4.515, 4.470, 4.421, 4.378 ($-CH_2-$, 2H, dd); 4.305, 4.290, 4.257, 4.240, 4.216, 4.203, 4.159, 4.146 ($-CH_2-$, 2H); 4.037, 4.021, 3.983, 3.968, 3.923, 3.904, 3.875, 3.855 ($-CH_2-$, 2H); 0.189, 0.163 ($SiCH_3$, 6H, s); 0.153, 0.143, 0.141, 0.136 ($OSiCH_3$, 42H, s); −0.403, −0.417, −0.443, −0.459, −0.480, −0.516, −0.653, −0.681 (CH_3Al, 15H, s). ^{13}C NMR (C_6D_6): 143.20, 141.80, 141.10, 139.98 (C=C): 61.29, 60.47, 60.31, 59.51 ($-CH_2-$); 1.91 ($OSiCH_3$); −0.15 ($SiCH_3$); −11.20, −13.48 (CH_3Al).

The reaction of Me_3Al with butendiol A (1:1)

The reaction was carried out as described above for the 3:2 reaction. A solution of 0.869 g (12 mmol) of Me_3Al in 20 ml of diethyl ether was added to a solution of 3.696 g (12 mmol) of butendiol A in 30 ml of diethyl ether; 22.5 mmol of methane evolved (93.7% of OH groups reacted). The product obtained after distilling off the solvent was a very viscous liquid. ^1H NMR (C_6D_6) (very broad signals): δ 6.44 (H–C=C); 4.85 ($-CH_2-$); 0.26 (CH_3Si, CH_3SiO); −0.32 (CH_3Al); integration of signals = 2 : 8 : 40 : 6. $\{[AlCH_3]_2[OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2\}_n$ calc.: 2:8:42:6. ^{13}C NMR (C_6D_6): 148, 126 (C=C); 64, 60 ($-CH_2-$); 2.0 (CH_3Si, CH_3SiO); −10 (CH_3Al).

Anal. Found: Me, 4.93 wt%, Al, 7.56 wt%. $\{[AlCH_3]_2[OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_2\}_n$ calc.: Me, 4.31 wt%; Al, 7.76 wt%.

The reaction of Me_3Al with butendiol A (2:3)

A solution of 1.848 g (6 mmol) of butendiol A in 40 ml of toluene was placed in a flask and cooled to −76°C. A mixture of 0.288 g (4 mmol) of Me_3Al, 1 ml of diethyl ether and 7 ml of toluene was cooled to −76°C and added to the flask. The reaction began at −76°C; 6 mmol of methane evolved. The reaction mixture was then warmed up to room temperature over 2 h. A further 3.7 mmol of methane evolved (together 80.3% of OH group reacted). The product was obtained as a colourless gel in toluene. After the solvent was distilled off, the product was an amorphous solid insoluble in organic solvent.

Anal. Found: Me, 1.9 wt%; Al, 5.39 wt%. $\{Al_2[OCH_2(SiMe(OSiMe_3)_2)C{=}C(H)CH_2O]_3\}_n$ calc.: Me, 0 wt%; Al, 5.56 wt%. It was calculated that 20% of the methyl groups bonded to aluminium remained unreacted.

References

1 F.J. Feher, T.A. Budzichowski and K.J. Weller, J. Am. Chem. Soc., 111 (1989) 7288.

2 G.H. Robinson, A.D. Rae, C.F. Campana and S.K. Byram, Organometallics, 6 (1987) 1227.

3 G.H. Robinson, M.F. Self, W.T. Pennington and S.A. Sangokoya, J. Am. Chem. Soc., 7 (1988) 2424.

4 G.H. Robinson, B. Lee, W.T. Pennington and S.A. Sangokoya, J. Am. Chem. Soc., 110 (1988) 6260.
5 S. Pasynkiewicz and W. Ziemkowska, J. Organomet. Chem., (1991) JOM 22117, in press.
6 The method for the synthesis of 2-[methyl-bis(trimethylsiloxy)silyl]but-2-ene-1,4-diol was worked out by Dr. W. Ziemkowska in the group of Professor G. Sonnek, Academy of Sciences of the GDR, Central Institute of Organic Chemistry, Berlin-Adlershof.