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Steric effects in alkylalane dioldiates [^{t}BuAl(OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O)]$_2$ a new (monoalkyl)alane *O*,*O*′-chelate complex

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Abstract

The dependence of the structure of alkylalane dioldiates on the steric bulk of the substituents on the aluminium, as well as steric hindrances of diol moiety is reported. Reactions of R$_3$Al [where R = ^{i}Bu, ^{t}Bu] with 2,4-dimethylpentane-2,4-diol, butane-1,4-diol and propane-1,3-diol lead to the formation of alkylalane dioldiates, [^{t}BuAl(OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O)]$_2$ (**1**), ^{i}Bu$_5$Al$_3$[(OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O)]$_2$ (**2**) [^{t}Bu$_2$Al(O(CH$_2$)$_4$OH)]$_2$ (**3**), ^{i}Bu$_5$Al$_3$(O(CH$_2$)$_4$O)$_2$ (**4**) and ^{t}Bu$_5$Al$_3$(O(CH$_2$)$_3$O)$_2$ (**5**). The molecular structures of **1** and **3** have been determined by single crystal X-ray diffraction. In the reactions of ^{i}Bu$_3$Al with diols the trinuclear complexes of the general formula [R$_5$Al$_3$(diol−(2H))$_2$] (**2** and **4**) are formed irrespective of the diol moiety steric hindrances. ^{t}Bu$_3$Al reacts with diols to yield the products depending on the length of diol backbone and steric hindrances of the diol moiety. The interaction of the sterically crowded 2,4-dimethylpentane-2,4-diol with ^{t}Bu$_3$Al gives the new (monoalkyl)alane *O*,*O*′-chelate complex **1**. In the case of unhindered aliphatic diols like butane-1,4-diol and propane-1,3-diol, the compound **3** with the strong intramolecular hydrogen bonding interaction and the trimetallic compound **5** were obtained, respectively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium; Diols; Steric effects

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1. Introduction

Steric effects of ligands and Al centre play important role in the chemistry of organoaluminium complexes influencing the structure of the products and coordination number on the aluminium atoms. Although typically aluminium centres are four-, five- and six-coordinate, the use of suitable bulky ligands such as mesityl [1], 2,6-di-*t*-butyl-4-methylphenoxide [2], or bis(trimethylsilyl)amide [3] allowed to obtain stable electron deficient three-coordinate organoaluminium compounds. On incorporating bulky substituents (R^1, R^2) at the nitrogen in the compounds R^{1}R^{2}NAlMe$_2$ Roesky and coworkers [4] has been able to prepare the first examples of methyl-bridged aminodimethylalanes albeit usually organoaluminium complexes are heteroatom-bridged. Recently, it has been reported by Barron and coworkers [5] that the bond distances in the compounds [R$_2$Al(μ-OC$_6$H$_4$-2-OMe)]$_2$ are controlled by the steric bulk of the aluminium alkyl substituents. Due to the potential possibility of the structure control of aluminium chelate complexes, the dependence of the organoalane chemistry from the steric factors led us to the further study of an influence of alkylaluminium groups bulkiness and steric hindrances of diol moieties on the structure of alkylalane diolates. It was earlier shown that the reactions of trimethyl- and triethylalanes with diols yield trinuclear complexes of the general formula [R$_5$Al$_3$(diol−(2H))$_2$] irrespective of steric hindrances of the diol moiety [6–11]. Although methyl- and ethylalane dioldiates are well known, the examples of *iso*-butyl- and *tert*-butylalane dioldiates are rare. It was

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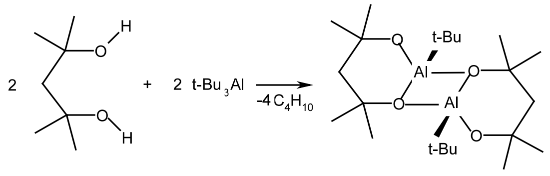
recently reported that the reaction of 2,2-dimethylpropane-1,3-diol with $^{t}Bu_3Al$ yields exclusively bimetallic complex $^{t}Bu_4Al_2(OCH_2C(CH_3)_2CH_2OH)_2$ with two unreacted hydroxyl groups. The complex is stabilised by the presence of two O–H···O intra-molecular hydrogen bonds [12].

In this work the dependence of the structure of alkylalane dioldiates on steric effects on the basis of the reactions of tri-*iso*-butyl- and tri-*tert*-butylalanes with sterically crowded and non-crowded aliphatic diols has been studied.

2. Results and discussion

The reaction of $^{t}Bu_3Al$ with one equivalent of 2,4-dimethylpentane-2,4-diol yields the unusual dimeric alkylalane dioldiate $[^{t}BuAl(OC(CH_3)_2CH_2C(CH_3)_2O)]_2$ (**1**) as the colourless solid (Eq. (1)).



(1)

1

The compound **1** has been spectroscopically and crystallographically characterised, see Section 3 and below. Data collection and structure analysis are presented in Table 1. The molecular structure of **1** is shown in Fig. 1; selected bond lengths and angles are given in Table 2. The structure of the compound **1** consists of Al_2O_2 dimeric core, each of the aluminium distorted tetrahedral coordination environment being completed by an oxygen and a carbon from ^{t}Bu group. The $OC(CH_3)_2CH_2C(CH_3)_2O$ moieties are mutually cis with respect to the Al_2O_2 core. The O(1) and O(2) atoms deviate from the C(1), Al(1), Al(2) and C(4), Al(1), Al(2) planes, respectively which is presumably caused by steric hindrances. The sums of the angles about the O(1) and O(2) atoms are equal 345.58 and 345.83°, respectively. The structural features of **1** are similar to a compound $[(Me_3Si)_3CAlO(CH_2)_4]_2$, where one oxygen atom at each Al atom is replaced by a CH_2 group and the two $Al–O–C_4$ rings take up a *cis* conformation [13].

It was found on the basis of the ^{1}H-NMR spectrum of the post-reaction mixture that unexpectedly only *cis* isomer is formed in the reaction. The further studies on the reaction of sterically hindered diols with Group 13 alkyl compounds are necessary to elucidate the factors influencing on the reaction course and products.

Table 1
Crystal data and data collection parameters for **1** and **3**

	1	**3**
Empirical formula	$C_{22}H_{46}Al_2O_4$	$C_{24}H_{54}Al_2O_4$
Formula weight	428.55	460.63
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbcn*
a (Å)	9.275(2)	20.916(4)
b (Å)	16.388(3)	14.319(3)
c (Å)	17.871(4)	10.251(2)
α (°)	90	90
β (°)	97.64(3)	90
γ (°)	90	90
V (Å^3)	2692.3(10)	3070.1(11)
Z	4	4
D_{calc} (g cm^{-3})	1.057	0.997
Absorption coefficient (mm^{-1})	0.129	0.117
$F(000)$	944	1024
Crystal size (mm)	0.25 × 0.22 × 0.18	0.40 × 0.38 × 0.30
θ Range for data collection (°)	3.62–25.00	3.25–24.99
Index ranges	$-6 \le h \le 12$, $-22 \le k \le 22$, $-24 \le l \le 24$	$-27 \le h \le 27$, $-19 \le k \le 11$, $-13 \le l \le 13$
Reflections collected	14 081	15 383
Independent reflections	4722 [$R_{int} = 0.0688$]	2697 [$R_{int} = 0.0479$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4641/0/300	2694/0/166
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0696$, $wR_2 = 0.1705$	$R_1 = 0.0535$, $wR_2 = 0.1319$
R indices (all data)	$R_1 = 0.1311$, $wR_2 = 0.2179$	$R_1 = 0.1142$, $wR_2 = 0.1680$
Goodness-of-fit on F^2	0.957	0.981°
Largest difference peak and hole (e Å^{-3})	0.318 and −0.320	0.164 and −0.140

Four-coordinate organoalanes are the mostly popular, however the compounds with aluminium atom bonded to the three oxygens and one carbon atom are rare. The structures of the earlier reported products mainly fall into two categories, monomers of the general formula $MeAlR_2 \cdot B$ where R is bulky alkoxy group, B is Lewis base possessing oxygen atom [14] and the cubane type compounds of the formulae $[R^1Al(O_3R^2)]_n$ where $R^1 = Me$, ^{i}Bu, ^{t}Bu, $R^2 = P(^{t}Bu)$, AsPh, 1,3-$(^{i}Pr)_2C_6H_3$-2-$N(SiMe_3)$, $n = 4$, 6 [15,16], $Al^{t}_6Bu_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_n$ where $R = OCCH_2C(H)(Me)O$, H [17], $[^{t}BuAl(\mu_3\text{-}O)]_n$ where $n = 6$, 9 [18] and $\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4$ [19]. Only one dimeric compound $\{[^{t}BuAl(SiR(OH)O_2)] \cdot THF\}_2$ with an eight-membered $Al_2Si_2O_4$ cycle was found [16].

Contrary to $^{t}Bu_3Al$, tri-*iso*-butylalane reacts with 2,4-dimethylpentane-2,4-diol yielding trimetallic compound $^{i}Bu_5Al_3[(OC(CH_3)_2CH_2C(CH_3)_2O)]_2$ (**2**) according to Eq. (2). The complex **2** was isolated by distillation as a colourless viscous liquid. Similar methylalane complex $Me_5Al_3[(OC(CH_3)_2CH_2C(CH_3)_2O)]_2$ was earlier crystallographically characterised and reported [10].

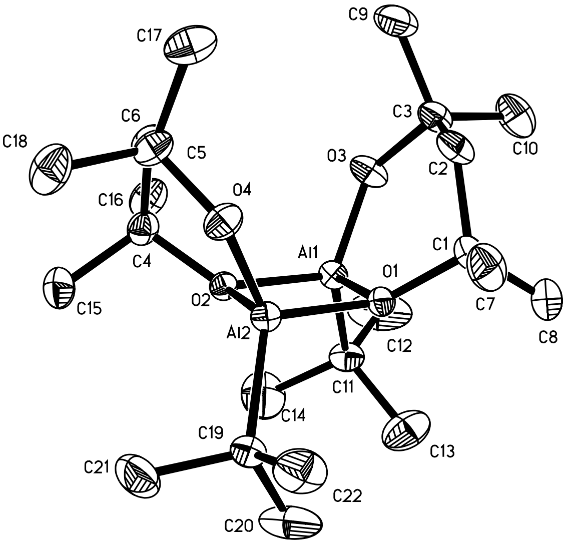
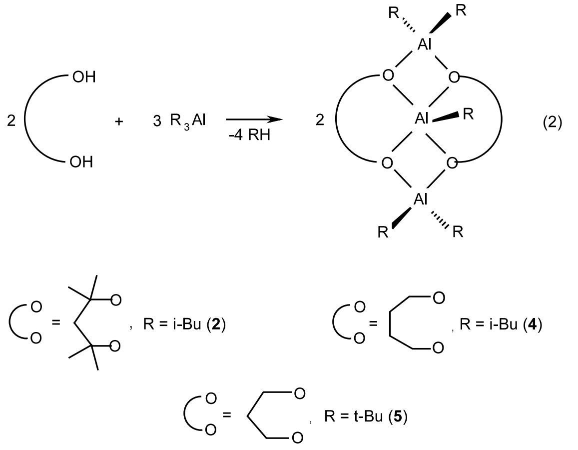


Fig. 1. The molecular structure of [^{t}BuAl(OC$(CH_3)_2CH_2C(CH_3)_2O$)]$_2$ (**1**). Thermal ellipsoids are shown at the 30% level, and all hydrogens are omitted for clarity.

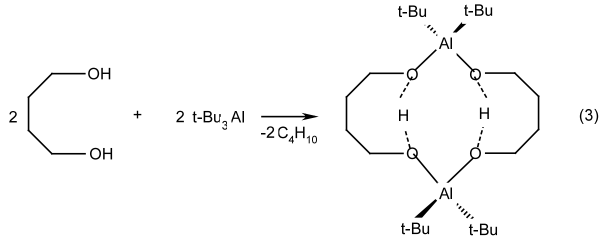
Table 2
Selected bond lengths (Å) and angles (°) in [^{t}BuAl(OC$(CH_3)_2$-$CH_2C(CH_3)_2O$)]$_2$ (**1**)

Bond lengths			
Al(1)–O(3)	1.702(3)	Al(2)–O(4)	1.702(3)
Al(1)–O(2)	1.839(3)	Al(2)–O(1)	1.845(3)
Al(1)–O(1)	1.847(2)	Al(2)–O(2)	1.848(2)
Bond angles			
O(3)–Al(1)–O(2)	116.50(14)	O(4)–Al(2)–O(2)	102.99(13)
O(3)–Al(1)–O(1)	103.18(13)	O(1)–Al(2)–O(2)	82.94(11)
O(2)–Al(1)–O(1)	83.13(11)	Al(2)–O(1)–Al(1)	96.88(11)
O(4)–Al(2)–O(1)	117.63(13)	Al(1)–O(2)–Al(2)	97.03(11)



The structure of **2** was determined on the basis of NMR spectra, molecular weight measurements and elemental analysis. ^{1}H-NMR spectrum reveals the signals of two ^{i}BuAl groups *syn* and the signals of two ^{i}BuAl groups *anti* (the doublets at 1.22 and 1.20, doublets at 0.29 and 0.26 ppm) to the ^{i}Bu group bonded to the central aluminium atom. The $(CH_3)_2C$ groups of the diol moiety are inequivalent and the CH_3 protons show two singlets at 1.38 and 1.28 ppm.

The reaction of ^{t}Bu$_3$Al with one equivalent of butane-1,4-diol allows for the isolation of the dimeric bimetallic product [^{t}Bu$_2$Al(O$(CH_2)_4$OH)]$_2$ (**3**) possessing two hydroxyl groups of diol moieties and stabilised by two intra-molecular hydrogen bonds.



3

In recent years, it has been demonstrated that inter- and intra-molecular hydrogen bondings play significant role in the structure engineering of Group 13 compounds incorporating multidentate ligands [20]. The NMR spectroscopy of the compound **3** is consistent with the formulation, see Section 3. The molecular structure of **3** has been determined by X-ray crystallography and is shown in Fig. 2a. Data collection and structure analysis are presented in Table 1; selected bond lengths and angles are given in Table 3. The molecule exists as a centrosymmetric dimer with asymmetrically bridging hydrogen atoms [O(1)–H(1) 1.09(4), O(2a)–H(1) 1.31(4) Å]. As may be seen from Fig. 2b, the central $Al_2O_4H_2$ eight-membered cycle is not planar. The compound **3** is the first alkylalane diolate with the located position of alcohol's protons in the difference map. The presence of the intra-molecular hydrogen bondings in the recently reported similar compound ^{t}Bu$_4$Al$_2$(OCH$_2$C$(CH_3)_2$CH$_2$OH)$_2$ was confirmed only spectroscopically [12]. The signal of alcohol's protons of **3** appears in ^{1}H-NMR spectrum as a singlet at 16.10 ppm.

As expected, butane-1,4-diol gives with ^{i}Bu$_3$Al a trinuclear product [^{i}Bu$_5$Al$_3$(O$(CH_2)_4$O)$_2$] (**4**) as a colourless viscous liquid (Eq. (2)). The structure of **4** was determined on the basis of NMR spectra, molecular weight measurements and elemental analysis (see Section 3). The ^{13}C-NMR spectrum of **4** shows three signals (at 29.07, 28.81 and 28.70 ppm) of AlCH$_2$CH(CH_3)$_2$ carbons and three signals (26.28, 26.15 and 26.11 ppm) of AlCH$_2$CH(CH$_3$)$_2$ carbons which indicates the presence of three kinds of inequivalent ^{i}Bu groups bonded to aluminium atoms. The ^{1}H-NMR spectrum of **4** reveals two multiplets of CH_2O and CH_2 protons (at 3.58 and 1.34 ppm) and two doublets of the protons of AlCH$_2$CH(CH_3)$_2$ groups (at 1.20 and 1.15 ppm) with a CH_2O–CH_2–AlCH$_2$CH(CH_3)$_2$ integration ratio of 8:8:30 which is fully consistent with the structure **4**.

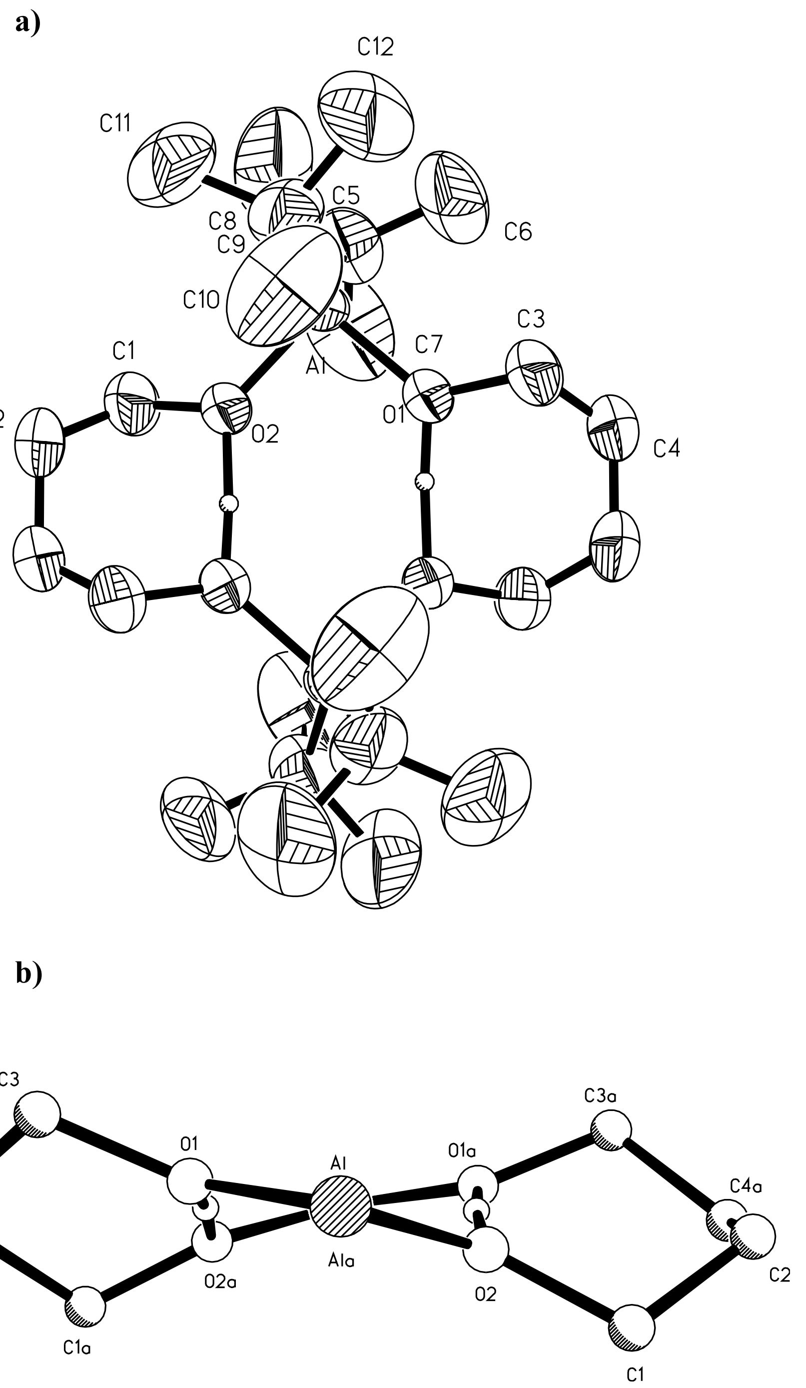


Fig. 2. (a) The molecular structure of $[{}^t\mathrm{Bu}_2\mathrm{Al}(\mathrm{O}(\mathrm{CH}_2)_4\mathrm{OH})]_2$ (**3**). All hydrogens (besides of OH) are omitted for clarity. (b) Partial coordination sphere of $[{}^t\mathrm{Bu}_2\mathrm{Al}(\mathrm{O}(\mathrm{CH}_2)_4\mathrm{OH})]_2$ (**3**) viewed along the Al···Al vector showing the central non-planar $\mathrm{Al}_2\mathrm{O}_4\mathrm{H}_2$ cycle.

Table 3
Selected bond lengths (Å) and angles (°) in $[{}^t\mathrm{Bu}_2\mathrm{Al}(\mathrm{O}(\mathrm{CH}_2)_4\mathrm{OH})]_2$ (**3**)

Bond lengths			
Al–O(2)	1.808(2)	O(1)–H(1)	1.09(4)
Al–O(1)	1.815(2)	O(2a)–H(1)	1.31(4)
Bond angles			
O(2)–Al–O(1)	94.03(9)	Al–O(1)–H(1)	126.0(18)
C(3)–O(1)–Al	128.8(2)	C(1)–O(2)–Al	128.0(2)
C(3)–O(1)–H(1)	105.2(18)		

One equivalent of propane-1,3-diol reacts with ^{t}Bu$_3$Al unexpectedly yielding the mixture of non-volatile organoaluminium oligomers as a main product. Besides the broadened multiptets of C*H*$_2$ and C(C*H*$_3$)$_3$ protons ^{1}H-NMR spectrum of the post-reaction mixture shows also the singlet at 15.32 ppm of O*H* protons and triplet at 3.44 ppm of C*H*$_2$ protons, which may indicate the traces of a product [^{t}Bu$_2$Al(O(CH$_2$)$_3$OH)]$_2$ similar to the compound **3**. Unfortunately, the attempts of isolation of the product failed.

The reaction of two equivalents of propane-1,3-diol with three equivalents of ^{t}Bu$_3$Al yields trinuclear complex of formula ^{t}Bu$_5$Al$_3$(O(CH$_2$)$_3$O)$_2$ (**5**) (Eq. (2)). The compound **5** may be isolated by crystallisation from hexane solution or by distillation from the post-reaction mixture under high vacuum. The crystals were unsuitable for X-ray measurements therefore the structure of **5** was determined on the basis of NMR spectroscopy, molecular weight measurements and elemental analysis. The NMR spectra are in very good agreement with the proposed structure. ^{1}H-NMR spectrum of **5** reveals three singlets of protons of AlC(CH$_3$)$_3$ groups at 1.25, 1.23 and 1.20 ppm with the integration ratio 2:1:2. The integration ratio of OCH$_2$–CH$_2$–AlC(CH$_3$)$_3$ group signals is the same as the ratio of protons in **5** and is equal 8:4:45. Two signals at 130 and 59 ppm present in the ^{27}Al-NMR spectrum of **5** confirm the existence of two kinds of aluminium atoms (four- and five-coordinate). The compound **5** is the first trinuclear alane aliphatic dioldiate with five ^{t}Bu groups bonded to aluminium atoms. The attempt of synthesis of ^{t}Bu$_5$Al$_3$(OCH$_2$C(CH$_3$)$_2$CH$_2$O)$_2$ compound failed due to the too small cavity of the intermediate ^{t}Bu$_4$Al$_2$(OCH$_2$C(CH$_3$)$_2$CH$_2$OH)$_2$ products [12]. Only the reaction of 1,2-catechol with ^{t}Bu$_3$Al led to the formation of ^{t}Bu$_5$Al$_3$(OC$_6$H$_4$O)$_2$ catecholate [21].

The comparison of **1**, **3** and **5** *tert*-butylalane aliphatic dioldiates shows that the structure of the products depends on the steric hindrances of diol moiety and the length of backbones of diols. Barron has previously reported that R$_4$Al$_2$(diol–(H))$_2$ type compounds stabilised by intra-molecular hydrogen bondings are the intermediate products in the reactions of R$_3$Al with diols [12]. We found that the stable complex possessing intra-molecular hydrogen bondings is formed only in the reaction with butane-1,4-diol (compound **3**). In the case of propane-1,3-diol presumably the decreasing of the length of the diol backbone restricts the formation of intra-molecular hydrogen bonding. Due to good accessibility of OH groups, the intermediate product [^{t}Bu$_2$Al(O(CH$_2$)$_3$OH)]$_2$ react with the excess of ^{t}Bu$_3$Al to give finally trimetallic complex (^{t}Bu$_5$Al$_3$(O(CH$_2$)$_3$O)$_2$ (**5**). In the case of the reaction carried out at 1:1 molar ratio of the reagents the molecules of the intermediate product react between themselves yielding the mixture of organoalane oligomers. The steric hindrances present in 2,4-dimethylpentane-2,4-diol moiety caused by methyl and *tert*-butyl groups make impossible the formation of stabilising intra-molecular hydrogen bonding in the reaction product with ^{t}Bu$_3$Al. On the other hand, due to the steric hindrances the OH groups of the intermediate product are inaccessible for the excess of ^{t}Bu$_3$Al. Therefore, hydroxyl groups can further react only with intra-molecular ^{t}Bu groups to form the compound [^{t}BuAl(OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O)]$_2$ (**1**).

In conclusion, the reactions of trimethyl-, triethyl- and tri-*iso*-butylalanes with diols yield trinuclear complexes of the general formula R$_5$Al$_3$(diol–(2H))$_2$ irrespective of the diol moiety steric hindrances. Tri-*tert*-butylalane reacts with diols yielding several products depending on the length of diol backbone and steric hindrances of the diol moiety. In the reaction of sterically crowded diols binuclear [^{t}BuAl(diol–(2H)]$_2$ type compounds are formed. In the case of unhindered aliphatic diols the strong intra-molecular hydrogen bonding interaction in the intermediate product competes with the reaction of OH groups with the excess of ^{t}Bu$_3$Al and inclusion of the third metal atom to form [^{t}Bu$_2$Al(diol–(H)]$_2$ and ^{t}Bu$_5$Al$_3$[diol–(2H)]$_2$ respectively.

3. Experimental

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere. ^{t}Bu$_3$Al, butane-1,4-diol, propane-1,3-diol and 2,4-dimethylpentane-2,4-diol were obtained from Aldrich. ^{t}Bu$_3$Al was synthesised as described in the literature [22]. ^{1}H-, ^{13}C- and ^{27}Al-NMR spectra were run on Mercury-400BB spectrometer. ^{1}H-NMR spectra were recorded at 400.09 MHz. Chemical shifts were referenced to the residual proton signal of C$_6$D$_6$ (7.15 ppm). ^{13}C-NMR spectra were run at 100.60 MHz (standard, C$_6$H$_6$ ^{13}CC$_5$D$_6$, 128 ppm). Chemical shifts of aluminium signals were referenced to the six-coordinate aluminium atom signal of Al(acac)$_3$ (0.0 ppm).

The molecular weight of the compounds was determined by cryoscopy in C$_6$H$_6$.

The products were purified by distillation off under vacuum from the post-reactions mixtures containing the solvents. The solvents are necessary for the transportation of viscous liquids from the condenser to the flask when the distillation is coming to the end. The method allows isolating even small amount of the product almost quantitatively.

3.1. The synthesis of [^{t}BuAl(OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O)]$_2$ (1)

A sample (1.659 g, 6.1 mmol) of ^{t}Bu$_3$Al·OEt$_2$ in 20 cm^3 of Et$_2$O was placed in 100 cm^3 two-necked flask and cooled to −78 °C. The solution of 0.780 g (6.0 mmol) of 2,4-dimethylpentane-2,4-diol in 20 cm^3 of Et_2O was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm to room temperature (r.t.) within 2 h. Evolution of gases was observed during the course of the reaction. After 24 h all volatiles were removed from the post-reaction mixture and the product **1** was sublimed off (120 °C, 10^{-3} Torr) from the residue as a white colourless solid (yield: 1.027 g, 2.4 mmol, 80%). M.p.: 147–149 °C.

The resulting solid was recrystallised from $n\text{-}C_6H_{14}$ at −25 °C to form X-ray quality crystals.

^{1}H-NMR (C_6D_6): δ 2.01 (2H, d, $^2J(\text{H–H}) = 14.8$ Hz, $C\mathit{H}_2$), 1.41 (2H, d, $^2J(\text{H–H}) = 14.8$ Hz, $C\mathit{H}_2$), 1.40 (6H, s, $OC(C\mathit{H}_3)_2$), 1.37 (6H, s, $OC(C\mathit{H}_3)_2$), 1.32 (6H, s, $OC(C\mathit{H}_3)_2$), 1.23 (6H, s, $OC(C\mathit{H}_3)_2$), 1.20 (18H, s, $AlC(C\mathit{H}_3)_3$). ^{13}C-NMR (C_6D_6): δ 77.95 ($O\mathit{C}(CH_3)_2$), 70.66 ($O\mathit{C}(CH_3)_2$), 53.74 ($\mathit{C}H_2$), 35.10 ($OC(\mathit{C}H_3)_2$), 33.64 ($OC(\mathit{C}H_3)_2$), 32.84 ($OC(\mathit{C}H_3)_2$), 31.05 ($OC(\mathit{C}H_3)_2$), 30.81 ($AlC(\mathit{C}H_3)_3$), 12.58 ($Al\mathit{C}(CH_3)_3$). ^{27}Al-NMR (C_6D_6): δ 110 (four-coord. Al) ppm.

Molecular weight (C_6H_6): Found: 435. Calc.: 428. Anal.: Found: Al, 12.45; hydrolysable *tert*-butyl groups, 26.32. Calc.: Al, 12.62; ^{t}Bu, 26.64 wt.%.

3.2. The synthesis of $^i Bu_5Al_3[(OC(CH_3)_2CH_2C(CH_3)_2O)]_2$ (2)

The compound **2** was obtained as described in Section 3.1 using 0.520 g (4.0 mmol) of 2,4-dimethylpentane-2,4-diol and 1.247 g (6.3 mmol) of $^i Bu_3Al$. The pure product **2** was isolated by distillation under high vacuum (200 °C, 10^{-3} Torr) as a thick colourless liquid (yield: 0.950 g, 1.5 mmol, 76%).

^{1}H-NMR (C_6D_6): δ 2.11 (5H, m, $AlCH_2C\mathit{H}(CH_3)_2$), 1.87 (2H, d, $^2J(\text{H–H}) = 15.2$ Hz, $C\mathit{H}_2$), 1.38 (12H, s, $C(C\mathit{H}_3)_2$), 1.28 (12H, s, $C(C\mathit{H}_3)_2$), 1.24 (6H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlCH_2CH(C\mathit{H}_3)_2$), 1.22 (12H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlCH_2CH(C\mathit{H}_3)_2$), 1.20 (12H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlCH_2CH(C\mathit{H}_3)_2$), 1.09 (2H, d, $^2J(\text{H–H}) = 15.2$ Hz, $C\mathit{H}_2$), 0.29 (4H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlC\mathit{H}_2CH(CH_3)_2$), 0.26 (4H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlC\mathit{H}_2CH(CH_3)_2$), 0.24 (2H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlC\mathit{H}_2CH(CH_3)_2$). ^{13}C-NMR ($C_6D_6$): δ 74.57 ($\mathit{C}(CH_3)_2$), 51.88 ($\mathit{C}H_2$), 33.55 ($C(\mathit{C}H_3)_2$), 31.55 ($C(\mathit{C}H_3)_2$), 29.23 ($AlCH_2CH(\mathit{C}H_3)_2$), 29.14 ($AlCH_2CH(\mathit{C}H_3)_2$), 29.06 ($AlCH_2CH(\mathit{C}H_3)_2$), 26.60 ($Al\mathit{C}H_2CH(CH_3)_2$ br), 26.39 ($AlCH_2\mathit{C}H(CH_3)_2$), 26.27 ($AlCH_2\mathit{C}H(CH_3)_2$), 25.65 ($Al\mathit{C}H_2CH(CH_3)_2$ br) ppm.

Molecular weight (C_6H_6): Found: 597. Calc.: 626. Anal.: Found: Al, 12.65; hydrolysable *iso*-butyl groups, 45.90; Calc. Al, 12.94; ^{i}Bu, 45.53 wt.%.

3.3. The synthesis of $[^t Bu_2Al(O(CH_2)_4OH)]_2$ (3)

A Et_2O solution (30 cm^3) containing $^t Bu_3Al\cdot OEt_2$ (1.387 g, 5.1 mmol) was added to a Et_2O solution (20 cm^3, at −78 °C) containing butane-1,4-diol (0.450 g, 5 mmol). The reaction mixture was warmed to r.t. within 2 h, filtered and the solvent removed in vacuo. The crude material was recrystallised from $n\text{-}C_6H_{14}$ at −25 °C (yield 0.748 g, 1.6 mmol, 65%).

^{1}H-NMR (C_6D_6): δ 16.10 (2H, m, $O\mathit{H}$), 3.41 (8H, m, $OC\mathit{H}_2$), 1.26 (8H, m, $C\mathit{H}_2$), 1.16 (36H, s, $AlC(C\mathit{H}_3)_3$). ^{13}C-NMR (C_6D_6): δ 62.64 ($O\mathit{C}H_2$), 31.53 ($\mathit{C}H_2$), 30.77 ($AlC(\mathit{C}H_3)_3$), 15.90 ($Al\mathit{C}(CH_3)_3$, broad) ppm.

M.p.: 139 °C. Molecular weight (C_6H_6): Found: 450. Calc.: 460. Anal. Found: Al, 11.50; hydrolysable *tert*-butyl groups, 48.98. Calc.: Al, 11.74; ^{t}Bu, 49.57 wt.%.

3.4. The synthesis of $^i Bu_5Al_3(O(CH_2)_4O)_2$ (4)

The compound **4** was obtained as described in Section 3.3 using 1.228 g (6.2 mmol) of $^i Bu_3Al$ and 0.360 g (4 mmol) of butane-1,4-diol. The pure product **4** was isolated by distillation under high vacuum (200 °C, 10^{-3} Torr) as a viscous colourless liquid (yield: 0.856 g, 1.6 mmol, 79%).

^{1}H-NMR (C_6D_6): δ 3.58 (8H, m, $OC\mathit{H}_2$), 2.04 (4H, m, $AlCH_2C\mathit{H}(CH_3)_2$), 1.94 (1H, m, $AlCH_2C\mathit{H}(CH_3)_2$), 1.34 (8H, m, $C\mathit{H}_2$), 1.20 (6H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlCH_2CH(C\mathit{H}_3)_2$), 1.15 (24H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlCH_2CH(C\mathit{H}_3)_2$), 0.21 (4H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlC\mathit{H}_2CH(CH_3)_2$), 0.14 (6H, d, $^3J(\text{H–H}) = 6.4$ Hz, $AlC\mathit{H}_2CH(CH_3)_2$). ^{13}C-NMR ($C_6D_6$): δ 62.98 ($O\mathit{C}H_2$), 30.57 ($\mathit{C}H_2$), 29.07 ($AlCH_2CH(\mathit{C}H_3)_2$), 28.81 ($AlCH_2CH(\mathit{C}H_3)_2$), 28.70 ($AlCH_2CH(\mathit{C}H_3)_2$), 26.28 ($AlCH_2\mathit{C}H(CH_3)_2$), 26.15 ($AlCH_2\mathit{C}H(CH_3)_2$), 26.11 ($AlCH_2\mathit{C}H(CH_3)_2$), 22.45 ($Al\mathit{C}H_2CH(CH_3)_2$, broadened), 21.37 ($Al\mathit{C}H_2CH(CH_3)_2$, broadened). ^{27}Al-NMR (C_6D_6): δ 62 (five-coord. Al) ppm.

Molecular weight (C_6H_6): Found: 547. Calc.: 542. Anal. Found: Al, 14.69; hydrolysable *iso*-butyl groups, 53.01. Calc.: Al, 14.94; ^{i}Bu, 52.58 wt.%.

3.5. The synthesis of $^t Bu_5Al_3(O(CH_2)_3O)_2$ (5)

The compound **5** was obtained as described in Section 3.3 using 1.251 g (4.6 mmol) of $^t Bu_3Al\cdot OEt_2$ and 0.228 g (3 mmol) of propane-1,3-diol. Based upon the ^{1}H-NMR spectrum the crude reaction product was a compound **5** contaminated by aluminium oligomers. The pure product **5** was isolated by distillation under high vacuum (200 °C, 10^{-3} Torr) as a colourless crystalline solid (yield: 0.655 g, 1.3 mmol, 85%).

^{1}H-NMR (C_6D_6): δ 3.61 (8H, m, $OC\mathit{H}_2$), 1.55 (2H, m, $C\mathit{H}_2$), 1.25 (18H, s, $AlC(C\mathit{H}_3)_3$), 1.23 (9H, s, $AlC(C\mathit{H}_3)_3$), 1.20 (18H, s, $AlC(C\mathit{H}_3)_3$), 1.07 (2H, m, $C\mathit{H}_2$). ^{13}C-NMR (C_6D_6): δ 64.59 ($O\mathit{C}H_2$), 33.36 ($\mathit{C}H_2$), 31.90 (AlC(CH_3)$_3$), 31.86 (AlC(CH_3)$_3$), 31.25 (AlC(CH_3)$_3$), 16.50 (AlC(CH$_3$)$_3$, br). ^{27}Al-NMR (C_6D_6): δ 59 (five-coord. Al), 130 (four-coord. Al) ppm.

Molecular weight (C_6H_6): Found: 530. Calc.: 514. Anal. Found: Al, 15.38; hydrolysable *tert*-butyl groups, 56.01. Calc. Al: 15.76; ^{t}Bu, 55.45 wt.%.

3.6. X-ray crystal structure analysis

Determination of the crystal structures of **1** and **3** were performed on a KUMA KM4CCD κ-axis diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation. The crystals were positioned at 62 mm from the KM4CCD camera. The frames were measured at 1.2° intervals with a counting time of 25 s. All of the data were corrected for Lp effects. No absorption correction was applied. Data reduction and analysis were carried out using the KUMA diffraction (Wrocław) programs. Structure of the investigated crystal was solved by the direct methods [23] and refined using SHELXL computer program [24]. All hydrogen atoms placed in the calculated positions and their thermal parameters were refined isotropically. The H atom bonded to the O atom was located from difference map and refined isotropically. Scattering factors were taken from the literature (Tables 6.1.1.4 and 4.2.4.2. [25]).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172042 and 172043 for compound **1** and **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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