SYNTHESIS AND STRUCTURE OF ALKYLALUMINIUM DERIVATIVES OF 1,2-CATECHOLS

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Abstract

Alkylaluminium 1,2-catecholates of formulae $R_5Al_3(OC_6H_4O)_2$ [**1** (R = Me), **2** (R = Et), **3** (R = *i*-Bu), and **4** (R = *t*-Bu)] and $R_5Al_3[4\text{-}(CH_3)_3C\text{-}OC_6H_3O]_2$ [**5** (R = Me) and **6** (R = Et)] were obtained in the reactions of 3 equiv. of trialkyaluminium with 2 equiv. of 1,2-catechols. The pure complexes were isolated and characterized by means of ^1H, ^{13}C, ^{27}Al NMR spectroscopy, molecular weight measurements and elemental analysis. The crystal structure of **4** has been determined by an X-ray diffraction study.

1. Introduction

Complexes of catechols with diethylzinc [1–7] are of interest as catalysts for epoxide polymerization, since they are found to exhibit catalytic activity in the alkylene oxide polymerization and propylene oxide – carbon dioxide copolymerization. Very recently it appeared that the products formed in the reactions of 1,2-catechol with triethylaluminium and diethylaluminium chloride are also effective catalysts for the polymerization of propylene oxide and for the copolymerization of propylene oxide and carbon dioxide [8]. The catalysts were generally used as post-reaction mixtures of unseparated complexes.

The aim of this paper is the detail the study of pure, fully characterized alkylaluminium derivatives of 1,2-catechol and 4-*tert*-butyl-1,2-catechol. The determination of the structure of the complexes will permit a better understanding of their role in the alkylene oxides polymerization.

2. Experimental

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere. t-Bu_3Al was synthesised as described in the literature [9].

^1H NMR spectra were recorded with a Varian-Mercury-400BB spectrometer, at 400.09 MHz. Chemical shifts were referenced to the residual proton signal of C_6D_6 (7.15 ppm). ^{13}C NMR spectra were run on the same instrument at 100.60 MHz (standard, benzene $^{13}CC_5D_6$, 128 ppm). ^{27}Al spectra were run on a Varian VXR 300 spectrometer at 78.2 MHz (standard $Al(acac)_3$ = 0.0 ppm). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. CCDC 141136 for compound **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, fax: +44(1223)336-033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

The molecular weight of the compounds was determined by cryoscopy in benzene.

2.1. Synthesis of $Me_5Al_3(OC_6H_4O)_2$ (1)

1.100 g (10 mmol) of 1,2-catechol in 30 cm^3 of toluene was placed in 250 cm^3 two-necked flask and cooled to –78°C. The solution of 1.087 g (15.1 mmol) of Me_3Al in 20 cm^3 of toluene was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm up to room temperature within 2 h. Evolution of gases was observed during the course of the reaction. The solvent was distilled off under vacuum. The complex (1.300g) was sublimed off (T = 150°C, p = 10^{-3}Torr) as a white solid from the post reaction mixture (Yield : 70%).

^1H NMR (benzene-d^6): δ 6.56 (m, 8H, H_{arom}, AA'BB' pattern typical for 1,2-substituted benzene), –0.15 (s, 6H, $AlCH_3$), –0.36 (s, 3H, $AlCH_3$), –0.82 (s, 6H, $AlCH_3$) ppm.

^{13}C NMR (benzene-d^6): δ 144.57, 123.56, 116.43 (C_{arom}), –9.79, –13.06 ($AlCH_3$) ppm.

^{27}Al NMR (benzene-d^6): δ 150 (four-coord. Al), 100 (five-coord. Al) ppm.

Molecular weight. Found: 372. Calc.: 372. Association degree: 1.0

Elemental anal. Found: Al, 21.65; hydrolysable methyl groups, 19.95; Calc.; Al, 21.77; Me, 20.16 wt%.

2.2. Synthesis of $Et_5Al_3(OC_6H_4O)_2$ (2)

Complex **2** was obtained as described in section 2.1 using 1.100g (10mmol) of 1,2-catechol and 1.721 g (15.1 mmol) of Et_3Al. 1.967 g (89%) of complex **2** was distilled off from the post reaction mixture (T = 180°C, p = 10^{-3} Torr) as a thick liquid.

^{1}H NMR (benzene-d^6): δ 6.61 (m, 8H, H_{arom}, AA'BB' pattern typical for 1,2-substituted benzene), 1.45 (t, 6H, $AlCH_2CH_3$), 1.19 (t, 3H, $AlCH_2CH_3$), 0.85 (t, 6H, $AlCH_2CH_3$), 0.49 (q, 4H, $AlCH_2CH_3$), 0.34 (q, 2H, $AlCH_2CH_3$), –0.09 (q, 4H, $AlCH_2CH_3$) ppm.
^{13}C NMR (benzene-d^6): 144.83, 123.52, 116.33 (C_{arom}), 8.56, 8.36, 8.27 ($AlCH_2CH_3$), –0.50, –2.40 ($AlCH_2CH_3$) ppm.
^{27}Al NMR (benzene-d^6): δ 167 (four-coord. Al), 96 (five-coord. Al) ppm.
Molecular weight. Found: 419. Calc.: 442. Association degree: 0.95.
Elemental anal. Found: Al, 18.11; hydrolysable ethyl groups, 32.72; Calc.: Al, 18.33; Et, 32.81 wt%.

2.3. Synthesis of i-$Bu_5Al_3(OC_6H_4O)_2$ (3)

Complex **3** was obtained as described in section 2.1. using 1.100 g (10 mmol) of 1,2-catechol and 2.990 g (15.1 mmol of *i*-Bu_3Al. A total of 2.561 g (88%) of thick liquid compound **3** was obtained by distillation (T = 160°C, p = 10^{-3} Torr) from the post reaction mixture.
^{1}H NMR (benzene-d^6): δ 6.71 (m, 8H, H_{arom}, AA'BB' pattern typical for 1,2-substituted benzene), 2.31 (m, 2H, $(CH_3)_2CHCH_2Al$), 2.06 (m, 1H, $(CH_3)_2CHCH_2Al$), 1.74 (m, 2H, $(CH_3)_2CHCH_2Al$), 1.29 (d, J = 6.8 Hz, 12H, $(CH_3)_2CHCH_2Al$), 0.98 (d, J =6.6 Hz, 6H, $(CH_3)_2CHCH_2Al$), 0.88 (d, 6.8 Hz, 12H, $(CH_3)_2CHCH_2Al$), 0.63 (d, J = 6.8 Hz, 4H, $(CH_3)_2CHCH_2Al$), 0.42 (d, 2H, J = 6.8 Hz, $(CH_3)_2CHCH_2Al$), –0.01 (d, J = 7.0 Hz, 4H, $(CH_3)_2CHCH_2Al$) ppm.
^{13}C NMR (benzene-d^6): δ 144.84, 123.56, 116.70 (C_{arom}), 28.46, 28.31, 27.80 ($(CH_3)_2CHCH_2Al$), 26.01, 25.56, 25.46 ($(CH_3)_2CHCH_2Al$), 22.91, 20.26 ($(CH_3)_2CHCH_2Al$) ppm.
^{27}Al NMR (benzene-d^6): δ 150 (four-coord. Al), 85 (five-coord.Al) ppm.
Molecular weight. Found: 570. Calc.: 582. Association degree: 0.98.
Elemental anal. Found: Al, 13.75; hydrolysable *iso*-butyl groups, 48.50; Calc.: Al, 13.92, *i*-Bu, 48.97 wt.%.

2.4 Synthesis of t-$Bu_5Al_3(OC_6H_4O)_2$ (4)

1.660 g (6.1 mmol) of t-$Bu_3Al{\cdot}OEt_2$ in 30 cm^3 of diethyl ether was placed in a 250 cm^3 two necked flask and cooled to –78°. The solution of 0.440 g (4 mmol) of 1,2-catechol in 20 cm^3 of diethyl ether was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm up to room temperature within 2 h. The solvent was removed by distillation under vacuum immediately after reaction. Complex **4** (1.162 g) was sublimed off (200°C, 10^{-3}Torr) from the post-reaction mixture as a white solid (yield 50%). Suitable crystals for X-ray measurements were obtained from the hexane – methylene dichloride solution at –25°C.
^{1}H NMR (benzene-d^6): δ 6.70 (m, 8H, H_{arom}, AA'BB' pattern typical for 1,2-substituted benzene), 1.41 (s, 18H, $(CH_3)_3Al$), 1.13 (s, 9H, $(CH_3)_3Al$), 0.91 (s, 18H, $(CH_3)_3Al$) ppm.
^{13}C NMR (benzene-d^6): δ 145.82, 123.90, 116.94 (C_{arom}), 31.21, 30.99, 30.73 ($(CH_3)_3CAl$), 17.20, 15.85 ($(CH_3)_3CAl$) ppm.
^{27}Al NMR (benzene-d^6): 150 (four-coord. Al), 67 (five-coord. Al) ppm.
Molecular weight. Found: 553. Calc.: 582. Association degree: 0.95.
Elemental anal. Found 13.71 Al, hydrolysable *tert*-butyl groups 48.02; Calc.: Al, 13.92, *t*-Bu, 48.97 wt.%.

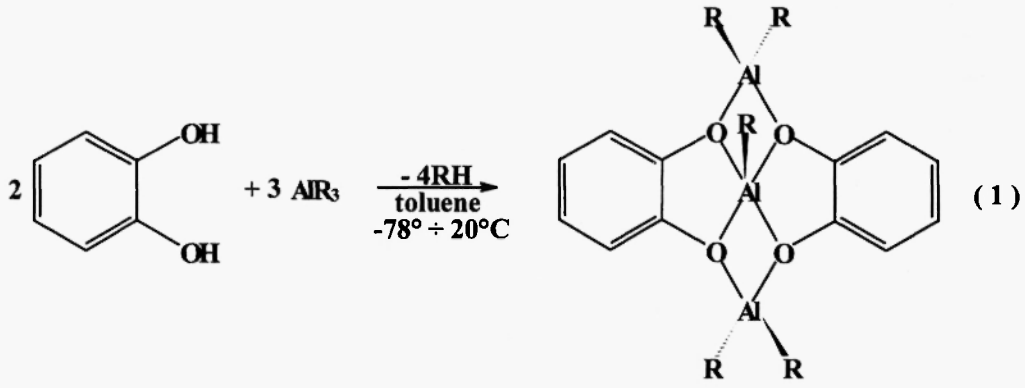
2.5. Synthesis of Me_5Al_3(4-t-Bu-$OC_6H_3O)_2$ (5)

1.087 g (15.1 mmol) of Me_3Al in 40 cm^3 of toluene was placed in a 250 cm^3 two-necked flask and cooled to –78°C. A solution of 1.660 g (10 mmol) of 4-*tert*-butyl-1,2-catechol in 40 cm^3 of toluene was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm up to room temperature within 2 h. Evolutions of gases was observed during the course the reaction. The solvent was removed by distillation under vacuum. The complex **5** (2.202 g) (cis and trans isomers) was distilled off (180°C, 10^{-3} Torr) from the post reaction mixture as a thick colourless liquid. (Yield 91%).
^{1}H NMR (benzene-d^6): δ 7.02 (d, J = 2.0 Hz, 2H, 3-H_{arom}), 6.74 (dd, J = 8.2 Hz, J = 1.9 Hz, 2H, 5-H_{arom}), 6.63 (d, J = 8.2 Hz, 2H, 6-H_{arom}), 1.09 (s, 18H, $(CH_3)_3C$), –0.04 (s, 1.5H, $AlCH_3$), –0.07 (s, 3H, $AlCH_3$), –0.09 (s, 1.5H, $AlCH_3$), –0.26 (s, 3H, $AlCH_3$), –0.65 (s, 1.5H, $AlCH_3$), –0.71 (s, 3H, $AlCH_3$), –0.75 (s, 1.5H, $AlCH_3$) ppm.
^{13}C NMR (benzene-d^6): δ 147.10, 147.15, 144.44, 144.49, 142.30, 142.26, 120.11, 120.04, 115.74, 115.56, 113.98, 113.78 (C_{arom}), 34.38 ($(CH_3)_3C$), 31.29 ($(CH_3)_3C$), –9.66, –12.98 ($AlCH_3$).
^{27}Al NMR (benzene-d^6): δ 150 (four-coord. Al.), 95 (five-coord. Al) ppm.
Molecular weight. Found: 487, Calc.: 484. Association degree: 1.0.
Elemental anal.: Found: Al, 16.44; hydrolysable methyl groups 15.65, Calc.: Al., 16.74; Me, 15.50 wt%.

2.6. Synthesis of Et_5Al_3(4-t-Bu-$OC_6H_3O)_2$ (6)

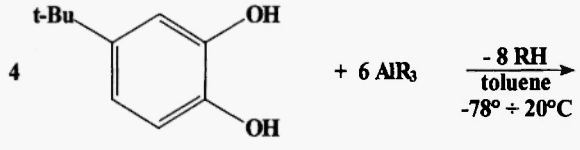
Complex **6** was obtained as described in section 2.5. using 1.721 g (15.1 mmol) of Et_3Al and 1.660 g (10 mmol) of 4-*tert*-butyl-1,2-catechol. 2.410 g (87%) of **6** (*cis* and *trans* isomers) was distilled off as a thick liquid.
^{1}H NMR (benzene-d^6): 7.08 (d, J = 2.0 Hz, 2H, 3-H_{arom}), 6.72 (m, 4H, 5,6-H_{arom}), 1.51, 1.50, 1.49 (three triplets, 6H, CH_3CH_2Al), 1.23 (t, 3H, CH_3CH_2Al), 1.12 (s, 18H, $(CH_3)_3C$), 0.94, 0.90, 0.87 (three triplets, 6H, $AlCH_2CH_3$), 0.57, 0.54, 0.52 (three quartets, 4H, $AlCH_2CH_3$), 0.39 (q, 2H, $AlCH_2CH_3$), 0.12, –0.03, –0.03 three quartets, 4H, $AlCH_2CH_3$) ppm.
^{13}C NMR (benzene-d^6): δ 147.05, 147.03, 144.62, 144.55, 142.55, 142.49, 120.04, 120.01, 115.64, 115.49, 113.93, 113.78 (C_{arom}), 8.67, 8.48, 8.36 ($AlCH_2CH_3$), –0.43, –2.23 ($AlCH_2CH_3$) ppm.

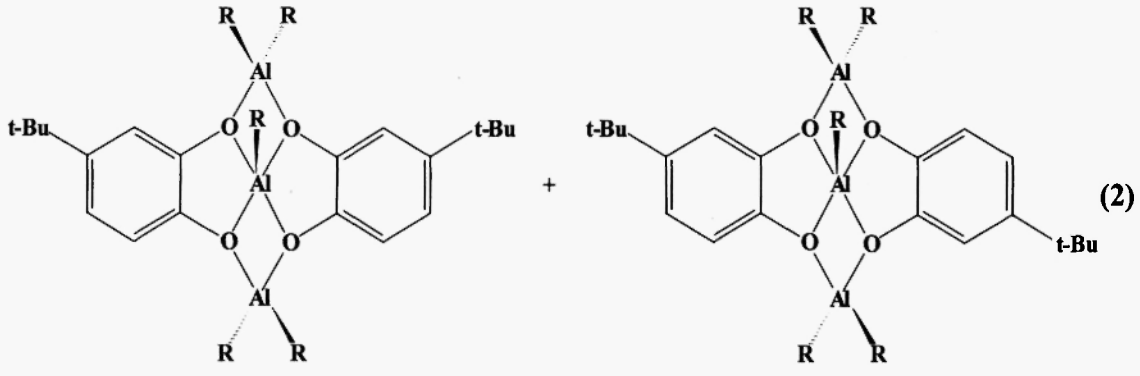
^{27}Al NMR (benzene-d^6): δ 160 (four-coord. Al), 85 (five-coord. Al) ppm.
Molecular weight. Found: 564. Calc.: 554. Association degree: 1.0.
Elemental anal.: Found: Al, 14.31; hydrolysable ethyl groups 26.35; Calc.: Al, 14.62; Et, 26.17 wt.%.



(1)

1 (R = Me) **3** (R = i-Bu)
2 (R = Et) **4** (R = t-Bu)





(2)

5 cis (R=Me) **5** trans (R=Me)
6 cis (R=Et) **6** trans (R=Et)

3.7. Crystal structure determination

The X-ray data were measured on a KM-4 KUMA diffractometer with graphite monochromated MoKα radiation. The data were collected at room temperature using ω–2θ scan technique. The intensity of the control reflections varied by less than 4% and the linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarisation effects, and for absorption [10] using an empirical procedure. The structure was solved by direct methods [11] and refined using SHELXL [12]. The refinement was based on F^2 for all reflections. The weighted R factor, wR, and the goodness-of-fit, S, are based on F^2. The non-hydrogen atoms were refined anisotropically, whereas the H–atoms were placed in their calculated positions and their thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables [13]. The details of X-ray measurements and structural computations and crystal data for compound **4** are given in Table 1.

3. Results and discussion

The reactions of 2 equiv. of 1,2-catechol with 3 equiv. of trimethyl-, triethyl-, tri-*iso*-butyl- and tri-*tert*-butylaluminium proceeded with the formation of **1, 2, 3** and **4** complexes (Eq. 1).

4-*tert*-Butyl-1,2-catechol reacted with trimethyl- and triethylaluminium yielded complexes **5** and **6** which demonstrated trans and cis ligand geometries (Eq. 2).

All complexes were isolated from the post-reaction mixtures either by sublimation (complexes **1** and **4**) and by distillation (complexes **2**, **3**, **5** and **6**) (T = 160-200°C, p = 10^{-3}Torr) in 50-90% yield. The complexes were characterized by means of ^{1}H, ^{13}C and ^{27}Al NMR spectra, molecular weight measurements and elemental analysis. The crystal structure of **4** was determined by an X-ray diffraction study. A perspective view of the molecule with the atom numbering system is shown in Fig. 1.

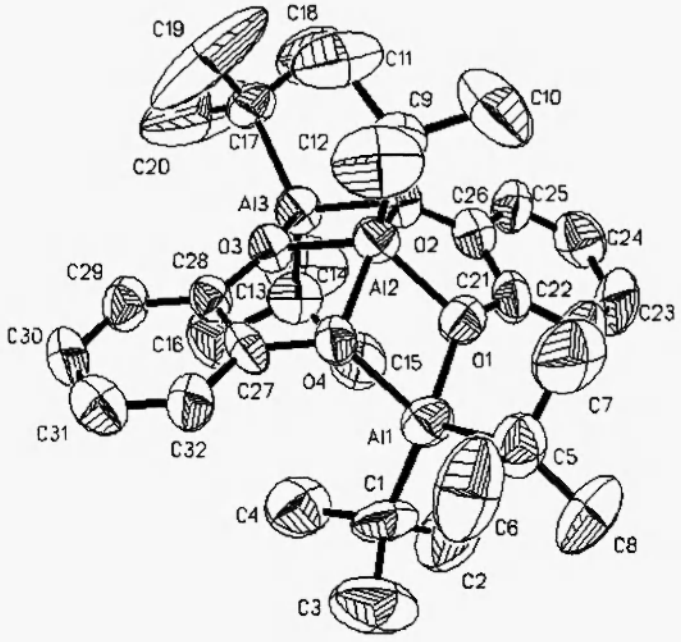


Fig.1. The molecular structure of **4** with the atom numbering scheme.
Hydrogen atoms were omitted for clarity.

Selected bond distances and bond angles are shown in Tables 2 and 3. The Al(2) atom in **4** exhibits square based pyramid geometry with four oxygen atoms in the basal sites. The base of the pyramid is a highly distorted rectangle with distances between O(1)–O(2) 2.485(6), O(2)–O(3) 2.348(6), O(3)–O(4) 2.504(5) and O(1)–O(4) 2.359(7) Å. The angles of O(1)–O(2)–O(3), O(2)–O(3)–O(4), O(3)–O(4)–O(1) and O(4)–O(1)–O(2) are 82.7(2)°, 95.3(2)°, 82.0(2)° and 95.6(2)° respectively. The five-coordinated aluminium atom is displaced 0.742 Å above the O_4 plane. The terminal aluminium atoms are in a four coordinate distorted tetrahedral environment, which results from strain in the four-membered Al_2O_2 rings. The oxygen atoms O(1) and O(3) are situated in the planes formed by Al(1), Al(2), C(21) and Al(2), Al(3) C(28) atoms respectively. The three X–O(1)–Y angles and the three X–O(3)–Y angles sum 360°. The O(2) and O(4) atoms deviate from the C(26), Al(2), Al(3) and C(27), Al(2), Al(1) planes, contrary to the comparable oxygen atoms in the related structures of $Me_5Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2$ [14] and $Cl_5Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2$ which have been published recently [15]. The sums of the angles about the O(2) and O(4) atoms are equal 339.2° and 342.5°, respectively. Further, the conformations of the five-membered AlOCCO rings may be described as an open envelope with a planar catecholoxide core and folded along the AlO_2 plane. The Al(2)–O(1)–C(21)–C(26), Al(2)–O(2)–C(26)–C(21), Al(2)–O(4)–C(27)–C(28) and Al(2)–O(3)–C(28)–C(27) torsion angles are –15.5(7)°, 9.8(7)°, 16.8(7)° and –11.1(7)°, respectively.

The complexes **1** - **6** possess one central five-coordinated and two terminal four-coordinated aluminium atoms. ^{27}Al NMR spectra of **1** - **6** revealed two broad signals: at about 150 ppm and in the region

of 65-100 ppm assigned to the four- and five-coordinated aluminium atoms, respectively. The signals of the five-coordinated aluminium atoms of **1**, **2** and **5** were significantly downfield shifted when compared to **3**, **4** and **6** and to those of other alkylaluminium diolates of the general formula $R_5Al_3[diol\text{-}(2H)]_2$ [14 - 20]. This was probably caused by the low electron density on the oxygen atoms in catecholates **1**, **2** and **5** due to the coupling with aromatic rings. The withdrawing electron effect of the aromatic rings was partially balanced by bulky substituents bonded to aluminium in the case of the complexes **3** and 4 and by the *tert*-butyl group of catechol and ethyl group bonded to aluminium in compound **6**.

Table 1. Crystal data and structure refinement for **4**

Empirical formula	$C_{32}H_{53}Al_3O_4$
Formula weight	582.68
Temperature (K)	293(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	9.931(2)
b(Å)	18.608(4)
c(Å)	18.559(4)
β(°)	99.59(3)
V(Å^3)	3381.7(12)
Z	4
D_{calc}(g cm^{-3})	1.144
Absorption coefficient (mm^{-1})	0.144
F(000)	1264
Crystal size (mm)	0.25×0.25×0.30
Θ range for data collection (°)	2.19 to 21.66
Index ranges	$0\leq h\leq 9, -14\leq k\leq 17, -19\leq l\leq 17$
Reflections collected	4787
Independent reflections	3099 [R_{int} = 0.1512]
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	3089 / 0 / 421
Goodness–of–fit on F^2	1.025
Final R indices [I>2σ(I)]	R_1 = 0.0695, wR_2 = 0.1540
R indices (all data)	R_1 = 0.1274, wR_2 = 0.1997
Extinction coefficient	0.0008(6)
Largest difference peak and hole (e Å^{-3})	0.254 and –0.359
Diffractometer	KM-4 KUMA
Weighting scheme	$w^{-1} = \sigma^2(F_0^2)+(0.0873P)^2+3.13P$ where $P = (F_0^2 + 2F_c^2)/3$
Programs used	SHELXL, SHELXS
Deposition number	CCDC 141136

Table 2. Selected bond distances [Å] for **4**

Al.(1)-O(4)	1.853(5)	Al(2)-O(2)	1.884(5)	O(2)-C(26)	1.356(9)
Al.(1)-O(1)	1.869(5)	Al(2)-C(9)	1.938(7)	O(3)-C(28)	1.359(7)
Al.(1)-C(1)	1.944(9)	Al(3)-O(2)	1.850(5)	O(4)-C(27)	1.328(8)
Al.(1)-C(5)	1.977(8)	Al(3)-O(3)	1.871(5)	C(21)-C(26)	1.383(10)
Al.(2)-O(1)	1.832(5)	Al(3)-C(17)	1.933(7)	C(27)-C(28)	1.401(9)
Al.(2)-O(3)	1.843(4)	Al(3)-C(13)	1.953(8)		
Al.(2)-O(4)	1.884(5)	O(1)-C(21)	1.355(8)		

Table 3. Selected bond angles (°) for **4**.

O(4)-Al(1)-O(1)	78.7(2)	O(3)-Al(2)-C(9)	118.9(3)	C(26)-O(2)-Al(2)	110.8(4)
O(4)-Al(1)-C(1)	112.6(3)	O(4)-Al(2)-C(9)	108.2(3)	Al(3)-O(2)-Al(2)	101.4(2)
O(1)-Al(1)-C(1)	118.6(3)	O(2)-Al(2)-C(9)	107.3(3)	C(28)-O(3)-Al(2)	112.7(3)
O(4)-Al(1)-C(5)	113.6(3)	O(2)-Al(3)-O(3)	78.2(2)	C(28)-O(3)-Al(3)	142.1(4)
O(1)-Al(1)-C(5)	108.4(3)	O(2)-Al(3)-C(17)	112.7(3)	Al(2)-O(3)-Al(3)	102.2(2)
C(1)-Al(1)-C(5)	118.5(4)	O(3)-Al(3)-C(17)	113.3(3)	C(27)-O(4)-Al(1)	131.4(4)
O(1)-Al(2)-O(3)	120.6(2)	O(2)-Al(3)-C(13)	113.5(3)	C(27)-O(4)-Al(2)	110.5(4)
O(1)-Al(2)-O(4)	78.8(2)	O(3)-Al(3)-C(13)	112.2(3)	Al(1)-O(4)-Al(2)	100.6(2)
O(3)-Al(2)-O(4)	84.4(2)	C(17)-Al(3)-C(13)	119.8(3)	O(1)-C(21)-C(26)	112.3(7)
O(1)-Al(2)-O(2)	83.9(2)	C(21)-O(1)-Al(2)	114.0(4)	C(21)-C(22)-C(23)	119.0(9)
O(3)-Al(2)-O(2)	78.1(2)	C(21)-O(1)-Al(1)	141.7(5)	O(2)-C(26)-C(21)	115.6(8)
O(4)-Al(2)-O(2)	144.5(2)	Al(2)-O(1)-Al(1)	101.9(3)	O(4)-C(27)-C(28)	115.7(6)
O(1)-Al(2)-C(9)	120.4(3)	C(26)-O(2)-Al(3)	127.0(4)	O(3)-C(28)-C(27)	112.8(6)

The ^{1}H NMR spectrum of **1** reveals AA'BB' pattern of aromatic protons and three singlets of methyl groups bonded to aluminium. The signals at –0.15 and –0.82 ppm are assigned to the four methyl groups bonded to two four-coordinated aluminium atoms and the signal at –0.57 ppm corresponds to one methyl group bonded to the central five-coordinated aluminium atom. The integration shows that the molecule consists of 8 aromatic protons and 5 methyl groups. The ^{13}C NMR spectrum reveals three signals of aromatic carbons and two broad signals at –9.79 and –13.06 ppm of methyl groups bonded to aluminium, which are consistent with the structure **1**.

The ^{1}H NMR spectrum of **2** shows the multiplet of aromatic protons, three triplets of $AlCH_2\underline{C}H_3$ groups and three quartets of $AlC\underline{H}_2CH_3$ groups. On the bases of the integration ratio the triplets at 1.45 and 0.85 ppm are assigned to the four ethyl groups bonded to the terminal aluminium atoms and the triplet at 1.19 ppm is assigned to the ethyl group bonded to the central aluminium. Similarly the quartets at 0.49 and –0.09 ppm correspond to the four $AlCH_2CH_3$ groups bonded to four-coordinated aluminium atoms and the quartet at 0.34 ppm is observed for the $AlCH_2CH_3$ group bonded to the five-coordinated aluminium. The ^{13}C NMR spectrum shows that the compound **2** possesses three different kinds of aromatic carbons (signals at 144.83, 123.52 and 116.33 ppm) and three different kinds of $AlCH_2CH_3$ groups (signals at 8.56, 8.36 and 8.27 ppm). The signals at –0.50 and –2.40 ppm of $AlCH_2CH_3$ methylene groups are observed in the region characteristic for the carbons bonded to aluminium.

In the ^{1}H NMR spectrum of compound **3** the following signals are present: a multiplet of aromatic protons, three multiplets at 2.31, 2.06 and 1.74 ppm of $AlCH_2C\underline{H}(CH_3)_2$, three doublets of $AlCH_2CH(C\underline{H}_3)_2$ and three doublets of $AlC\underline{H}_2CH(CH_3)_2$ groups. The multiplets of $AlCH_2CH(CH_3)_2$ protons are formed by the splitting of the signals by six $AlCH_2CH(CH_3)_2$ and two $AlCH_2CH(CH_3)_2$ neighbouring protons. On the bases of the integration the multiplet at 2.06 ppm is assigned to the *iso*-butyl group bonded to the five-coordinated aluminium atom, and the remaining two multiplets correspond to the groups bonded to the four-coordinated aluminium atoms. The integration of the doublets of $AlCH_2CH(C\underline{H}_3)_2$ and $AlC\underline{H}_2CH(CH_3)_2$ protons shows that the molecule consists of one *iso*-butyl group bonded to the central aluminium and four *iso*-butyl groups bonded to the terminal aluminium atoms. The ^{13}C NMR spectrum shows that the product is an individual compound. The aromatic carbons are observed as singlets at 144.84, 123.56 and 116.70 ppm. Three singlets at 28.46, 28.31 and 27.80 ppm and three singlets at 26.01, 25.56 and 25.46 ppm correspond to the $AlCH_2CH(\underline{C}H_3)_2$ and $AlCH_2\underline{C}H(CH_3)_2$ carbons respectively. The $Al\underline{C}HCH_2(CH_3)_2$ carbons were recorded at 22.91 and 20.26 ppm as broad signals due to a quadrupole effect.

The ^{1}H NMR spectrum of the compound **4** has typical for *ortho*-substituted benzene AA'BB' pattern of aromatic protons and three singlets of $(CH_3)_3CAl$ groups. The integration of the signals shows that the molecule consists eight aromatic protons and five *tert*-butyl groups. The signals at 1.41 and 0.91 ppm are assigned to the *tert*-butyl groups bonded to the four-coordinated aluminium atoms. The singlet at 1.13 ppm corresponds to the *tert*-butyl group bonded to the five-coordinated aluminium. The ^{13}C NMR spectrum of **4** reveals three singlets of aromatic carbons, three singlets of $(\underline{C}H_3)_3CAl$ carbons and two broad signals of $(CH_3)_3\underline{C}Al$ carbons bonded to aluminium which is in agreement with the proposed structure **4**.

Complexes **5** and **6** were mixtures of two isomers. In ^{1}H NMR spectrum of **5** seven singlets of $AlCH_3$ groups were present instead of expected eight signals, probably due to overlapping of two signals. It can be

stated, based on the integration, that the signals at –0.07 and –0.71 ppm correspond to the four methyl groups bonded to the terminal aluminium atoms of **5 trans** isomer. It seems that the signal at –0.26 ppm was formed by overlapping of the singlet of $AlCH_3$ group of **5 trans** bonded to the central aluminium and the signal of one methyl group of **5 cis**. The remaining signals at –0.04, –0.09, –0.65 and –0.75 ppm are assigned to the isomer **5 cis**. The protons of *tert*-butyl groups appear as one singlet at 1.09 ppm. Aromatic protons show typical AMX pattern. The ^{13}C NMR spectrum is in agreement with the proposed structure **5**. Aromatic carbons are observed as 12 singlets in the region from 147.10 to 113.78 ppm. The carbons $(CH_3)_3C$ and $(CH_3)_3C$ appear as two singlets at 34.38 and 31.29 ppm respectively. The methyl groups bonded to aluminium are recorded at –9.66 and –12.98 ppm as two broad signals, due to a quadrupole effect.

It can be concluded, on the bases of the integration of proton signals of the compound **6**, that the molecule consists of two *tert*-butyl groups and five ethyl groups bonded to aluminium. The signal of *tert*-butyl protons appears as the singlet at 1.12 ppm. The assignment of the signals to the particular ethyl groups is impossible, due to overlapping of the signals. The signal of 3-H_{arom} is a doublet at 7.08 ppm. The multiplet of the remaining aromatic protons at 6.72 ppm appears as the result of overlapping of the signals. The ^{13}C NMR spectrum reveals 12 signals of aromatic carbons, which is the evidence of the presence of two isomers. The characteristic signals of carbons bonded to aluminium appear as two broad singlets at –0.43 and –2.23 ppm.

The association degrees of complexes **1** – **6** calculated on the basis of the molecular weight determination were about 1. The satisfactory elemental analyses were obtained for all complexes; for details see Experimental section.

The alkylaluminium catecholates react with Lewis bases yielding complexes of trialkylaluminium with bases and organoaluminium oligomers. It seems that the reactivity of alkylaluminium catecholates is caused by low basicity of the oxygen atoms in comparison with other alkylaluminium diolates. Additionally, the strain in two five-membered rings facilitates the cleavage of Al–O bonds. Lewis bases form donor-acceptor bonds with aluminium atoms and decomposes the molecules of **1** –**6**. The study on the structure of decomposition products will be continued.

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