REACTIONS OF ALKYLALUMINIUM DIOLATES AND CATECHOLATES WITH LEWIS BASES AND DIOLS

Wanda Ziemkowska* and Andrzej Sawicki

Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland
<ziemkows@chemix.ch.pw.edu.pl>

Abstract

Alkylaluminium complexes with 1,2-catechols of formulae $R_5Al_3(OC_6H_4O)_2$ [**1** (R = Me), **2** (R = Et), **3** (R = *i*-Bu)] and $R_5Al_3[4\text{–}(CH_3)_3C\text{–}OC_6H_3O]_2$ [the mixture of **cis** and **trans** isomers] [**4** (R = Me), **5** (R = Et)] undergo the decomposition reaction in the presence of Lewis bases yielding the complexes $R_3Al{\cdot}B$ [where B = Et_2O, THF, py] and organoaluminium oligomers. The reaction of the alkylaluminium catecholates and diolates with diols proceeds similarly to the reaction with Lewis bases. The alkylaluminium catecholates $R_5Al_3(OC_6H_4O)_2$ [**3** (R = *i*-Bu), **9** (R = *t*-Bu)] and methylaluminium-1,3-propanediolate $Me_5Al_3(O(CH_2)_3O)_2$ [**6**] in the presence of diols undergo the decomposition to the intermediate [$R_3Al{\cdot}$diol] complexes which subsequently react forming trimetallic complexes R_5Al_3(diol–(2H))$_2$ [where R = *i*-Bu, Me] or bimetallic products R_4Al_2(diol–(H))$_2$ [where R = *t*-Bu].

1. Introduction

Trialkylaluminium compounds react easily with diols and 1,2-catechols yielding often trimetallic complexes of general formula $R_5Al_3[X\text{-}(2H)]_2$ (where R = Me, Et, *i*-Bu, *t*-Bu; X = diol or 1,2-catechol) [1 - 6]. The complexes are mostly stable in the presence of Lewis bases like diethyl ether or tetrahydrofurane. Recently a first example of decomposition reaction of the complex of 2-hydroxybenzyl alcohol with trialkylaluminium in diethyl ether was reported [7]. The complex undergoes the disproportionation reaction yielding $R_3Al{\cdot}OEt_2$ and white amorphous solid. The same reaction with Lewis bases was observed for dimethylaluminium methoxide, which undergoes the decomposition partially in THF and completely in pyridine yielding $MeAl(OMe)_2$ and the complexes of trimethylaluminium with Lewis bases [8]. Moreover similar decomposition reaction proceeds in the case of the complex of dimethylcyclopentadienylaluminium with THF and hemialkoxides Me_5Al_2OR [9, 10]. Dialkylaluminium acetylacetonates react with Lewis bases yielding $R_3Al{\cdot}B$ and $Al(acac)_3$ (where R = Me, Et, *i*-Bu; B = Et_2O, THF, Py, 2,6-dimethylpyridine, DMSO, HMPT) as disproportionation products [11, 12].

In an effort to gain a greater understanding of the stability of alkylaluminium catecholates and diolates an investigation of reactions of the complexes with Lewis bases like diethyl ether, tetrahydrofurane and pyridine and with diols has been undertaken.

2. Experimental section

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere. Alkylaluminium catecholates (**1** – **5**, **9**), methylaluminium-1,3-propanediolate **6** and methylaluminium-2,4-dimethyl-2,4-pentanediolate **7** were synthesised as described in the literature [4 – 6].

^{1}H NMR and spectra were recorded with a Varian VXR 300 spectrometer and Gemini – 200BB. Chemical shifts were referenced to the residual proton signal of C_6D_6 (7.15 ppm). ^{13}C NMR spectra were run on a Mercury-400BB spectrometer at 100.60 MHz (standard, benzene $^{13}CC_5D_6$, 128 ppm. ^{27}Al NMR spectra were run on Varian VXR 300 spectrometer, Gemini – 200BB and Unityplus – 500 Varian 500 (standard $Al(acac)_3$ = 0.0ppm). Molecular weight of the complexes was determined by the cryoscopy in benzene.

2.1. The reactions of methylaluminium-1,2-catecholate 1 with Lewis bases

1 g of the pure complex **1** was completely dissolved in 5 cm^3 of diethyl ether. In a few seconds the solution became turbid and white solid of organoaluminium oligomer has slowly precipitated. After 7 days the solid was separated by decantation, washed by diethyl ether and dried under vacuum. Elemental anal. Found: Al, 17.56; hydrolysable methyl groups, 11.44. Molar ratio Al : CH_3 = 1 : 1.18

The soluble part of the post-reaction mixture was concentrated and $Me_3Al{\cdot}OEt_2$ was obtained. The presence of the complex was confirmed by means of NMR spectroscopy. The ^{1}H NMR spectrum of the isolated product is in agreement with the literature data [13].

The reaction of **1** with THF was carried out as described above for diethyl ether. The white solid of the organoaluminium oligomer was obtained. Elemental anal. Found: Al, 17.67; hydrolysable methyl groups 11.28 wt%. Molar ratio Al : CH_3 = 1 : 1.15.

The soluble part of the post-reaction mixture contains only the complex $Me_3Al{\cdot}THF$. The stoichiometry of the compound was confirmed by ^{1}H NMR spectrum [14].

The reaction of **1** with pyridine was carried out as described above. The complex $Me_3Al{\cdot}py$ and the excess of pyridine was distilled off (10^{-3}Torr, 120°C, 10 h) and the light-yellow solid of organoaluminium oligomers was obtained. Elemental anal. Found: Al, 17.32; hydrolysable methyl groups 11.74 wt%. Molar ratio: Al : CH_3 = 1 : 1.22.

The distillate was concentrated and the complex $Me_3Al{\cdot}py$ was separated. The stoichiometry of the compound was confirmed by ^{1}H NMR spectrum [14].

2.2. The reactions of ethylaluminium-1,2-catecholate 2 with Lewis bases

The reaction of the pure complex **2** with diethyl ether was carried out as described for **1**. The solvent and volatile products were distilled off (10^{-3} Torr, 120°C, 10 h) and the white solid of organoaluminium oligomer was isolated. Elemental anal. Found: Al, 15.80; hydrolysable ethyl groups, 23.76 wt%. Molar ratio Al : C_2H_5 = 1 : 1.40.

The volatile product contains only the complex $Et_3Al{\cdot}OEt_2$, which was confirmed by ^{1}H NMR spectroscopy [14].

The disproportionation reaction of **2** with THF was carried out as described above. The white solid of organoaluminium oligomers was obtained. Elemental anal. Found: Al, 16.00; hydrolysable ethyl groups, 23.03 wt%. Molar ratio Al : C_2H_5 = 1 : 1.34.

The formation of the complex $Et_3Al{\cdot}THF$ as a sole volatile product was confirmed by ^{1}H NMR spectroscopy [14].

The disproportionation reaction of **2** with pyridine was carried out as described above. Light-yellow solid of the organoaluminium oligomer was obtained. Elemental anal. Found: Al, 15.70; hydrolysable ethyl groups, 20.81 wt%. Molar ratio Al : C_2H_5 = 1 : 1.24.

The complex $Et_3Al{\cdot}py$ was an exclusive volatile reaction product. The ^{1}H NMR spectrum confirmed the stoichiometry of the complex [14, 15].

2.3. The reactions of iso-butylaluminium-1,2-catecholate 3 with Lewis bases

The reaction of the pure complex **3** with diethyl ether was carried out as described for **1**. After 10 days the precipitation of the organoaluminium oligomer was not observed. Then diethyl ether was distilled off and unchanged complex **3** was obtained. ^{1}H NMR spectrum of the residue after distillation was the same as the spectrum of **3** [6].

The reaction of the pure complex **3** with THF was carried out as described for **1**. The white solid of organoaluminium oligomer was precipitated. Elemental anal. Found: Al., 13.40; hydrolysable *iso*-butyl groups, 31.07 wt%. Molar ratio Al : $(CH_3)_2CHCH_2$ = 1 : 1.08.

Only *i*-$Bu_3Al{\cdot}THF$ complex was present in the volatile products distilled off from the post-reaction mixture. The stoichiometry of the compound was confirmed by ^{1}H NMR spectrum [16].

The reaction of **3** with pyridine was carried out as described above and the light-yellow solid of organoaluminium oligomers was obtained. Elemental anal. Found: Al, 13.78; hydrolysable *iso*-butyl groups, 36.6 wt%. Molar ratio Al : *i*-Bu = 1 : 1.25.

The volatile product was only the complex *i*-$Bu_3Al{\cdot}py$. The ^{1}H NMR spectrum of the isolated product is in agreement with the literature data [16].

*2.4. The reactions of methylaluminium-4-tert-butyl-1,2-catecholate **4** (the mixture of **cis** and **trans** isomers) with Lewis bases*

The reaction of **4** with diethyl ether was carried out as described for **1**. Then 0.5 cm^3 of the solution was placed in the other flask and carefully concentrated under vacuum. The NMR spectra of the post-reaction mixture showed the presence of $Me_3Al{\cdot}OEt_2$ and organoaluminium oligomer. ^{1}H NMR (C_6D_6): δ 7.50 - 6.60 (m, Haromat.), 3.25 (m, $O(C\underline{H}_2CH_3)_2$), 1.30 - 0.85 (m, $(CH_3)_3C$, $O(CH_2CH_3)_2$), 0.10 - –0.50 (m, $AlCH_3$), –0.42 (s, $(CH_3)_3Al{\cdot}OEt_2$) ppm. ^{27}Al NMR (C_6D_6): δ 188 (four-coord. Al of $(CH_3)_3Al{\cdot}OEt_2$ and oligomer), 150 (four-coord. Al of the complex **4**), 92 (five-coord. Al of the complex 4), 10 (six-coord. Al of the oligomer) ppm.

The volatile complex $Me_3Al{\cdot}OEt_2$ was distilled off from the post-reaction mixture under vacuum (10^{-3} Torr, 120°C, 10 h) and the white amorphous solid of organoaluminium oligomer soluble in organic solvents was obtained. ^{1}H NMR (C_6D_6): δ 7.20 – 6.60 (m, Haromat.), 3.25 (m, 2H, $O(C\underline{H}_2CH_3)_2$, 1.30 – 0.90 (m, 21 H, $(CH_3)_3C$, $O(CH_2C\underline{H}_3)_2$), –0.07 - –0.72 (m, 10.5 H, $AlCH_3$) ppm. ^{27}Al NMR (C_6D_6): δ 185 (four-coord. Al of the oligomer), 55 (five-coord. Al of the oligomer), 14 (six-coord. Al of the oligomer) ppm. Elemental anal. Found: Al, 14.75; hydrolysable methyl groups, 12.1 wt%; Molar ratio Al : CH_3 = 1 : 1.48. Molecular weight: 1757.

The reaction of **4** with tetrahydrofuran was carried out as described for **1**. The composition of the post-reaction mixture was investigated by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 7.60 – 6.60 (m, H aromat.), 4.60 – 3.40 (m, $C\underline{H}_2O$(THF)), 1.00 – 1.25 (m, $(CH_3)_3C$, CH_2(THF)), –0.46 (s, $(CH_3)_3Al$ THF), 0.10 - –1.00(m, $AlCH_3$) ppm. ^{27}Al NMR (C_6D_6): δ 186 (four-coord. Al, $(CH_3)_3Al$ THF and the oligomer), 55 (five-coord. Al of the oligomer), 24 (six-coord. Al of the oligomer) ppm.

The solvent and $Me_3Al{\cdot}THF$ complex were distilled off from the post-reaction mixture (10^{-3} Torr, 120°C, 10 h) and white amorphous solid of organoaluminium oligomer was obtained. ^{1}H NMR (C_6D_6): δ 7.40 – 6.60 (m, H aromat.), 4.60 – 3.20 (4H, m, CH_2O(THF)), 1.40 – 1.00 (22H, m, $(CH_3)_3C$, CH_2(THF)), 0.00 - –1.00 (5.5H, m, $AlCH_3$) ppm. ^{27}Al NMR (C_6D_6): δ 62 (five-coord. Al), 20 (six-coord. Al) ppm. Elemental anal. Found: Al., 13.87; hydrolysable methyl groups 8.09 wt%. Molar ratio Al : CH_3 = 1 : 1.05. Molecular weight: 2008.

The reaction of 4 with pyridine was carried out as described for **1**. The composition of the post-reaction mixture has been studied by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 8.27 – 6.40 (m, H aromat. of the oligomer and pyridine), 1.22 (m, $(CH_3)_3C$), –0.25 (s, $(CH_3)_3Al{\cdot}py$), –0.10 - –0.80 (m, $AlCH_3$)ppm. ^{27}Al NMR (C_6D_6): δ 175 (four-coord. Al of $(CH_3)_3Al$ py and the oligomer), 54 (five-coord. Al), 24 (six-coord. Al) ppm. Pyridine and $Me_3Al{\cdot}py$ complex were distilled off from the post-reaction mixture (10^{-3} Torr, 150°C, 10 h) and light-yellow amorphous solid of the oligomer was obtained. ^{1}H NMR (C_6D_6): δ 8.30 – 6.40 (H aromat. of the oligomer and pyridine), 1.20 (m, $(CH_3)_3C$), 0.08 (s, $AlCH_3$), –0.45 (s, $AlCH_3$), –0.50 - –1.00 (m, $AlCH_3$) ppm. ^{27}Al NMR (C_6D_6): δ 150 (four-coord. Al of the oligomer), 50 (five-coord. Al), 19 (six-coord. Al) ppm. Elemental anal. Found: Al., 14.17; hydrolysable methyl groups, 8.27 wt%. Molar ratio Al : CH_3 = 1 : 1.05. Molecular weight: 1107.

*2.5. The reactions of ethylaluminium-4-tert-butyl-1,2-catecholate 5 (the mixture of **cis** and **trans** isomers) with Lewis bases*

The reaction of **5** with diethyl ether was carried out as described for the complex **1**. The mixture of the complex $Et_3Al{\cdot}OEt_2$ and organoaluminium oligomer was isolated. ^{1}H NMR (C_6D_6): δ 7.50 - 6.50 (m, H aromat.), 4.10 – 3.40 (m, $O(C\underline{H}_2CH_3)_2$), 3.40 (q, $\underline{O}(CH_2CH_3)_2{\cdot}Et_3Al$), 1.40 – 0.80 (m, $(CH_3)_3C$, $AlCH_2C\underline{H}_3$, $O(CH_2C\underline{H}_3)_2$), 0.50 – 0.00 (m, $AlC\underline{H}_2CH_3$) ppm. ^{27}Al NMR (C_6D_6): δ 175 (four-coord.Al, $Et_3Al{\cdot}OEt_2$) 150 (four-coord. Al of the oligomer), 53 (five-coord. Al), 7 (six-coord. Al) ppm.

The complex $Et_3Al{\cdot}OEt_2$ was distilled off under vacuum and the white solid of oligomer was obtained. Elemental anal. Found: Al, 12.73; hydrolysable ethyl groups, 19.14 wt%. Molar ratio Al : C_2H_5 = 1 : 1.40.

The reaction of **5** with THF was carried out as described for the complex **1**. The post-reaction mixture of oligomer and $Et_3Al{\cdot}THF$ complex was investigated by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 7.60 – 6.60 (m, H aromat.), 3.41 (m, CH_2O(THF)), 1.41 (t, $Al(CH_2CH_3)_3{\cdot}THF$), 1.40 – 0.80 (m, $(CH_3)_3C$), 1.12 (m, CH_2(THF)), 0.18 (q, $Al(CH_2CH_3)_3{\cdot}THF$) ppm. ^{27}Al NMR (C_6D_6): δ 176 (four-coord. Al, $Et_3Al{\cdot}THF$), 41 (five- coord. Al) ppm.

The complex $Et_3Al{\cdot}THF$ was distilled off under vacuum and the white solid of oligomer was obtained. ^{1}H NMR (C_6D_6): δ 7.60 – 6.60 (m, H aromat.), 4.50 – 3.37 (m, CH_2O(THF)), 1.50 –0.60 (m, $(CH_3)_3C$, $AlCH_2CH_3$), 0.40 – 0.00 (m, $AlC\underline{H}_2CH_3$) ppm. ^{27}Al NMR (C_6D_6): δ 179 (four- coord. Al, $AlOEt_2{\cdot}THF$), 10 (six-coord. Al) ppm. Elemental anal. Found: Al, 12.95; hydrolysable ethyl groups, 14.42 wt%. Molar ratio Al : C_2H_5 = 1 : 1.04. Molecular weight: 1790.

The reaction of **5** with pyridine was carried out as described for **1**. The post-reaction mixture of the oligomer and $Et_3Al{\cdot}py$ complex has been studied by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 8.10 – 6.30 (m, H aromat., py and oligomer), 1.43 (t, $Al(CH_2C\underline{H}_3)_3{\cdot}py$), 1.50 – 0.60 (m, $(CH_3)_3C$, $AlCH_2C\underline{H}_3$), 0.41 (q, $Al(CH_2CH_3)_3{\cdot}py$) ppm. ^{27}Al NMR (C_6D_6): δ 171 (four-coord. Al, $AlEt_3{\cdot}py$), 54 (five- coord. Al), 24 (six-coord. Al) ppm.

$Et_3Al{\cdot}py$ complex was distilled off from the post-reaction mixture) and the light-yellow solid was obtained. ^{27}Al NMR (C_6D_6): δ 54 (five-coord. Al), 15 (six-coord. Al) ppm. Elemental anal. Found: Al, 12.65; hydrolysable ethyl groups, 14.60 wt%. Molar ratio Al:C_2H_5 = 1:1.07. Molecular weight: 1340.

2.6. The reaction of methylaluminium-1,3-propanediolate 6 with 2,4-dimethyl-2,4-pentanediol

To a diethyl ether solution of methylaluminium-1,3-propanediolate 6 (1.105 g, 3.7 mmol), at –76°C, was added the diethylether solution of 2,4-dimethyl-2,4 pentanediol (0.480 g, 3.6 mmol). The reaction mixture was allowed to warm up to room temperature within 2 h. After 24 h the solvent was distilled off from the transparent post-reaction mixture. Methylaluminium-2,4-dimethyl-2,4-pentanediolate 7 was sublimed off under vacuum as a white solid (0.154 g, 0.37 mmol, yield 20%).

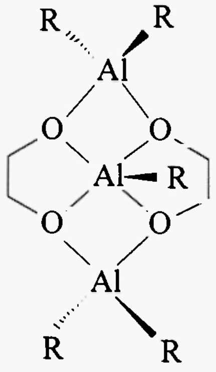
^{1}H NMR (C_6D_6): δ 1.75 (d, ^2J(H–H) = 14.8 Hz, 2H, CH_2), 1.26 (s, 12H, $(CH_3)_2C$), 1.16 (s, 12H, $(CH_3)_2C$), 0.96 (d, ^2J(H–H) = 14.8 Hz, 2H, CH_2), –0.37 (s, 6H, CH_3Al), –0.38 (s, 6H, CH_3Al), –0.40 (s, 3H, CH_3Al) ppm. ^{13}C NMR (C_6D_6): δ 74.50 ($(CH_3)_2\underline{C}O$), 51.45 (CH_2), 33.65, 30.83 ($(\underline{C}H_3)_2C$), –5.40, –6.40 (CH_3Al) ppm. ^{27} Al NMR (C_6D_6): δ 155 (four-coord. Al), 65 (five-coord. Al) ppm.

2.7. The reaction of methylaluminium-2,4-dimethyl-2,4-pentanediolate 7 with 1,3-propanediol

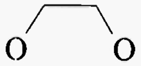
To a diethyl ether solution of methylaluminium-2,4-dimethyl-2,4-pentanediolate 7 (0.844 g, 2.1 mmol), at –76°C, was added the diether solution of 1,3-propanediol (0.153 g, 2.0 mmol). The reaction mixture was allowed to warm up to room temperature within 2 h, than after 24 h a white amorphous solid precipitated from the post-reaction mixture. The solution under the solid was determined by ^{1}H NMR spectroscopy to be the solution of the unreacted complex 7 [5]. The insoluble solid was isolated by decantation and dried under vacuum. Elemental anal. Al, 2.30; hydrolysable methyl groups, 16.85 wt%. Molar ratio Al : Me = 1 : 0.25.

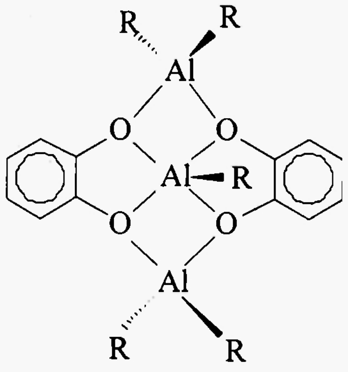
2.8. The reaction of iso-butylaluminium-1,2-catecholate 3 with 2,2'-di(hydroxymethyl)biphenyl

To a diethyl ether solution of *iso*-butylaluminium 1,2-catecholate **3** (1.755 g, 3.0 mmol), at –76°C, was added a toluene solution of 2,2'-di(hydroxymethyl)biphenyl (0.610 g, 2.9 mmol). The reaction mixture was allowed to warm up to room temperature within 2 h, that after this time the volatiles were removed under vacuum. The residue was crystallised from hexane-toluene to give a white powder of **8** (0.521 g, 0.7 mmol, 22% yield).

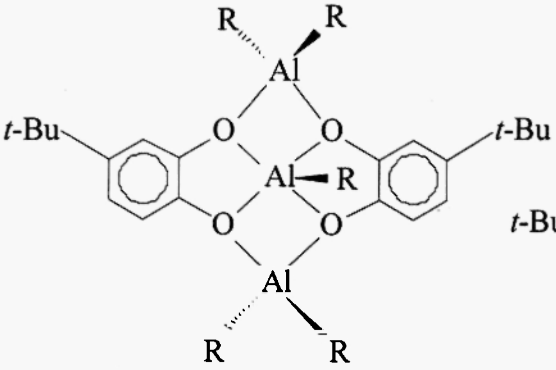


I

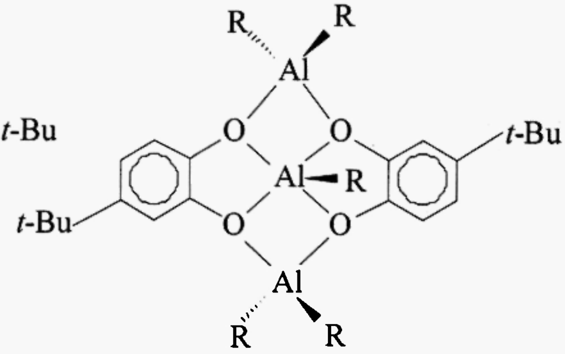

= diol - (2H), R = Me, Et



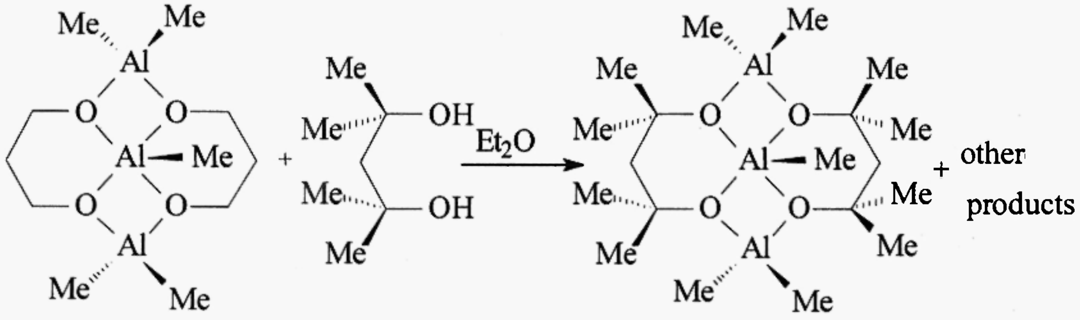
1 (R = Me)
2 (R = Et)
3 (R = *i*-Bu)



4 cis (R = Me)
5 cis (R = Et)



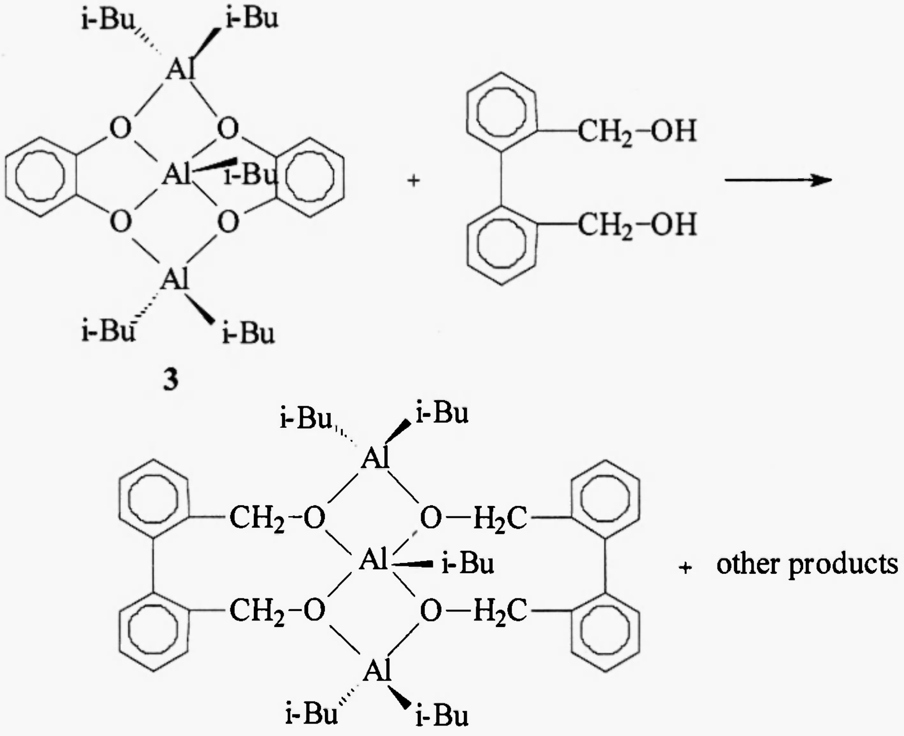
4 trans (R = Me)
5 trans (R = Et)



6

7

(1)



3

(2)

8

^{1}H NMR (C_6D_6): δ 7.91 (d, 2H ^3J(H–H) = 7.8 Hz, Haromat.), 7.61 (d, 2H ^3J(H–H) = 7.6 Hz, Haromat.), 7.30 6.90 (m, 12H, Haromat.) 4.80 (d, 2H, ^2J(H–H) = 12.8 Hz, CH_2O), 4.63 (d, 2H, ^2J(H–H) = 12.9 Hz, CH_2O), 4.62 (d, 2H, ^2J(H–H) = 11.7 Hz, CH_2O) 4.39 (d, 2H, ^2J(H–H) = 11.7 Hz, CH_2O), 2.38 (m, 2H, $(CH_3)_2CHCH_2$), 1.63 (m, 2H, $(CH_3)_2C\underline{H}CH_2$), 1.55 (m, 1H, $(CH_3)_2C\underline{H}CH_2$), 1.37 (d, 12H, ^3J(H–H) = 6.4 Hz, $(C\underline{H}_3)_2CHCH_2$), 0.92 (d, 6H, ^3J(H–H) = 6.4 Hz, $(C\underline{H}_3)_2CHCH_2$), 0.90 (d, 6H, ^3J(H–H) = 6.4 Hz, $(C\underline{H}_3)_2CHCH_2$), 0.72 (d, 6H, ^3J(H–H) = 6.6 Hz, $(C\underline{H}_3)_2CHCH_2$), –0.03 (m, 10H, $(CH_3)_2CHC\underline{H}_2$) ppm. ^{13}C NMR ($C_6D_6$): δ 141.23, 139.54, 137.43, 136.16, 130.92, 130.69, 130.58, 130.31, 129.18, 128.60, 128.44, 128.54 (Caromat.), 63.30, 62.70 (CH_2O), 29.03, 28.72, 25.65 ($(\underline{C}H_3)_2CHCH_2$), 27.94, 26.53, 22.94 ($(CH_3)_2\underline{C}HCH_2$), 20.07 ($(CH_3)_2CH\underline{C}H_2$, broad) ppm.

Elemental anal. Found: Al, 9.98; hydrolysable *iso*-butyl groups, 35.88; Calc.: Al, 10.25; *i*-Bu, 36.08 wt%.

2.9. The reaction of tert-butylaluminium 1,2-catecholate 9 with 2,2'-di(hydroxymethyl)biphenyl

To a toluene solution of *tert*-butylaluminium 1,2-catecholate **9** (0.500 g, 0.9 mmol), at –76°C, was added a toluene solution of 2,2'-di(hydroxymethyl)biphenyl (0.185 g, 0.9 mmol). The reaction mixture was allowed to warm up to room temperature within 2 h, that after this time the volatiles were removed under vacuum. The residue was crystallised from hexane to give a white powder of the mixture of **10a** and **10b** contaminated by organoaluminium oligomers (0.134 g, 21% yield).

^{1}H NMR (C_6D_6): δ 7.40 – 6.60 (m, broadened, H arom); **10a**: 16.04 (t, 2H, ^3J(H-H) = 3.2 Hz, OH), 4.62 (d, 4H, ^2J(H-H) = 10.1 Hz, CH_2), 4.54 (dd, 4H, ^2J(H-H) = 10.1 Hz, ^3J(H-H) = 3.2 Hz, CH_2), 0.92 (s, 36H, $(CH_3)_3C$); **10b**: 16.30 (t, 2H, ^3J(H-H) = 4.8 Hz, OH), 4.43 (d, 4H, ^2J(H-H) = 11.6 Hz, CH_2), 4.31 (dd, 4H, ^2J(H-H) = 11.6Hz, ^3J(H-H) = 4.8 Hz, CH_2), 1.19 (s, 18H, $(CH_3)_3C$), 0.95 (18H, s, $(CH_3)_3C$) ppm. ^{13}C NMR (C_6D_6): δ **10a**: 141.99, 135.94, 131.53, 129.09, 128.76, 128.52 (C arom), 64.72 (CH_2O), 31.01 ($(\underline{C}H_3)_3C$), 15.35 ($(CH_3)_3\underline{C}$) **10b**: 63.85, 62.84 (CH_2), 31.42, 31.23 ($(\underline{C}H_3)_3C$) ppm.

3. Results and discussion

Alkylaluminium diolates **I** are stable in the presence of popular Lewis bases. In the contrary to the complexes **I** alkylaluminium catecholates **1** – **5** show lower stability. The complexes **1**, **2** and **3** dissolved in diethyl ether, tetrahydrofuran and pyridine undergo decomposition reaction with the precipitation of amorphic organoaluminium oligomers insoluble in organic solvents. Moreover the complexes of trialkylaluminium with Lewis bases [$R_3Al{\cdot}B$] [where B = Et_2O, THF, py] were isolated and their formation during the course of the reaction was confirmed by NMR spectroscopy. The reactivity of alkylaluminium catecholates towards Lewis bases is different depending on the bulk of the aluminium alkyl groups. Methylaluminium catecholate **1** undergoes disproportionation reaction immediately after dissolution in diethyl ether whereas the reaction of the complex **3** with Et_2O was not observed.

The elemental analyses of organoaluminium oligomers precipitated in the disproportionation reaction show the contents of hydrolysable aluminium alkyl groups from 1.08 to 1.40 moles per 1 mol of aluminium.

On the contrary to **1**, **2** and **3** the complexes **4** (**cis** + **trans**) and **5** (**cis** + **trans**) undergo disproportionation reaction yielding the organoaluminium oligomers soluble in organic solvents. The pure organoaluminium oligomer was isolated from the post-reaction mixture of **4** with THF by distillation off the solvent and $Me_3Al{\cdot}THF$ complex under vacuum. The ^{27}Al NMR spectrum of the oligomer reveals two broad signals at 62 and 20 ppm of five- and six-coordinate aluminium atoms respectively. In the ^1H NMR spectrum besides the signals of $AlCH_3$ groups, tert-butyl groups and aromatic protons, very broad multiplet of THF protons in the region 3.2-4.6 ppm is observed. It was calculated from the integration ratio of THF protons to tert-butyl protons that the oligomer consists about 1 mol of THF per 2 moles of diol residue. It means that tetrahydrofuran co-ordinates to aluminium atoms in the oligomer after disproportionation reaction. Lewis bases complexed with organoaluminium oligomers were observed in NMR spectra of all products isolated from the post-reactions mixtures of **4** and **5** with diethyl ether, tetrahydrofurane and pyridine.

As expected, in comparison with THF and pyridine the weak base Et_2O reacts slowly with **4** and **5**. After 7 days besides the new signals of $R_3Al{\cdot}OEt_2$ and oligomer, in the ^{27}Al NMR spectrum of the post-reaction mixture the signal of four- and five-coordinate aluminium atoms of unreacted complexes **4** and **5** are present. The molar ratio of alkyl groups to aluminium calculated on the basis of elemental analysis is equal about 1.40:1. For comparison the oligomers obtained in the reactions with THF and pyridine contain about 1.1 moles of alkyl groups per one mole of aluminium.

Molecular weights of the isolated organoaluminium oligomers determined cryoscopically enclose in the range 1100-2000 $g{\cdot}mol^{-1}$.

The reactivity of alkylaluminium catecholates towards Lewis bases is caused by low basicity of the oxygen atoms in comparison with the alkylaluminium diolates. Additionally the strain in two five-membered rings AlOCCO facilitates the cleavage of Al–O bonds. Presumably the first step of the reaction is the formation of the complex of alkylaluminium catecholate with Lewis base $[R_5Al_3(catechol\text{-}(2H))_2{\cdot}B]$, then the decomposition of the complex to $R_3Al{\cdot}B$ and to the species with unsaturated aluminium atoms which associate yielding organoaluminium oligomers.

It appeared unexpectedly that diols react with alkylaluminium diolates and catecholates similarly to the presented above Lewis bases. In the presence of the diols, alkylaluminium diolates and catecholates undergo the disproportionation reaction, and the decomposition products react further with the diols. The reaction of methylaluminium-1,3-propanediolate **6** with 2,4-dimethyl-2,4-pentanediol proceeds with the formation of organoaluminium oligomer and the complex **7**, which was distilled off from the post-reaction mixture (yield 20%) (Eq. 1). It was confirmed on the basis of NMR spectra and elemental analysis that the product **7** is the earlier reported complex of trimethylaluminium with 2,4-dimethyl-2,4- [5].

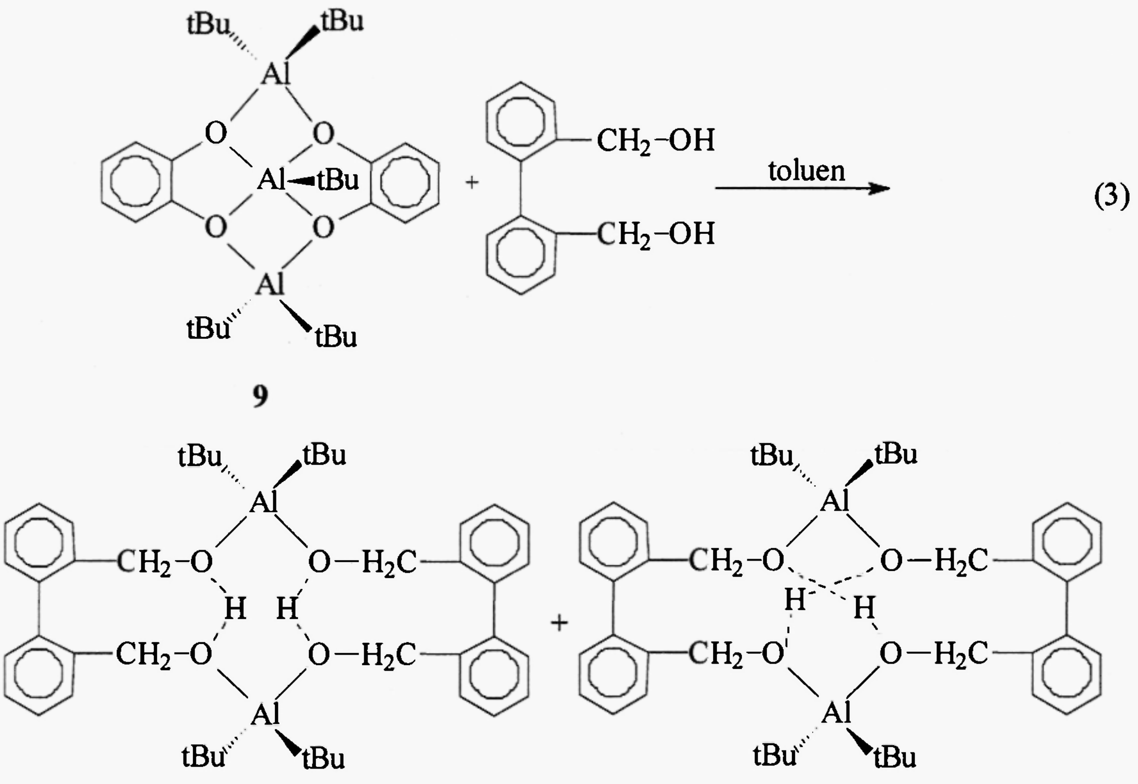
The compound **7** reacts slowly with 1,3-propanediol yielding only organoaluminium oligomers, which precipitates from the post-reaction mixture as a white amorphous solid. The compound **6** was not found in the post-reaction mixture. On the other hand the complex **7** was stable in the presence of 2,4-dimethyl-2,4-pentanediol even when the reaction was carried out in refluxing toluene. It is probably caused by steric hindrances of the diol.

As shown above *iso*-butylaluminium catecholate **3** undergoes the disproportionation reaction in THF and pyridine to the complex $i\text{-}Bu_3Al{\cdot}B$ and organoaluminium oligomer. In the presence of 2,2'-di(hydroxymethyl)biphenyl the compound **3** reacts yielding a complex **8** which was isolated by crystallisation from the post-reaction mixture with the yield 22% [Eq. 2]. Besides **8** the mixture of other unidentified oligomeric products is formed.

It was found by means of NMR spectroscopy and elemental analysis that the product **8** possesses the same structure as a complex obtained in the reaction of $i\text{-}Bu_3Al$ with 2,2'-di(hydroxymethyl)biphenyl [17].

The compound **7** reacts slowly with 1,3-propanediol yielding only organoaluminium oligomers, which precipitates from the post-reaction mixture as a white amorphous solid. The compound **6** was not found in the post-reaction mixture. On the other hand the complex **7** was stable in the presence of 2,4-dimethyl-2,4-pentanediol even when the reaction was carried out in refluxing toluene. It is probably caused by steric hindrances of the diol.

The ^1H NMR spectrum of **8** reveals the following signals of $(CH_3)_2CHCH_2Al$ groups: doublet at 1.37 ppm (J = 6.4 Hz) and two doublets at 0.92 (J = 6.4 Hz) and 0.90 (J = 6.4 Hz) ppm of *iso*-butyl groups bonded to four- coordinate aluminium atoms and doublet at 0.72 pm (J = 6.6 Hz) of *iso*-butyl group bonded to the central pentacoordinated aluminium atom.



9

10a

10b

$$R_5Al_3[diol^1\text{-}(2H)]_2 \;+\; diol^2 \longrightarrow [R_3Al\cdot diol^2] \;+\; \begin{array}{l}\text{unidentified}\\ \text{products}\end{array}$$

$$3\,[R_3Al\cdot diol^2] \xrightarrow[R=Me,\ i\text{-}Bu]{-4RH} R_5Al_3[diol^2\text{-}(2H)]_2 \;+\; diol^2$$

Scheme 1. Proposed pathway for the reaction of alkylaluminium diolates and catecholates with diolates.

Tert-butylaluminium derivative of 1,2-catechol **9** reacts with 2,2'- di(hydroxymethyl)biphenyl forming two products **10a** and **10b** [Eq. 3]. The products contaminated by organoaluminium oligomers were isolated by crystallisation from the post-reaction mixture. On the contrary to the *iso*-butylaluminium catecholate **3**, the compound **9** reacts with 2,2'- di(hydroxymethyl)biphenyl yielding bimetallic products **10a** and **10b** with two OH groups.

$$2\,[R_3Al\cdot diol^2] \xrightarrow[R=t\text{-}Bu]{-2RH} R_4Al_2[diol^2\text{-}H]_2$$

The ^1H NMR spectrum reveals two downfield shifted triplets at 16.07 and 16.34 ppm, which were assigned to the OH protons forming intramolecular hydrogen bondings of the major product **10a** and minor product **10b** respectively. Moreover the spectrum shows the doublet at 4.64 and doublet of doublets at 4.56 ppm of CH_2 protons and the singlet at 0.94 ppm of $(CH_3)_3C$ of the complex **10a**. The signals of the methylene and *tert*-butyl groups of the product **10b** are also present in the spectrum (see Experimental section).

It has been recently appeared that the complexes **10a** and **10b** are the only products formed in the reaction of t-Bu$_3$Al with 2,2'-di(hydroxymethyl)biphenyl irrespective of the t-Bu$_3$Al : diol ratio [18]. The formation of a trimetallic product t-$Bu_5Al_3(OCH_2C_{12}H_8CH_2O)_2$ was not observed. It was confirmed on the basis of the ^1H and ^{13}C NMR spectra that the reaction products of **9** with 2,2'-di(hydroxymethyl)biphenyl are the same as the reaction product of t-Bu$_3$Al with 2,2'-di(hydroxymethyl)biphenyl.

It was proposed on the basis of the isolated products, that the diol causes first the decomposition of the alkylaluminium diolate or catecholate to the intermediate [$R_3Al{\cdot}diol^2$] complex and unidentified organoaluminium oligomers (Scheme 1). Then the complex [$R_3Al{\cdot}diol^2$] reacts yielding trimetallic complex $R_5Al_3(diol^2\text{-}(2H))_2$ (where R = Me, *iso*-Bu) or bimetallic product $R_4Al_2(diol^2\text{-}(H))_2$ (where R = *tert*-Bu).

References

1. S. Pasynkiewicz, W. Ziemkowska, *J. Organomet. Chem.*, **423** (1992) 1.
2. S. Pasynkiewicz, W Ziemkowska, *J. Organomet. Chem.*, **437** (1992) 99.
3. W. Ziemkowska, S Pasynkiewicz, E Kalbarczyk, *J. Organomet. Chem.*, **465** (1994) 93.
4. W. Ziemkowska, S Pasynkiewicz, *J. Organomet. Chem.*, **508** (1996) 243.
5. W. Ziemkowska, S. Pasynkiewicz, T. Glowiak, *J. Organomet. Chem.*, **562** (1998) 3.
6 W Ziemkowska, *Main Group Met. Chem.*, **23** (2000) 389.
7. W. Ziemkowska, S. Pasynkiewicz, T. Skrok, *Main Group Met. Chem.*, **21** (1998) 105.
8. T. Mole, *Australian J. Chem.*, **19**(1966) 373.
9. W. R. Kroll, W. Naegele, *Chem. Commun.* (1969) 246.
10. E. A. Jeffery, T. Mole, *Australian J. Chem.* **23** (1970) 715.
11. S. Pasynkiewicz, K. Dowbor, *J. Organomet. Chem.* **39** (1972) C1.
12. S. Pasynkiewicz, J. Lewinski, *J. Organomet. Chem.* **290** (1985) 15.
13. T. Mole, *Australian J. Chem.*, **17** (1964) 1050.
14. K. Hatada, H Yuki, *Tetrahedron Lett.,* (1968) 213.
15. L. Petrakis et al., *J. Phys. Chem.* **72** (1968) 546.
16. B. Sen et al., *J. Inorg. Nucl. Chem.* **35** (1973) 2207.
17. W. Ziemkowska, submitted for publication.
18. W. Ziemkowska, *J. Organomet. Chem.* submitted for publication.

Received: January 19, 2001 - Accepted: February 1, 2001 - Accepted in publishable format: February 6, 2001