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The cyclopentadienylaluminium etheralkoxide derivative $[(\eta^1\text{-}C_5H_5)_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$; synthesis and structure

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Abstract

The reaction of $[Cl_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (**1**) with NaCp leads to the formation of etheralkoxy bridged dimer $[(\eta^1\text{-}C_5H_5)_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (**2**) containing five-coordinate aluminium atoms. The compound was characterised by ^1H-, ^{13}C- and ^{27}Al-NMR spectra and its crystal structure was determined by single crystal X-ray diffraction studies. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium; Bifunctional; Cyclopentadienyl; 2-Propoxyethanol

1. Introduction

Though the first cyclopentadienylaluminium compound was synthesised in 1961 [1] only several alkoxy- and phenoxycyclopentadienylaluminium derivatives are known [2–5].

A few years ago we described the synthesis and the structure of dicyclopentadienylaluminium isopropoxide obtained from the reaction of CpNa and $Cl_2AlO\text{-}^iPr$. [3] The compound was found to be a dimer both in the solution and the solid state. The cyclopentadienyl ligands are bonded to aluminium atom in η^1 manner. The η^1 bonding mode of cyclopentadienyl ring was also observed in $[(C_5Me_4H)AlCl(\mu\text{-}O^iPr)]_2$ [4]. This compound was obtained from the reaction of $(C_5Me_4H)_2Mg$ and $Cl_2AlO\text{-}^iPr$. It was found that in the reaction only one chlorine atom was replaced by the bulky C_5Me_4H group. The formation of $[Cp_2Al(BHT)]_x$ and $CpAl(BHT)_2$ cyclopentadienyl derivatives was found in the reaction of Cp_3Al with one equivalent of 2,6-di-*tert*-butyl-4-methylphenol. Due to the instability of $[Cp_2Al(BHT)]_x$ only $CpAl(BHT)_2$ could be fully characterised which was found to be monomeric in the solid state with an η^5-Cp geometry [5].

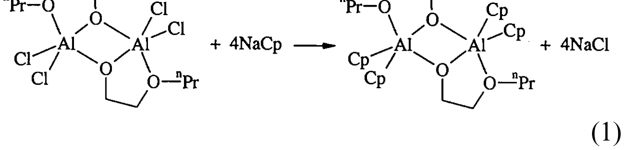
Organoaluminium derivatives of (O,O′) bifunctional ligands have been investigated for many years due to their practical and fundamental importance. These compounds are used as catalysts and precursors of catalysts in polymerisation processes [6,7] and organic reactions [8].

In this paper we report the synthesis and the structure characterisation of the first five-coordinate cyclopentadienylaluminium complex with (O,O′) 2-propoxyethanolato chelate ligand.

2. Results and discussions

2.1. Synthesis, properties and NMR analysis

$[(\eta^1\text{-}C_5H_5)_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (**2**) was obtained with high yield at room temperature in toluene from the reaction of $[Cl_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (**1**) and NaCp according to equation (1):



(1)

In the studied reaction both chlorine atoms are replaced by cyclopentadienyl ligands. In the reaction of

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tert-butoxyaluminium dichloride with NaCp [9] or *iso*-propoxyaluminium dichloride with $(Me_4CpH)_2Mg$ [4] one chlorine atom only was found to be replaced by cyclopentadienyl ring due to the steric hindrance. We found that the substitution of both chlorine atoms of $[Cl_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (**1**) by Cp ligands occurs despite overcrowding in aluminium atom coordination sphere.

In the literature the dimer–monomer as well as closed-dangling (O,O′) ligands equilibrium in dialkylaluminium chelates are considered (Scheme 1) [10].

We showed earlier [11] that in dimeric dialkyl compounds containing etheralkoxy ligands the $Al\text{–}O_{etheral}$ bonds are the weakest ones what causes that complex retains dimeric structure in solution and closed-dangling (O,O′) ligand equilibrium is preferred. We think that such equilibrium facilitates the replacement of the chlorine atoms in **1** by cyclopentadienyl ligands and $[(\eta^1\text{-}C_5H_5)_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (**2**) is formed exclusively.

Pure compound **2** was separated by crystallisation from toluene as colourless crystals. The compound is air and moisture sensitive. In the presence of oxygen a brown solid is formed.

Compound **2** was found to be a dimer ($n = 2.01$) in benzene solution. The molecular weight was measured cryometrically.

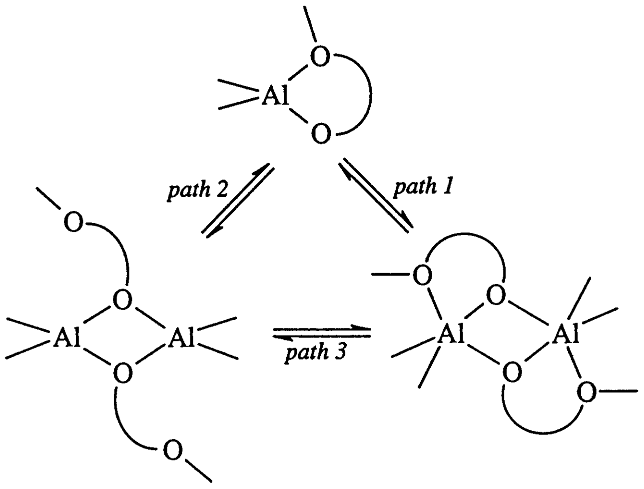
^{1}H- and ^{13}C-NMR spectra of **2** show five groups of signals characteristic for the 2-propoxyethanolato substituent and one signal for the cyclopentadienyl ligands. The spectroscopic data are consistent with the chemical formula of the compound but they are not sufficient for determination of the Cp–Al bond nature. The equivalence of cyclopentadienyl hydrogen and carbon atoms on the NMR time scale can result from rapid ring 'whizzing' [12]. The low temperature NMR spectra could not be measured because the studied cyclopentadienyl compound precipitated from toluene solution at this condition.

^{27}Al-NMR measurements of **2** show a broad signal at 89 ppm. In the literature, for $[Me_2Al(\mu\text{-}OCH_2CH_2OMe)]_2$ and $[Me_2Al(\mu\text{-}OCH(Me)COOEt)]_2$ the signals at 121 [10] and 114 ppm [11] were found, respectively and five-coordinate aluminium atom proposed. In our opinion the chemical shift and broad character of the signal observed for **2** suggest occurrence of five- and four-coordinate aluminium. This is consistent with the equilibrium showed on Scheme 1 (path 3).

2.2. Crystal and molecular structure of $[(\eta^1\text{-}C_5H_5)_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$ (2)

The compound **2** crystallises in monoclinic system in $P2_1/n$ symmetry space group (Table 1). The molecular structure with atom numbering scheme is shown in Fig. 1.

The X-ray structure analysis revealed the alkoxide-bridged dimeric molecules. The asymmetric unit comprises one half of the dimer, the other half being generated by the centre of symmetry. Thus, the overall



Scheme 1.

Table 1
Crystallographic data for compound **2**

Empirical formula	$C_{30}H_{42}Al_2O_4$
Formula weight	520.60
Temperature (K)	293(2)
Wavelength (Å)	Mo–K_α ($\lambda = 0.71073$ Å), graphite-monochromated
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
Unit cell dimensions	
a (Å)	7.9066(11)
b (Å)	11.4330(14)
c (Å)	16.506(2)
β (°)	91.839(11)
V (Å^3)	1491.3(3)
Z	2
D_{calc} (Mg m^{-3})	1.159
Absorption coefficient (mm^{-1})	0.129
F(000)	560
Crystal size (mm)	$0.14 \times 0.16 \times 0.26$
θ range for data collection (°)	2.17–25.06
Index ranges	$0 \le h \le 9$, $0 \le k \le 13$, $-19 \le l \le 19$
Reflections collected	2830
Independent reflections	2628 ($R_{int} = 0.0291$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2628/0/205
Goodness-of-fit on F^2	0.999
Reflections with $I > 2\sigma(I)$	1497
Final R indices ($I > 2\sigma(I)$) [a]	$R_1 = 0.0634$, $wR_2 = 0.1651$
R indices (all data) [a]	$R_1 = 0.1149$, $wR_2 = 0.1965$
Largest difference peak and hole (eÅ^{-3})	+0.407 and −0.254

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = (\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^4)^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.1135P)^2$ where $P = (F_o^2 + 2F_c^2)/3$.

molecule is crystallographically constrained to possess C_i point group symmetry. No short intermolecular contacts between dimers are observed.

The aluminium atom in **2** is five-coordinate and the geometry of the coordination sphere can be described as a distorted trigonal bipyramid.

The equatorial plane is defined by the C(6) and C(11) carbon atoms of cyclopentadienyls and O(1) alkoxide oxygen atom of the chelating ligand. The Al(1)–O(1) bond length of 1.822(3) Å is the one of the shortest Al–O bond observed for five-coordinate dialkylaluminium complexes [10,11,13]. The equatorial angles range from 116.1(3) to 124.3(2)° and the first is the C(6)–Al(1)–C(11) angle. The Al(1) atom lies almost exactly in the plane defined by O(1), C(6) and C(11) atoms with the displacement of 0.063(3) Å towards axial O(1′) bridging alkoxide atom. The second axial position is occupied by an etheral oxygen O(2) atom with Al(1)–O(2) bond length of 2.108(2) Å whereas the Al(1)–O(1′) bond length is much shorter (1.889(2) Å). The observed differentiation is in agreement with previously described five-coordinate etheralkoxide dimeric alkylaluminium complexes, e.g. 2.268 and 1.891 Å for $Me_2Al(\mu\text{-}OCH_2CH_2O\text{-}Me)]_2$ [10a]. Thus for both structures the external axial oxygen atom forms the weakest Al–O bond what points at proposed equilibrium (Scheme 1 path 3). The angle O(1′)–Al(1)–O(2) between the axial substituents is 153.4(1)° and the displacement of both Al(1)–O(2) and Al(1)–O(1′) bonds from the normal to the equatorial meanplane is due to the constraints in the five-membered AlOCCO chelate ring and in the four-membered Al_2 (μ-O)$_2$ bridging central core. The Al_2 (μ-O)$_2$ ring is planar with the bond angles Al(1)–O(1)–Al(1′) and O(1)–Al(1)–(O1′) equal to 104.41 and 75.59(11)°, respectively. The five-membered ring AlOCCO of the chelate is twisted on C(1)–C(2) with the torsion angle Al(1)–O(2)–C(2)–C(1) value of 37.2(4)° what can be assigned to sp^3 coordination sphere of the etheral O(2) oxygen atom (Fig. 1.) Selected bond lengths, bond angles and torsion angles are collected in Tables 2 and 3

The cyclopentadienyl ligands are bonded to aluminium atoms in η^1 manner with Al–C distances equal to 2.044(5) and 2.047(5) Å for Al(1)–C(6) and Al(1)–C(11), respectively. For η^1-Cp–Al complexes described in the literature the Al–C bond lengths vary from 1.976 [4] to 2.080 Å [14] with the mean equal to 2.029 Å. The C–C bond lengths analysis for cyclopentadienyl ligands showed that in one cyclopentadienyl ring two bonds are shorter (C(12)–C(13) 1.355(9); C(14)–C(15) 1.354(8) Å) with the remaining distances as follows: C(11)–C(15) 1.439(8); C(11)–C(12) 1.436(7); C(13)–C(14) 1.396(10) Å. The observed differentiation of C–C bond lengths is consistent with η^1 bonding type of Cp to a metal. Examination of C–C distances in the second ring showed extreme bond shortening (Table 2)

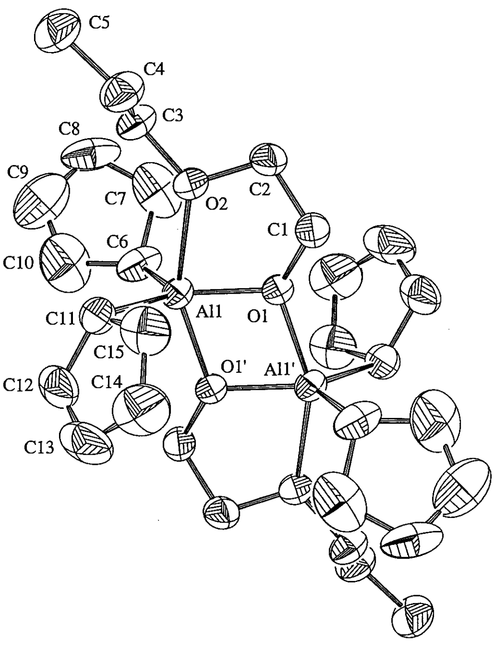


Fig. 1. An ORTEP [18] diagram of **2** showing 40% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths and non-bonded contacts (Å) for **2** [a]

Al(1)–O(1)	1.822(3)	O(1)–C(1)	1.433(4)
Al(1)–O(1′)	1.889(2)	O(2)–C(2)	1.438(5)
Al(1)–O(2)	2.108(2)	O(2)–C(3)	1.450(4)
Al(1)–C(6)	2.044(5)	Al(1)–C(11)	2.047(5)
Al(1)···C(10)	2.783(7)	Al(1)···C(15)	2.707(6)
Al(1)···C(7)	2.987(7)	Al(1)···C(12)	2.902(5)
C(6)–C(10)	1.370(9)	C(11)–C(15)	1.439(8)
C(6)–C(7)	1.478(9)	C(11)–C(12)	1.436(7)
C(7)–C(8)	1.412(9)	C(12)–C(13)	1.355(9)
C(8)–C(9)	1.295(11)	C(13)–C(14)	1.396(10)
C(9)–C(10)	1.243(10)	C(14)–C(15)	1.354(8)

[a] Atoms labelled with prime belong to the centrosymmetric counterparts of the dimer.

Table 3
Selected bond angles and torsion angles (°) for **2** [a]

O(1)–Al(1)–C(6)	119.3(2)	Al(1)–O(1)–Al(1′)	104.41(11)
O(1)–Al(1)–C(11)	124.34(19)	C(1)–O(1)–Al(1)	121.0(2)
C(6)–Al(1)–C(11)	116.1(3)	C(1)–O(1)–Al(1′)	131.9(2)
O(1′)–Al(1)–O(2)	153.42(11)	C(2)–O(2)–Al(1)	111.6(2)
O(1)–Al(1)–O(1′)	75.59(11)	C(3)–O(2)–Al(1)	129.1(3)
O(1)–Al(1)–O(2)	78.24(10)	C(2)–O(2)–C(3)	114.9(3)
O(1′)–Al(1)–C(6)	97.65(17)		
O(1′)–Al(1)–C(11)	102.87(16)	O(1)–C(1)–C(2)–O(2)	44.3(5)
C(6)–Al(1)–O(2)	99.08(17)	Al(1)–O(2)–C(2)–C(1)	−37.2(4)
C(11)–Al(1)–O(2)	88.08(15)	C(3)–O(2)–C(2)–C(1)	164.1(3)

[a] Atoms labelled with prime belong to the centrosymmetric counterparts of the dimer.

what is the result of the observed high anisotropy of the thermal parameters of carbon atoms caused by ring motion.

3. Experimental

3.1. General procedures

All experiments were carried out under argon using standard Schlenk techniques. Solvents were distilled under argon over potassium benzophenone ketyl. NaCp was obtained from the reaction of freshly distilled CpH and NaH in THF and used after vacuum-drying. 2-Propoxyetoxyaluminium dichloride was obtained by the method described in the literature [15]. NMR spectra were measured on Varian VXR-300 (^{1}H, ^{13}C, ^{27}Al).

3.2. Synthesis of $[(\eta^1\text{-}C_5H_5)_2Al(\mu\text{-}OCH_2CH_2O\text{-}^nPr)]_2$

2-Propoxyetoxyaluminium dichloride (2.11 g, 0.0105 mol) was added at room temperature to slurry of cyclopentadienylsodium (2.31 g, 0.026 mol) in 150 ml of toluene. The reaction mixture was stirred overnight. Clear toluene solution was separated by decantation. The solvent was evaporated under vacuum and the residue washed with hexane (5 ml) to yield light-pink solid (2.1 g; 77%). The solid was crystallised from toluene. Anal. Found: Al, 10.29; M_w (cryometrically in benzene): 522 ($n = 2.01$) $C_{15}H_{21}O_2Al$. Calc. for Al, 10.37 M_w: 260. ^{1}H-NMR (C_6D_6) δ 0.63 (t, $J = 7.5$, 3H, $CH_3CH_2CH_2$); δ 1.28 (m, $J = 7.5$, 2H, $CH_3CH_2CH_2$); δ 2.82 (t, $J = 5.0$, 2H, $ROCH_2CH_2O$); δ 3.13 (t, $J = 7.5$, 2H, $CH_3CH_2CH_2$); δ 3.18 (t, $J = 5.0$ Hz, 2H, $ROCH_2CH_2O$); δ 6.20 (s, 10H, C_5H_5). ^{13}C-NMR (C_6D_6) δ 10.00 ($CH_3CH_2CH_2$); δ 21.59 ($CH_3CH_2CH_2$); δ 63.87 ($ROCH_2CH_2O$); δ 67.97 ($CH_3CH_2CH_2$); δ 73.33 ($ROCH_2CH_2O$); δ 113.62 (C_5H_5). ^{27}Al-NMR (C_6D_6) δ 88.87 ($\omega_{1/2} = 5435$ Hz).

3.3. X-ray structure determination

A colourless well-shaped crystal of **2** was placed in a thin-walled capillary tube (Lindemann glass) in an inert atmosphere and centred on Siemens P3 diffractometer. The unit cell parameters were obtained by least-squares refinement of the angular settings of 42 randomly find reflections in the 2θ range from 15 to 30°. Data were collected at ambient temperature by the $\theta - 2\theta$ technique. The measured intensities were corrected for the Lorentz-polarization effects and the crystal decay. The structure was solved by direct methods using SHELXS-86 [16], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares method against F^2 (SHELXL-97 [17]). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms of cyclopentadienyl rings were included in calculated positions with isotropic U equal to 1.2 times the equivalent isotropic displacement parameter of the parent carbon atom. The positions of hydrogen atoms of the methyl group were calculated and refined with common displacement parameter. For remaining H atoms positional and isotropic thermal parameters were refined. The cyclopentadienyl groups showed large anisotropic displacement parameters and significant electron density features close to the carbon atoms what implied some kind of disorder but no satisfactory multisite model was derived. The refinement converged to $R_1 = 0.0634$ and $wR_2 = 0.1651$.

4. Supplementary material

Listings of crystal and refinement data, atomic coordinates, bond distances and angles, thermal parameters for compound **2** are available from Cambridge Crystallographic Data Centre, CCDC no. 143645. 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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