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Synthesis, structural characterisation of new oligomeric alkyl aluminium (2,2′-methylene-*p*-chloro-bisphenoxides) and application as catalysts in polymerisation reactions involving cyclohexene oxide

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Abstract

The synthesis, spectroscopic characterisation and X-ray structure determination of the first aluminium *para*-chloro-bisphenoxides $[Al_2(mbpcp)_2(C_2H_5)_2(THF)_2]$ and $[Al_3(mbpcp)_2(C_2H_5)_5]$ (mbpcp = 2,2′-methylenebis(4-chlorophenol) are reported. 2,2′-Methylene-bis(4-chlorophenol) was reacted with triethyl aluminium to yield under liberation of ethane, aluminium *para*-chloro-2,2′-methylene-bis-phenoxides with different molecular complexities: a dinuclear and a trinuclear specie, both displaying two bridging bisphenoxide ligands. The nature of the solvent (coordinating or not) influences the aggregation degree of the final product. The use of a coordinating solvent like THF yields a dimeric structure with a bisphenol:metal ratio of 1 to 1 which displays a trigonal-bipyramidal coordination geometry around the aluminium atoms whereas using an apolar, weak-coordinating solvent like diethyl ether yields a trinuclear species with a bisphenol:metal ratio of 2 to 3, displaying aluminium atoms with both tetrahedral and trigonal-bipyramidal coordination geometries. These compounds were tested in preliminary screening tests as catalysts of the homopolymerisation of cyclohexene oxide (CHO) and copolymerisation of CHO with carbon dioxide. Both aluminium bisphenoxides are highly active in the ring opening polymerisation of CHO (RT, reaction time <5 min, M_n ranging from 31 000 to 40 700 g/mol, polydispersities from 1.2 to 1.4). Both compound are also active in the copolymerisation of CHO with CO_2 although the carbonate amount remains low (75 bar, 90 °C, reaction time 8 h, M_n ranging from 6800 to 15 200 g/mol, polydispersities from 1.9 to 2.5).
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Keywords: Aluminium alkoxide; NMR-spectroscopy; 2,2′-Methylene-bisphenoxide; X-ray structure; Aliphatic polycarbonate; Poly(cyclohexene oxide)

1. Introduction

Aluminium alkoxides play an important role as soluble Lewis acid catalysts in the organic synthesis [1]. For instance aluminium tri-isopropoxide is commonly used in the polymer chemistry, e.g. the ring opening polymerisation of cyclic anhydrides [2], ε-caprolactone [3] and lactides [4] as well as a catalyst of the Meerwein–Ponndorf–Verley reduction [5] and in the conversion of aldehydes into esters (Claisen–Tishchenko) [6]. We recently reported that this

bulk aluminium alkoxide can be also used as a catalyst in the copolymerisation of cyclohexene oxide with carbon dioxide [7]. Aluminium alkoxides are well-known to display complex molecular structures ranging from dimeric to polymeric aggregates [8]. Aluminium tri-isopropoxide for instance is found as a dimer in the gas phase, as a symmetric Mitsubishi logo-shaped tetramer in apolar solvents and as a trimer in freshly distilled samples [9]. In order to gain more information on the active aluminium species involved in different catalytic processes and to have a better control on the reactions' course, a "simplification" of the catalytic systems is often necessary. The use of chelating alkoxo ligands can elegantly provide a structurally well-defined aluminium catalyst. Bulky 2,2′-methylene-

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bisphenols constitute a versatile and easy-to-handle toolbox for the coordination chemist. The synthesis on a larger scale of these chelating ligands from formaldehyde and the corresponding bulky phenols is relatively easy and allows the rapid development of a ligand library [10]. Aluminium 2,2′-methylene-bisphenoxides were already extensively studied by the groups of Okuda [11], Lin [12], Chisholm [13] and newly Lewinski [14] in ring opening polymerisation of lactones, in Diels–Alder coupling reactions, and in the Meerwein–Ponndorf–Verley reduction. Additionally related aliphatic and aromatic chelating diols yielding aluminium compounds with a constrained geometry have been recently reviewed, confirming that the synthesis of tailored aluminium-containing Lewis acids attracts an increasing interest [15].

During the course of our studies on new potential catalysts of the copolymerisation of CO_2 and epoxides, we became interested in systems involving aluminium bisphenoxides and synthesized, structurally characterized and eventually tested different new aluminium compounds [16]. Within this context, it was interesting to synthesize aluminium bisphenoxides having a high Lewis acidity through the presence of electron-withdrawing substituents. Surprisingly structural characterizations of aluminium bisphenoxides bearing single electron-withdrawing groups (considered here is only the −I inductive effect) like Cl, MeO or NO_2 have so far not been reported. Similarly the structural characterization of aluminium bisphenoxides bearing no ancillary sterically demanding groups at location 6 (ortho) of the bisphenoxide is scarcely documented. One single related example involving a sulfide-bridge bisphenol, 2,2′-thiobis {4-(1,1,3,3-tetramethylbutyl)phenol} was reported by Janas et al. [17], the aluminium based-thio-bisphenoxides presenting dimeric features. An other, although remotely related, structure exhibiting an unshielded bisphenol moieties was reported by Stryker and co-workers [18]. In that particular case, the ligand used, tetrakis(2-hydroxyphenyl)ethane, is a tetradentate displaying coordinating abilities similar to those found in calix[4]arenes derivatives. For all these reasons we decided to focus on the chelating 2,2′-methylenebis(4-chloro-phenol) and investigate the resulting aluminium para-chloro-bisphenoxides. By reacting triethyl aluminium with the chelating bisphenol mbpcp [mbpcp: 2,2′-methylenebis(4-chlorophenol)], we performed the synthesis of two aluminium complexes displaying different molecular complexities (dinuclear and trinuclear complexes). Herein, we report the syntheses and X-ray structure determinations of a new family of aluminium complexes supported by the mbpcp ligand as well as the preliminary catalytic tests in polymerisation reactions involving cyclohexene oxide.

2. Results and discussion

When triethyl aluminium was reacted with 0.95 molar equiv of 2,2′-methylenebis(4-chloro-phenol in THF or diethyl ether at 5 °C, an evolution of ethane was observed.

The reaction mixture was allowed to warm up until room temperature (3–5 h) and the different aluminium para-chloro-bisphenoxides were obtained in good yields as yellowish crystals (small needles) upon concentration of the solution. Separate crystallization attempts were run with diluted solution of the dinuclear and trinuclear compounds at −25 °C and small crystals of both chloro-bisphenoxides could be eventually isolated. The use of a relatively strong coordinating solvent like THF instead of affording, as might be expected, a monomeric tetra-coordinated species, leads to the formation of a dimeric specie [(THF)Al(C_2H_5)-(mbpcp)]$_2$. The absence of sterically demanding groups in position 6 of the aromatic rings and the capability of the aluminium center to easily adopt different coordination geometries lead to the formation of this dimer. Supporting this, the use of a weak coordinating solvent like diethyl ether lead to the formation of a higher oligomer, the trinuclear bisphenoxide [$Al_3(C_2H_5)_5$(mbpcp)$_2$] (Scheme 1).

2.1. Spectroscopic characterisation of the aluminium bisphenoxides 1–2

Interestingly the ^{1}H and COSY NMR data of the dinuclear and trinuclear compounds, 1 and 2, suggest that these compounds behave differently once in solution (Table 1).

The dinuclear compound, 1, gives rise to ^{1}H spectra with a low resolution at room temperature confirming the presence of an ethyl-aluminium moiety, of the bisphenol ligand and of THF molecules in the isolated solid. At room temperature, the hydrogen atoms of the methylene bridge are not well resolved in the ^{1}H spectra and are partly overlapped by the strong NMR-signal from the THF's methylene groups in α-location of the oxygen atom. However, the non-equivalence of the two hydrogen atoms in the methylene bridge of the chelating bisphenol is clearly seen in 2D-spectra (^{1}H COSY and gHMQC in CD_2Cl_2). At room temperature, the two magnetically non-equivalent hydrogens of the bridging methylene group are barely detectable as two doublet ($^2J_{HH}$: 15.26 Hz) at ca. 3.6 ppm for the hydrogens exo and 4.2 ppm for the hydrogens endo [endo: pointing towards the Al atom; exo: not pointing towards Al]. The "bad resolution"-issue was also found in the ^{13}C NMR and DEPT135 spectra of 1. The Al-bound ethyl groups can be noticed as broad signals at ca. 9.0 ppm (methyl) and −2.9 ppm (broad, methylene), whereas the ^{13}C-signals of the aromatic region and of the THF were recorded as broad signals at 121.8, 128.1, 130.4 ppm (C–H) and 132.5, 154.8 ppm (quaternary carbons) and at 69.7 and 25.8 ppm, respectively. The bridging methylene group of the bisphenol was found as a broad signal at ca. 33.1 ppm. Generally, recording the spectra at lower temperature did not yield better resolved spectra.

In comparison, the trinuclear compound 2 reveals well-resolved, albeit complex, NMR-spectra clearly showing in ^{13}C/DEPT 135 spectra two sets of resonances for the phenyl rings in the 2,2′-methylenebis(chloro-phenoxide) ligands [two sets of six narrow signals at: 120.46/121.11
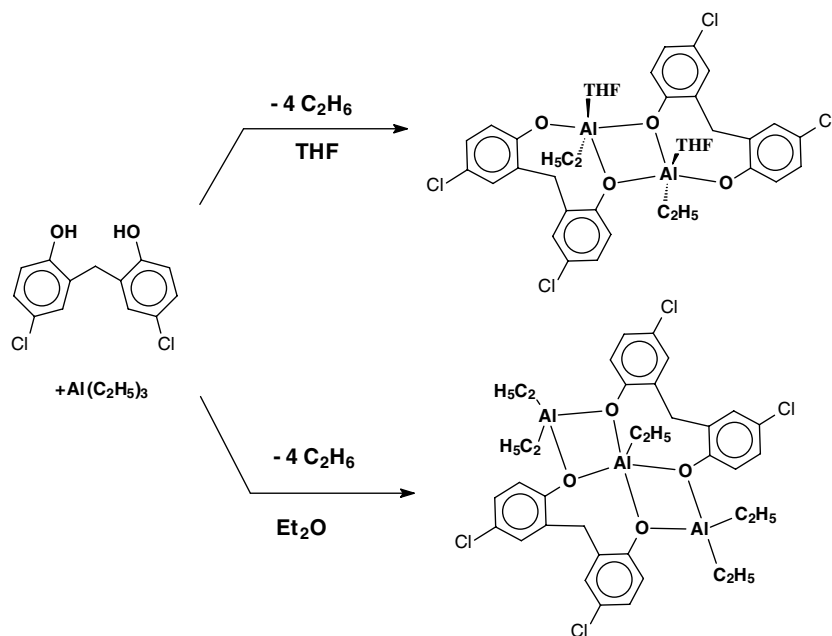
Scheme 1. Formation of the oligomeric aluminium –*para*-chloro-bisphenoxides.

Table 1
^{1}H and ^{13}C NMR data for dinuclear [Al$_2$(mbpcp)$_2$(C$_2$H$_5$)$_2$(THF)$_2$]·(THF) and trinuclear [Al$_3$(mbpcp)$_2$(C$_2$H$_5$)$_5$] bisphenoxides recorded in CD$_2$Cl$_2$

Location → Compound	1	2	3	4	5	6	–CH$_2$– bridge	Al-Ethyl CH$_2$	Al-Ethyl CH$_3$
Ligand									
^{1}H	–	–	6.86 (d 2.7 Hz)	–	6.73 (dd)	6.43 (d, 8.4 Hz)	3.60	–	–
^{13}C	152.1	126.5	130.9	129.5	128.5	117.8	30.6	–	–
1-Dinuclear									
^{1}H	–	–	7.26 (broad)	–	7.0 (broad)	6.78 (broad)	4.3; 3.6 (d:15 Hz)	0.0	0.96
^{13}C	154.8	132.5	130.4	?	128.1	121.8	33.1	−2.9	9.0
2-Trinuclear									
^{1}H	–	–	6.9–7.4 (complex pattern)	–	6.9–7.4 (complex pattern)	6.9–7.4 (complex pattern)	4.3, 3.6 (d:15 Hz)	−0.63, −0.30 0.0, 0.12	0.44, 0.73, 0.94
^{13}C	148.52, 152.09	128.23, 128.70	128.96, 129.31	130.29, 130.74	131.68, 131.84	120.47, 121.11	33.2	1.32, 0.55	8.0, 8.6, 9.9

Numbering scheme used for the bisphenoxo–aluminum–ethyl moities
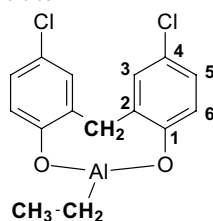
(C–H); 128.23/128.70 (quaternary C); 128.96/129.31 (C–H); 130.29/130.74 (quaternary C); 131.68/131.84 (C–H) and 148.52, 152.09 ppm (quaternary C); recorded in CD$_2$Cl$_2$]. Considering the solid state structure of compound **2** (vide infra, Fig. 2), one set of resonances can be tentatively attributed to the phenol rings located perpendicular to the pseudo-C2 symmetry axis and the other to the phenol rings oriented along this axis. Accordingly, only one signal was recorded at 33.09 ppm for the bridging methylene of the bisphenoxide ligand. We proposed an attribution of the ^{1}H and ^{13}C chemical shifts within the 2,2′-methylene-para-chloro-bisphenol ligand in compounds 1 and 2 (see Section 4 for comprehensive list) using NMR data reported by Yildiz et al. in the case of *para*-chloro-2,2′-methylene bisphenoxy-phosphazene derivatives [19].

For compound **2** several ^{13}C NMR signals are found for the ethyl groups bound to the aluminium atoms, as expected at high-field, at 0.55 ppm, and 1.32 ppm for the methylene groups and 8.03, 8.58 and 9.87 for the methyl groups suggesting a structure in solution with different types of ethyl groups. In ^{1}H and [1]H-based 2D spectra of trinuclear **2** (COSY, gHMQC a.o.), the hydrogen atoms of the methylene bridge are anew observed to be magnetically non-equivalent with two distinct chemical shifts at 2.9 ppm for the hydrogens *exo* and 4.2 ppm for the hydrogens *endo* ($^2J_{HH}$ of 15.3 Hz). The values obtained for the hydrogen *endo* and *exo* are similar to the ones reported for other aluminium bisphenoxides displaying a constrained geometry [11–13]. The assessment of the *endo–exo* character for the non-equivalent hydrogens of the methylene bridge was done according to the literature [12b]. The aluminium bound ethyl groups in complex **2** occurred in the ^{1}H spectrum as a complex pattern of overlapping multiplets (methylene groups) and triplets (methyl groups) ranging from −0.63 to 0.94 ppm. In the gCOSY and gHMQC spectra of compound **2**, corroborating the ^{13}C NMR data, three different signal sets belonging to ethyl groups could be noticed: (i) two ethyl groups displaying most probably a constrained geometry, the two hydrogens of the methylene groups being magnetically not equivalent (CH_3 at 0.45 ppm [3H] and CH_2 at −0.31 ppm [1H] and −0.63 ppm [1H]), (ii) two ethyl groups displaying a free rotation around the aluminium–carbon axis (CH_3 at 0.94 ppm [3H] and CH_2 at 0.11 ppm [2H]) and, (iii) one last ethyl group displaying a "slightly" constrained geometry (CH_3 at 0.74 ppm [1.5H] and CH_2 between 0.1 and −0.1 ppm [broad, ca. 1H]). This again suggests the presence in solution of, at least, three different types of ethyl groups. A similar complex situation was already encountered in the literature with related trinuclear ethyl-aluminium 2′2-di(hydroxymethyl) bisphenoxides [20].

In comparison the aluminium-bound ethyl groups in dinuclear complex **1** displayed a simpler pattern with two ^{1}H NMR signals at ca. 0.1 (CH_2) and 0.9 ppm (CH_3). The ^{13}C NMR signals of the ethyl groups bound to the aluminium atoms in bisphenoxide **1** are found as a broad singlet at ca. −3 ppm for the methylene groups and ca. 9.0 ppm for the methyl groups. The lower complexity of the spectra was expectable considering the symmetric dimeric structure of compound **1** (see Fig. 1). On the other hand, the overall poorer resolution of the recorded spectra (broader signals) can be tentatively explained by some dynamic processes involving a dimer–monomer exchange [(bisphenol)(THF)Al-Et]$_2$ ↔ 2(bisphenol)(THF)Al-Et].

To complement this study, ^{27}Al NMR spectra were recorded between −200 and +400 ppm in order to assess symmetry and coordination geometries around the aluminium atoms of compounds **1** and **2** once in solution. Unfortunately the spectra delivered few structural information and displayed at room temperature only very broad signals ranging from 45 to 56 ppm ($w_{1/2}$ ranging from 8000 to 11 000 Hz), the ^{27}Al-background spectra of the NMR-

probe head (Al-based alloy) being logically taken into account. Nevertheless the chemical shifts found are within the range for four- and five-coordinate aluminium alkoxides according to the literature [21].

2.2. Molecular structures of compounds 1 and 2

Suitable crystals for a structural determination of **1** and **2** were obtained from slowly cooling hot THF, respectively diethyl ether solutions down to −25 °C. The thermal ellipsoid plots of the dinuclear and trinuclear bisphenoxides are provided in Figs. 1 and 2. Experimental data for the crystal structures of compounds **1** and **2** are listed in Table 2, as well as selected bond lengths and bond angles in Table 3.

The structure of **1** shows dimeric features with five-coordinated aluminium atoms displaying a distorted trigonal bipyramidal geometry, with the phenoxydic oxygen atoms occupying axial and equatorial positions and the oxygen atom of THF occupying the remaining axial position [O(1)–Al(1)–O(3) = 163.72(11)°]. The bisphenoxide ligands are coordinated in a bridging mode through the oxygen atom O1. The Al–O bond lengths are all compatible with the bond lengths reported for aluminium bisphenoxides containing bulky *ortho*-substituents [11–13]: Al–O(2)(bisphenoxy): 1.729(3) Å, Al–O(1) (bisphenoxy): 1.829(2) Å, Al–O(3)(THF): 2.047 Å (3). The Al–C bond length of 1.958 Å is clearly within the range expected for Al–C terminal bond distances. The Al–O(3) bond distances associated with the coordinated THF bond are notably longer than the Al–O bisphenoxide distances as might be expected for dative bonds and are also longer than the Al–O(#1) bridging distances involved in the formation of the dimer (Table 4): Al–O(1#) (bisphenoxy): 2.004(2) Å. As expected the longest aluminium–oxygen bonds involve the oxygen atoms located in apical position: Al–O(1#) (bisphenoxy): 2.004(2) Å and Al–O(3): 2.047(3) Å.
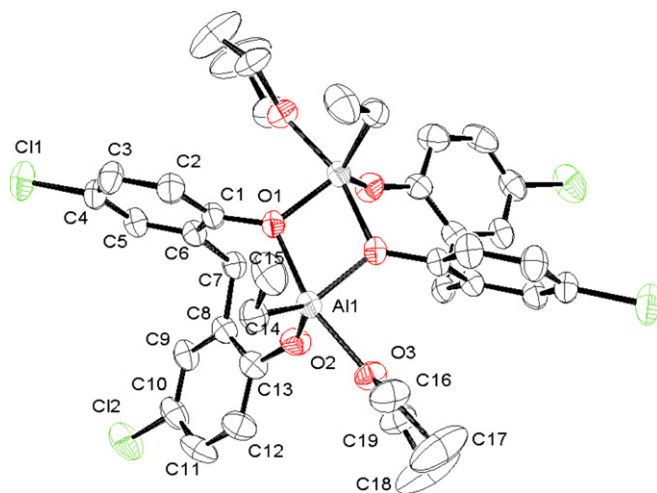

Fig. 1. ORTEP drawings (30% probability) of the dinuclear compound [Al$_2$(mbpcp)$_2$(C$_2$H$_5$)$_2$(THF)$_2$]·(THF). Solvent molecule omitted for sake of clarity.
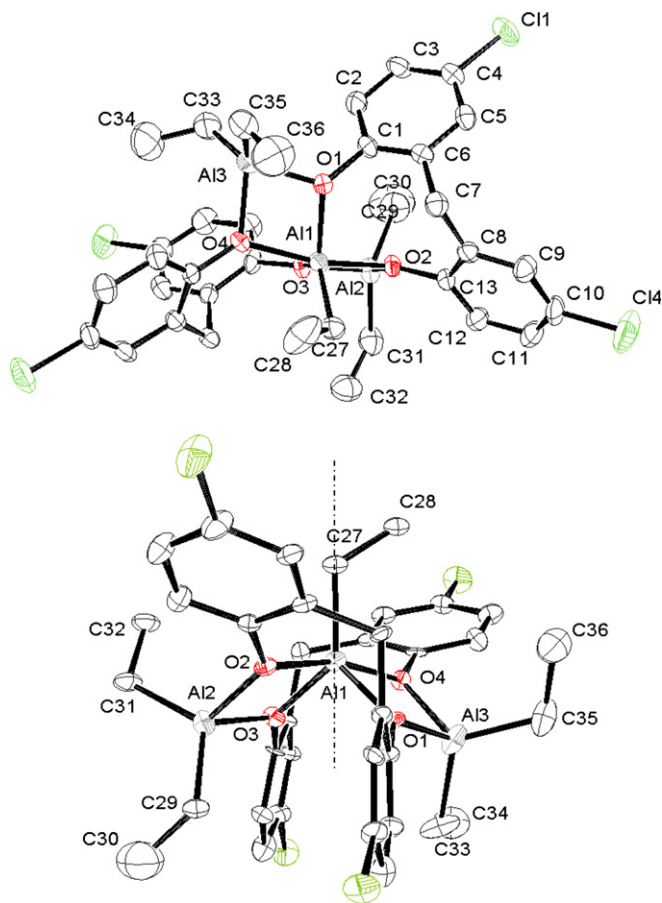
Fig. 2. ORTEP drawings (30% probability) of the trinuclear compound [Al₃(mbpcp)₂ (C₂H₅)₅].

Table 2
Experimental data for the crystal structures of the dinuclear [Al₂(mbpcp)₂(C₂H₅)₂(THF)₂] · (THF) and trinuclear [Al₃(mbpcp)₂ (C₂H₅)₅]

	Dinuclear 1	Trinuclear 2
Crystal data		
Empirical formula	$C_{38}H_{42}Al_2Cl_4O_6 \cdot C_4H_8O$	$C_{36}H_{41}Al_3Cl_4O_4$
Molecular mass	431.29	760.43
Crystal color	Colorless	Colorless
Crystal size (mm)	$0.4 \times 0.5 \times 0.05$	$0.3 \times 0.3 \times 0.05$
Crystal system	Orthorhombic	Triclinic
Space group	$Iba2$ (No. 45)	$P\bar{1}$ (No. 2)
a (Å)	15.0671(11)	10.170(3)
b (Å)	16.8044(13)	12.322(4)
c (Å)	16.8539(13)	16.273(5)
α (°)	90	71.32(3)
β (°)	90	86.68(3)
γ (°)	90	79.61(2)
V (Å³)	4267.3(6)	1900.0(10)
Z	8	2
D_{calc} (g cm⁻³)	1.343	1.329
μ (mm⁻¹)	0.367	0.418
$F(000)$	1808	792
Wavelength (Å)	0.71073	0.71073
T (K)	200(2)	200(2)
θ-Range (°)	1.82–28.32	1.32–28.31
Index ranges	$-19 \leqslant h \leqslant 19$,	$-13 \leqslant h \leqslant 13$,
	$-22 \leqslant k \leqslant 22$,	$-16 \leqslant k \leqslant 16$,
	$-22 \leqslant l \leqslant 22$	$-21 \leqslant l \leqslant 21$
Solution and refinement		
Number of reflections measured	25 002	22 330
Number of independent reflections	5257	9174
GOF	1.053	1.017
$R\ [I \cdot 2\theta(I)]$	0.0617	0.0824
$wR_2\ [I \cdot 2\theta(I)]$	0.1365	0.1811
Largest e-max, e-min (e Å⁻³)	0.489 and −0.547	1.390 and −0.661

The structure of compound 2 exhibits a trinuclear feature, the core of the complex is based on two Al₂O₂ rhombuses mutually bound to a third central aluminium atom displaying a trigonal bipyramidal coordination geometry (O(1), O(3), C(27) and Al(1) situated within the same plane O(2)–Al(2)–O(4): 165.2(11)°). The two terminal aluminium atoms adopt a slightly distorted tetrahedral coordination geometry. The overall structure is comparable to the structure of trinuclear alkyl-aluminium 2′2-di(hydroxymethyl) bisphenoxides reported by Ziemkowska [20]. The bisphenoxide ligands are coordinated in a bridging mode through both oxygen atoms (O(1), O(2)) of the ligand. As already evoked in the NMR study the phenol rings of the bisphenoxide ligands are oriented in such a way that two phenol rings of two distinct ligands are perpendicular to a pseudo-C2 symmetry axis and the remaining halves of the bisphenoxide ligands are oriented along this axis (see Fig. 2). Interestingly this structural feature can explain the non-equivalence found in the ¹H NMR spectra for some aluminium-bound methylene groups: the bisphenoxide's halves oriented along the axis neighbour two terminal-bound ethyl groups [C(29)–C(30) and C(33)–C(34)] thus hampering their free rotation. In comparison the remaining terminal ethyl groups [C(31)–C(32) and C(35)–C(36)] are not that hindered and display isochrone methy-

lene groups. The last "central" ethyl group, C(27)–C(28), bordered by the remaining bisphenoxide's halves and the methylene bridges of the bisphenoxide ligand is slightly hindered, explaining the "in-between" non-equivalence of the methylene group's hydrogens noticed in ¹H NMR.

In the trinuclear compound, the oxygen–aluminium distances are roughly equivalent within the two Al₂O₂ moieties and can be sorted in two main categories: (i) standard aluminium–oxygen bonds ranging from: 1.850(4) (Al(1)–O(1)) to 1.883(4) Å (Al(2)–O(3)) in agreement with other reported tetrahedrally coordinated aluminium bisphenoxides and, (ii) two long aluminium–oxygen bonds found within the coordination sphere of the trigonal-pyramidal-coordinated aluminium atom and involving both apical oxygen atoms: Al(1)–O(2): 1.962(4) Å; Al(1)–O(4): 1.960(4) Å. The Al–C bond lengths range from 1.910(7) Å (Al(3)–C(35)) to 1.989(7) Å (Al(3)–C(33)), in good agreement with the values found usually in the literature. In both aluminium *para*-chloro bisphenoxides, the C–C, C–Cl and C–O bond lengths measured within the 2,2′methylene bis 4-chloro-phenol ligands are similar to the values found in the literature [19].

Table 3
Comparison of selected bond distances (Å) and bond angles (°) for **1** and **2**

1 Dinuclear *para*-chlorobisphenoxide [(THF)Al(C₂H₅)(mbpcp)]₂ · THF		**2** Trinuclear *para*-chlorobisphenoxide [Al₃(C₂H₅)₅(mbpcp)₂]			
Bonds/Angles	Å/°	Bonds	Å	Angle	°
Al–O1	1.829(2)	Al1–O1	1.850(4)	O1–Al1–O4	76.29(15)
Al–O1#	2.004(2)	Al1–O2	1.962(4)	O2–Al1–O3	76.76(15)
Al–O2	1.729(3)	Al1–O3	1.852(4)	O2–Al1–O4	165.2(11)
Al–O3	2.047(3)	Al1–O4	1.960(4)	O1–Al1–C27	129.9(2)
Al–C7	3.796(9)	Al1–C27	1.958(5)	O2–Al2–O3	78.72(15)
Al#–C7	3.899(9)	Al2–O2	1.853(4)	O2–Al2–Al1	38.29(11)
Al–Al#	3.048(8)	Al2–O3	1.883(4)	C29–Al2–C31	122.5(3)
Al–C14	1.958(4)	Al2–C29	1.945(6)	O4–Al3–O1	78.48(16)
		Al2–C31	1.952(6)	O1–Al3–Al1	37.58(11)
		Al3–O1	1.867(4)	C33–Al3–C35	118.3(3)
C14–Al–O1#	124.84(18)	Al3–O4	1.856(4)	Al(3)–Al(1)–Al(2)	122.22(8)
C14–Al–O1	97.04(17)	Al3–C33	1.989(7)		
C14–Al–O2	122.71(18)	Al3–C35	1.910(7)		
C14–Al–O3	94.52(17)	Al1–Al3	2.938(3)		
O1–Al–O2	94.76(14)	Al1–Al2	2.939(2)		
O1–Al–O3	163.72(11)	Al–C7	3.332(7)		
O2–Al–O3	88.56(15)				
Al–O1–Al#	105.23(11)				
O1#–Al–O1	74.61(11)				

Table 4
Polymerisation reaction involving cyclohexene oxide as substrate

Catalyst	Polymer yield (%)	CO₃ content (%)[a]	M_n (g/mol)[b]	M_w/M_n	P (bar)[c]	T (°C)
1/CHO/CH₂Cl₂	62	–	31400	1.25	–	From 4 °C up to RT
2/CHO/CH₂Cl₂	51	–	40700	1.38	–	From 4 °C up to RT
1/CHO + CO₂	24	11.9	15220	1.92	75	93[c]
2/CHO + CO₂	53	8.7	6770	2.49	78	90[c]
Ref. [23]/CH₂Cl₂[d]	71	–	6000	2.1	–	20[c]
Ref. [24]/bulk	85–88	–	23800–37000	2.11–2.83	–	25[c]

Experimental conditions: cyclohexene oxide: 20 ml (0.1976 mol); (ROP) catalyst-to-substrate molar ratio 1:4000, compound **1**:21.3 mg; compound **2**:37.6 mg; (copolymerisation) catalyst:epoxide molar ratio 1:300; ca. 25 g CO₂ (0.57 mol) i.e. epoxide:CO₂ molar ratio ca. 1:3.

[a] Evaluated via ¹H NMR: Carbonate % = int(H_methine polycarbonate)/[int(H_methine polycarbonate) + int(H_methine polyether)].
[b] Evaluated via gel permeation chromatography.
[c] Read after 8 h reaction time.
[d] Catalyst 2.5% w/w to monomer.

2.3. Catalytic screening of the aluminium para-chloro-bisphenoxides in polymerisation reaction involving cyclohexene oxide

First catalytic screening tests showed that these aluminium compounds are highly active in the ring opening polymerisation of cyclohexene oxide (CHO) and not that efficient in the copolymerisation of CHO with carbon dioxide (see Table 4).

The tests for the ROP's were performed with a substrate-to-catalyst molar ratio of 4000 to 1. The tests were performed firstly at 4 °C and diluted with methylene chloride due to the high exothermic reaction with cyclohexene oxide. The catalysts were dissolved in dry methylene chloride and cooled down to 4 °C under argon. CHO was then slowly added to the vigorously stirred catalyst's solution. The dinuclear *para*-chloro bisphenoxide barely reacted at 4 °C whereas the trinuclear counterpart reacted violently at the same low temperature. Allowing the reaction mixture containing compound **1** to warm up to room temperature ended with a vigorous reaction bringing the solvent to ebullition. This is most likely due to the fact that, in compound **1**, THF molecules initially occupy the coordination sites of the catalyst and compete with the epoxide. The molecular weights of the isolated polymers (number average, M_n, and weight average, M_w) and the related polydispersities were obtained via gel permeation chromatography (see Section 4 for more details). The polymerisation reaction yields are relatively high (12 g polymer with **1** and 10 g polymer with **2**, ca. 62% and 51% yield, respectively) as well as the chain lengths: around 31 400 g/mol for the dinuclear compound and 40 700 g/mol in the case of the trinuclear one. Interestingly the isolated long-chained polymers display in both cases (dinuclear and trinuclear complexes) narrow polydispersity indexes (1.25–1.38). The long polymers chains and the narrow molecular weight distribution suggest either the presence of a definite, single reaction site at the catalyst or a very rapid polymer chains

exchange at the aluminium center (more rapid than the increasing of the polymer chain through insertion into the Al–O$_{Polymer}$ bond) [22]. The similar reactivity observed for dinuclear and trinuclear compounds is, at this stage of the reactivity's study, difficult to explain: whereas dinuclear compound **1** can be expected to build a reactive monomeric specie, (bisphenoxide)Al(C$_2$H$_5$)(CHO), the trinuclear derivative **2** is not likely to undergo a rearrangement to a monomeric specie with ligand migration. More work is actually in progress to understand the exact nature of the intermediates involved in the catalysis.

DSC thermograms of the isolated poly(cyclohexene oxide)s are characterized by one broad endotherm between 66 and 100 °C (max at 70 °C) which can be attributed to a melting of the polymers. The maximal value of the melting point is comparable to the value found by Yahiaoui et al. in the case of poly(1,2-cyclohexene oxide) prepared with an acid-exchanged montmorillonite [23]. In our case, neither a clear glass transition temperature (i.e. an inflection point of the curve in the endothermic direction) nor an exothermic peak due to a crystallization of the polymer was observed strongly suggesting that the isolated PCHO's are amorphous. The homogeneous aluminium catalysts based on the *para*-dichloro bisphenol logically display a higher activity than the heterogeneous catalytic system reported in the studies of Yahiaoui and coworkers (M_n ranging from 6000 to 8800, PDI 2.1–2.8). Compared to other homogeneous aluminium-based catalytic system involving cyclohexene oxide as substrate like e.g. the multinuclear aluminium–yttrium isopropoxides of Spassky and Thiam [24] (M_n 23 800–37 000, PDI 2.11–2.83, CHO/ Catalyst from 250 up to 550), it can be noticed that the aluminium *para*-bisphenoxides are promising catalysts due to

a significant better molecular weight distribution. To complete the data gained from the DSC, the stereochemistry of the isolated poly(1,2-cyclohexene oxide) was investigated with ^{1}H NMR spectroscopy according to the literature [25]. Fig. 3 shows the ^{1}H NMR spectrum of a PCHO recorded in C$_6$D$_6$; interestingly the spectra recorded for both polymers obtained with dinuclear and trinuclear aluminium catalysts are identical. The methine hydrogens in α-location of the ether bridges (O–CR(H)–CR(H)–O) are located around 3.8 ppm whereas the methylene groups of the cyclohexyl fragment are located between 1.4 and 2.2 ppm. The signals of the methine protons appear in the form of three peaks (3.88, 3.78, and 3.66 ppm) which can be attributed to syndiotactic (RR), heterotactic (MR and RM), and isotactic (MM) triads, respectively.

Fig. 4 typically shows the ^{13}C NMR spectrum for a poly(cyclohexene oxide) obtained after a ROP catalysed by an aluminium *p*-chloro-bisphenoxide. In a comparable manner, three main signals were found in ^{13}C NMR spectra for the methine carbons at 78.6, 78.0 and 76.6 ppm confirming the presence of several regions of different tacticity in the polymers [24]. The remaining methylene groups of the cyclohexane moieties belonging to the polymer backbone were found in two main groups ranging from 29.0 to 30.1 ppm and 23.4 and 22.2 ppm.

A high catalytic activity in the ring opening polymerisation of cyclohexene oxide does not implicitly mean a high catalytic activity in the copolymerisation of cyclohexene oxide with CO$_2$. Copolymerisation tests were run with compound **1** and **2** in a 1 to 1000 catalyst:epoxide molar ratio and yielded only poly(cyclohexene oxide). We had to increase the catalyst loading to generate a measurable amount of carbonate linkages in the copolymer
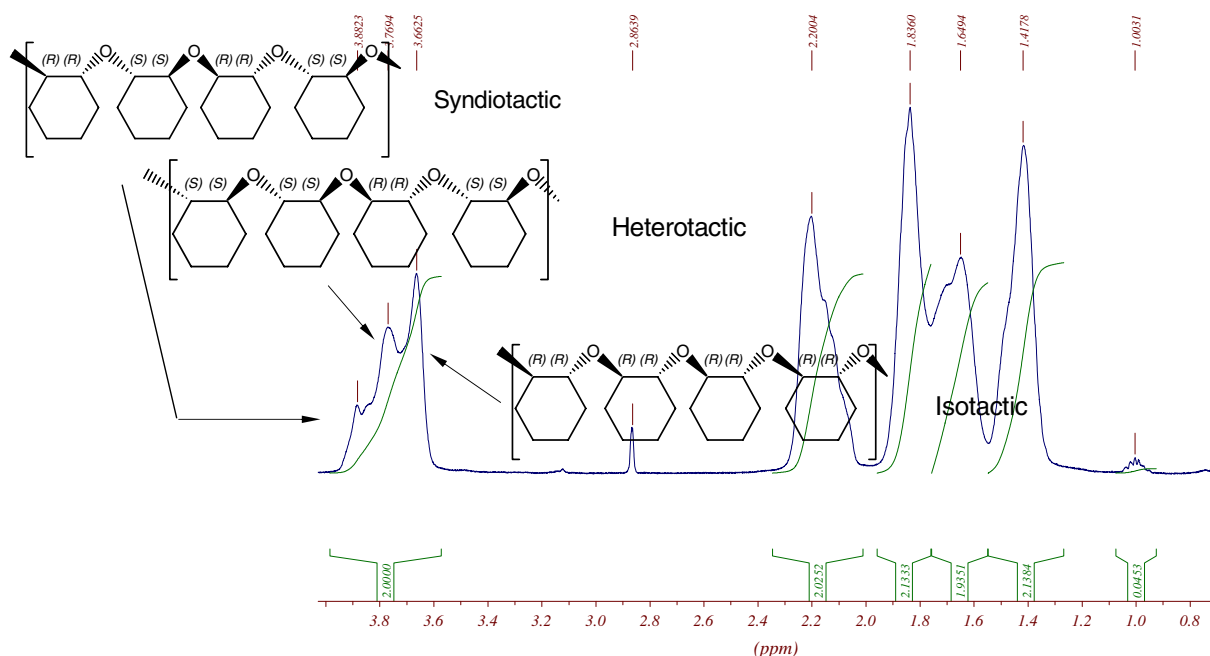

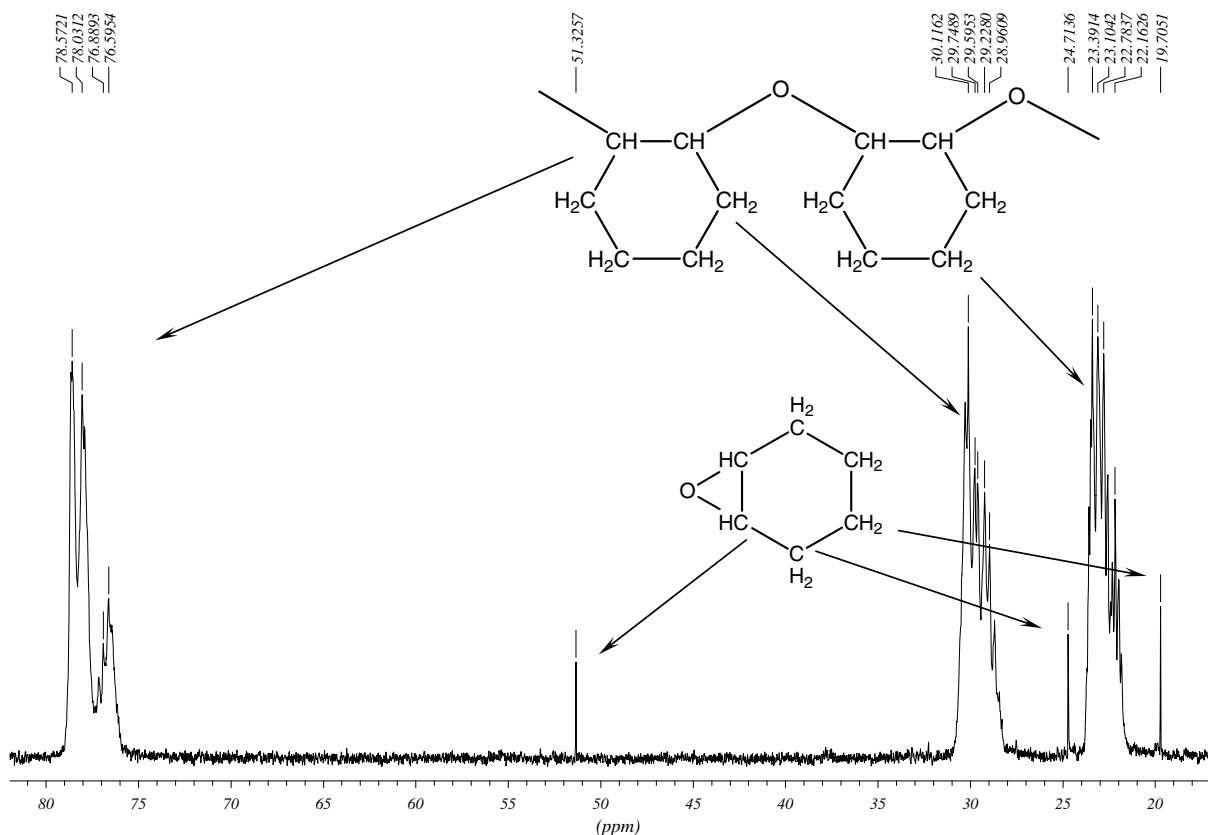Fig. 3. Typical ^{1}H NMR spectrum of poly (cyclohexene oxide) obtained with compound **1** or **2**, recorded in C$_6$D$_6$.

Fig. 4. Typical ^{13}C NMR spectrum of a poly (cyclohexene oxide) in C_6D_6 (with remaining traces of the substrate) (NMR spectra of PCO obtained with compound **1** or **2** are comparable).

(catalyst:epoxide = 1–300). The tests were typically conducted in stainless steel autoclaves equipped with standard Swagelock fittings and a separate loop made of stainless steel tubing which can be operated independently of the main reactor body. Owing to the high Lewis acidity of the aluminium bisphenoxides and their ability to also catalyse a homopolymerization of the epoxide, the catalyst was first dissolved under argon into ca. 1 ml of an unreactive solvent (CH_2Cl_2) and introduced into the separate loop. After establishing the communication with the epoxide/CO_2 mixture in the autoclave, the solution was allowed to diffuse into the reaction mixture through gravity. This procedure though time-consuming was necessary to get reproducible results and clearly evaluate the reactivity of the catalyst in pure copolymerization reactions.

The insertion of carbon dioxide into an epoxidic C–O bond with formation of a carbonate is easily evaluated via IR spectroscopy [26]. The copolymers synthesized with the help of aluminium *p*-chloro-bisphenoxides contained no cyclic carbonate and showed a medium $v(C=O)$ band (at 1740 cm^{-1}), characteristic of the presence of some polycarbonate linkages in the copolymer together with a strong absorption band at 1200 cm^{-1} ($v(C–O)$).

The quantification of the CO_2 insertion in the final copolymers (i.e. the ether- to carbonate-linkage ratio) can be readily performed via ^1H NMR spectroscopy and directly taken from the integration's ratio between methine protons of the polycarbonates units (4.7 ppm) and the polyether units (3.4 ppm) [27]. Both dinuclear and trinuclear complexes are able to catalyse in some extent a copolymerisation although the carbonate amounts in the polymers remain relatively low and are generally lower than those reported with other aluminium-bisphenoxides-based catalysts [16]. The isolated copolymers contain mostly ether linkages separated by short carbonate regions, confirming that the higher Lewis acidity of these *para*-chloro bisphenoxides dramatically shift the polymerisation reaction towards a pure homopolymerization of the epoxide (Scheme 2). The selectivity towards a CO_2 insertion is for both aluminium dichloro-bisphenoxides within the same order of magnitude: carbonate to ether linkage ratio of 1 to 13.1 for the dinuclear compound and 1 to 10.5 for the trinuclear compound (resp. 7.1% and 8.7% carbonate in the copolymer). The average molecular weights of the isolated copolymers are not as high as in the case of a pure homopolymerization and range from 6770 to 15 220 g/mol with a broader molecular weight distribution ranging from 1.92 to 2.49, which suggest the presence of more than one active site and a more complicated mechanism than in the case of a pure ROP of the epoxide.

In order to improve the catalytic system toward a pure copolymerisation, we run a couple of experiments at higher CO_2-pressure (up to 130 bar) without significant improve-
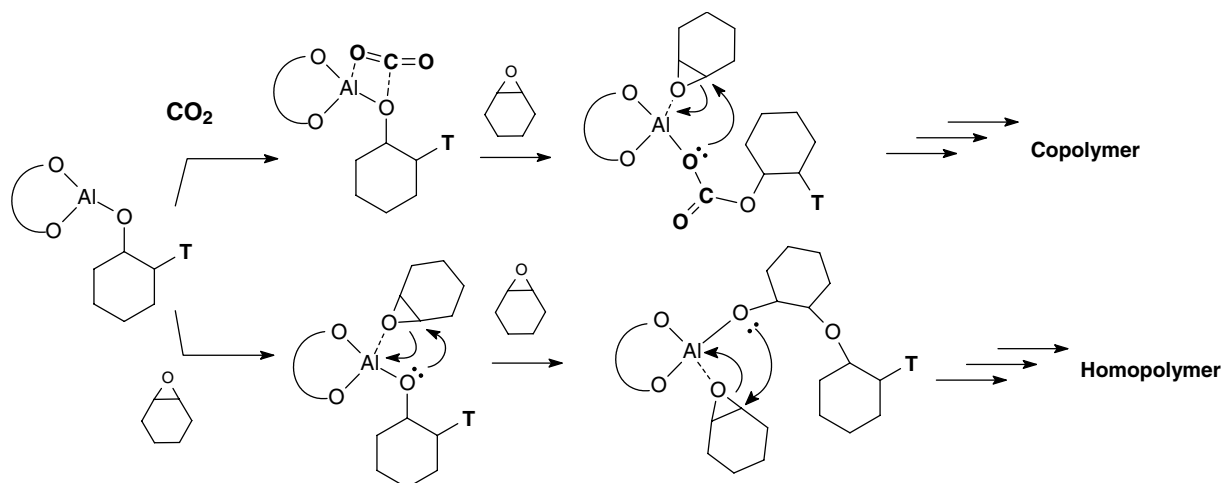
Scheme 2. Two concurrent Al-catalysed reactions: copolymerisation of epoxide with carbon dioxide and ring opening polymerisation of the epoxide (**T** stands for C_2H_5).

ment of the CO_2-incorporation into the copolymer. A poor solubility of these aluminium bisphenoxide catalysts in a CO_2-rich phase or in supercritical CO_2 might be the cause for this lack of reactivity and has to be assessed more in detail.

3. Conclusion

To sum up, we have synthesised new aluminium *para*-chloro-bisphenoxides displaying different molecular complexities, and for the first time could structurally characterized *para*-chloro-bisphenoxides via X-ray diffraction on single crystals. These Lewis acids are highly effective catalysts of the ring opening polymerisation of cyclohexene oxide. Unfortunately the compounds display a limited reactivity in copolymerisation of cyclohexene oxide with carbon dioxide. More work is currently in progress to optimise the polymerisation reactions (e.g. ROP at lower temp.) and to better understand the structure of the intermediates involved in both polymerisation mechanisms.

4. Experimental

Commercially available triethyl aluminium (Aldrich, reagent grade 97%) was used without further purification. 2,2′-methylene-bis(4-chlorophenol) (Aldrich, reagent grade 97%) was dissolved in an anhydrous hexane/$CHCl_3$/THF mixture and filtrated on Celite 521 (Aldrich). The solution was then let at RT overnight, the obtained waxy yellowish crystals were then collected and eventually dried under vacuum at 100 °C. CH_2Cl_2, THF, *n*-hexane and MeOH were dried by standard methods [28] and store under argon. Carbon dioxide (Messer Griesheim, purity 99.9990%) was used without further purification. NMR deuterated solvents (Chemotrade, Germany) were degassed, dried over Molecular sieves Linde 4 Å and stored under argon.

4.1. General procedures

The NMR spectra of the catalysts and copolymer were recorded with a Varian Inova 400 spectrometer as solutions in C_6D_6, CD_2Cl_2 or toluene D_8 (^1H 399,81 MHz, ^{13}C: 100.54 MHz). TMS was used as internal standard (^{13}C, ^1H) with different deuteriated solvents. The chemical shifts δ (in ppm) are then given relative to the residual signal of the solvent for all these runs. The ^{27}Al NMR (104 207 MHz) spectra of the aluminium catalysts were recorded in tol. D8 and referenced relative to a saturated solution of aluminium nitrate $Al(NO_3)_3$ in D_2O used as a standard. Infrared spectra (KBr pellets and thin films between KBr plates) were recorded on a BIORAD 175C FT-IR spectrometer in the range of 4000–400 cm^{-1}. Molecular weights and MWD of the polymers were measured using a Merck gel permeation chromatograph (Lichograph Gradient pump L-6200 with thermostat, LaChrom RI detector L-7490), equipped with a pre column and two different columns (PSS SDV 5 m 1000 Å and 100 Å). THF was used as eluent, and calibration was performed using polystyrene standards. The X-ray analyses were performed using a Siemens SMART CCD 1000 diffractometer with an irradiation time of 10–20 s per frame, thus collecting a full sphere of data using an ω-scan technique with $\Delta\omega$ ranging from 0.3° to 0.45°. The data were corrected for Lorentz and polarisation effects. An experimental absorption correction has been performed [29]. The structures were solved with direct methods and refined against F^2 [30]. For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used [31].

4.2. Synthesis and characterisation

4.2.1. Bis[(tetrahydrofuran)-ethyl-{2,2′-methylenebis(4-chlorophenato)} aluminium (III)], [Al_2(mbpcp)_2(C_2H_5)_2(THF)_2] · (1)

A solution of the aluminium precursor (Et_3Al) (0.92 g/ 8.1 mmol) solved in anhydrous THF was added to an

ice-cold solution (0 °C) of 2,2'-methylenebis (4-chlorophenol) (2.30 g/8.55 mmol) in 60 ml of anhydrous THF. The mixture was stirred for 3 h and then dried in vacuum. The solid was washed twice with a small amount of the solvent, concentrated and stored in −20 °C to furnish yellowish crystals in good yield of 2.43 g/71.8%.

IR (nujol, cm^{-3}): 2925 (s), 2857 (s), 1462 (s), 1379 (m), 1276 (m), 1243 (m), 1043 (m), 861 (m), 768 (m), 648 (m); ^1H NMR in CD_2Cl_2: δ (ppm) = 0.0, (AlCH_2CH$_3$), 0.94 (AlCH$_2$CH_3), 1.6 (OCH$_2$CH_2- in THF); 3.4 (OCH_2CH$_2$- in THF), 4.3 and 3.6 (d, 1H, –CH$_2$–, $J = 15$ Hz); 6.80 (C$_6$-H), 6.99 (C$_5$-H), 7.26 (C$_3$-H); ^{13}C NMR: δ (ppm) = −2.9 (AlCH$_2$CH$_3$), 9.0 (AlCH$_2$CH_3), 27.15 (O–CH$_2$CH$_2$– in THF), 33.1 (–CH$_2$–), 71.08 (O–CH$_2$CH$_2$– in THF), 121.8 (C$_6$), 128.1 (C$_5$), 129.8 (C$_4$–Cl), 130.4 (C$_3$), 132.5 (C$_2$–CH$_2$–), 154.8 (C$_1$–O–Al); ^{27}Al NMR: δ (ppm) = 56 ($w_{1/2}$ ca. 11 000 Hz). Elem. anal. calc. for $C_{38}H_{42}O_6Al_2Cl_4$: (calc.) C (%) 57.74, H (%) 5.35; (found) C (%) 57.94, H (%) 5.60.

4.2.2. Aluminium (III), bis[μ³-[2,2'-methylenebis(4-chlorophenato)(2-)-κO:κO:κO':κO']] pentaethyltri-, stereoisomer; [Al₃(mbpcp)₂(C₂H₅)₅] (2)

To an ice-cold solution (0 °C) of 2,2'-methylenebis(4-chlorophenol) (1.72 g/6.41 mmol) in 60 ml of anhydrous Et$_2$O, a solution of Et$_3$Al (0.77 g/6.73 mmol) in Et$_2$O was added. The mixture was stirred for 3 h and then dried under vacuum to give a colourless powder, which was then extracted three times with 60 ml of Et$_2$O (3×20 ml), concentrated to ca. 15 ml and then stored at −20 °C to furnish colorless crystals. Yield of isolated crystals: 1.29 g/75.4%.

IR (nujol, cm^{-3}): 2930 (s), 2855 (s), 1467 (s), 1375 (s), 1230 (m), 1172 (m), 1118 (m), 926 (m), 818 (m), 788 (m), 685 (m); ^1H NMR: δ (ppm) = −0.63, −0.30, 0.00 and 0.12 (AlCH_2CH$_3$), 0.44, 0.73 and 0.94 (AlCH$_2$CH_3); 4.31 and 3.6 (d 1H, –CH$_2$–, $J = 15.1$ Hz), 6.96, 7.01(C$_6$-H), 7.19 (C$_5$-H); 7.38 (C$_3$-H); ^{13}C NMR in CD_2Cl_2: δ (ppm) = 0.55, 1.32 (Al-CH$_2$CH$_3$); 8.0, 8.6, 9.9 (Al-CH$_2$CH_3), 33.1 (–CH$_2$–); 120.47/121.11 (C6), 128.96/129.31 (C$_3$), 130.29/130.74 (C4), 131.68/131.84 (C5), 128.23/128.70 (C2) 148.52/ 152.09 (C1); ^{27}Al NMR: δ (ppm) = 45 ($w_{1/2}$ ca. 8000 Hz). Elem. anal. calc. for $C_{36}H_{41}O_4Al_3Cl_4$: (calc.) C (%) 56.86, H (%) 5.43; (found) C (%) 56.80, H (%) 5.39.

4.3. General procedure for the polymerisation experiments

The ring opening polymerisation reactions were run in standard glassware under Argon (Schlenk tubes technique). Typically, the catalyst was dissolved in dry methylene chloride and cooled down to 4 °C under argon (catalyst-to-substrate molar ratio 1:4000, compound 1:21.3 mg; compound 2:37.6 mg). CHO (20 ml:0.1976 mol) was then slowly added to the vigorously stirred catalyst's solution. The reaction mixture was then allowed to reach room temperature and, in the case of an exothermic reaction, further diluted with 20 ml methylene chloride. In both cases (dinuclear and trinuclear compounds) the reaction

mixture became rapidly syrupy. Within ca. 30 min the reaction mixture was allowed to cool down to RT. In order to isolate the final product of the reaction, poly(cyclohexene oxide) and separate it from the catalyst, the reaction mixture was further diluted with methylene chloride and added drop wise to a vigorously stirred methanol/HCl mixture. The so-obtained white sticky "pancake" was vigorously stirred for 2 h and regularly cut into smaller pieces to be eventually filtered and dried under vacuum at ca. 80 °C. The remaining methanol phases once dried delivered only very small amounts of short-chained poly(cyclohexene oxide). The copolymerisation reactions involving cyclohexene oxide and carbon dioxide were run in a "multi-reactor" system involving four stainless steel high pressure reactors equipped with magnetically coupled stirring systems, standard Swagelock fittings and electrical heating mantles. Temperature and pressure were monitored via a digital multimeter (HP 34970A) connected to a personal computer. CHO (20 ml:0.1976 mol; catalyst:epoxide molar ratio 1:300, ca. 25 g CO_2 i.e. epoxide:CO_2 molar ratio ca. 1:3), the experimental set-up and work-up of the co-polymers have been already reported in detail in earlier contributions [7,16].

Appendix A. Supplementary data

CCDC 292015 and 292016 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.019.

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