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Further investigation of the ring-opening polymerization of propylene oxide. Catecholate derivatives of Zn(II) and Al(III)

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Abstract

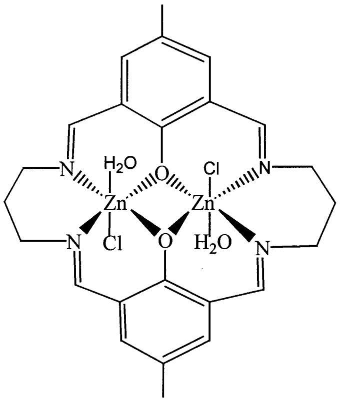
Ring-opening polymerization of propylene oxide, PO, by binuclear complexes of zinc and aluminum has been investigated. The preparation and crystal structure of a dinuclear catecholate $Al_2(O\cdots O)_2Cl_2\cdot 4THF$ (where $O\cdots O$ = 3,5-di-*tert*-butylcatechol) is reported together with its reactivity towards PO.

1. Introduction

Single-site metal catalysis has contributed significantly in the development of polyolefins [1]. We are keen to determine whether similar strategies can be applied to polyoxygenates. For this to be successful, the *cis*-migratory insertion reaction must be operative [2]. Of course, this works well for the insertion of olefins into metal–carbon bonds and seems to be effective in the ring-opening polymerization (ROP) of lactides and related cyclic esters by single-site catalyst precursors [3]. However, in the ROP of epoxides, single-site metal alkoxides seem ineffective as evidenced from our studies of monomeric magnesium, zinc and aluminum alkoxides [3]. See Fig. 1.

It is, however, well known that 'cluster' metal alkoxides are capable of catalyzing the ROP of propylene oxide, as for example in the reaction between $ZnEt_2$ and the alcohols $HOCH_2CH_2OMe$ and $HOCH_2CHMeOMe$ [4]. Furthermore, based on the work of Inoue, it is known that (porphyrin)Al(OR) compounds initiate the living polymerization of PO by a bimolecular mechanism in [Al] [5]. We, therefore, believed that it was appropriate to synthesize dinuclear complexes wherein one metal center could coordinate the epoxide and the other transfer the nucleophilic alkoxide ligand. See Scheme 1. Loosely described, the reaction in Scheme 1 involves a six-membered ring for ROP.

One ligand system that brings two metals together in a planar manner and has active axial sites is seen in Robson's ligand and the binuclear zinc complex shown in **I** below is a known compound [6]. From the work of Inoue, it is well known that Zn–Cl or Al–Cl bonds may be used to initiate polymerization. The metal–oxygen (alkoxide) group than acts as a propagating species with carbon–chlorine bond as the head group.



I

Another attractive ligand is catecholate(2−) which can occupy both bridging and terminal sites and is well suited for binuclear formation, as seen in **II** below. We

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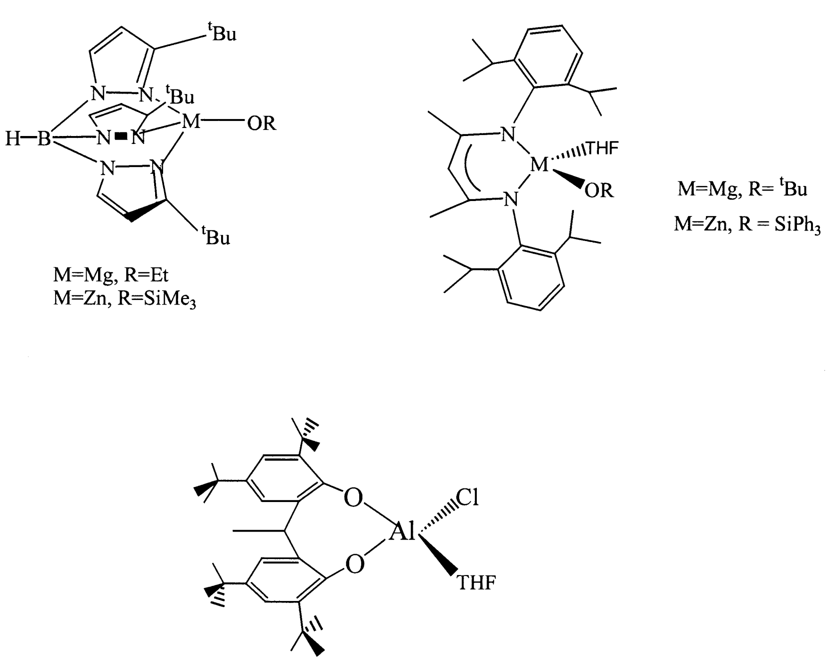
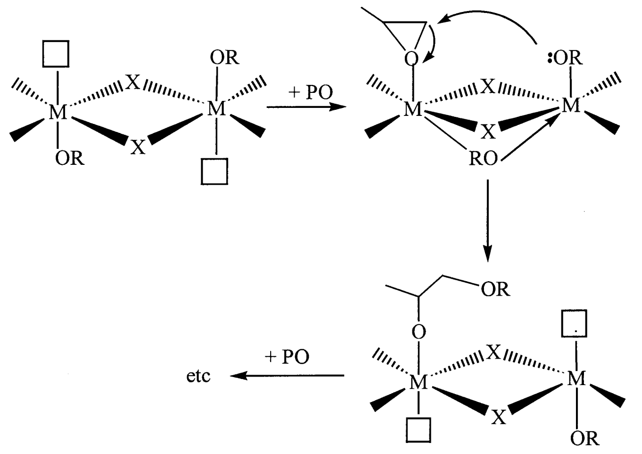
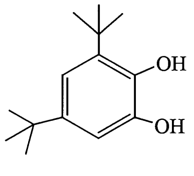


Fig. 1. Single-site Mg, Zn and Al catalyst precursors.



Scheme 1. A possible ROP mechanism by a binuclear catalyst system.

describe herein results that were prompted by these considerations.



II

2. Experimental

All syntheses were done under an Argon atmosphere using standard Schlenk-line and drybox techniques. Toluene and hexanes were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from calcium hydride. Propylene oxide was stirred over calcium hydride for 24 h and distilled under nitrogen. Diethylaluminum chloride and dimethylzinc (Aldrich) were used as received. The ligand 3,5-di-*tert*-butylcatechol was purchased from Aldrich and recrystallized from hexanes prior to use. Methylmagnesium was prepared from MeMgCl and dioxane. Synthesis of compound **4**, $Zn_2LCl_2 \cdot 2H_2O$ (L = macrocycle formed from condensation of 2 equiv. of 2,6-diformyl-4-methylphenol with 2 equiv. of 1,3-diaminopropane) was done according to literature procedures [6].

^1H, ^{13}C and Dept NMR experiments were carried out with Bruker DPX-400 and Bruker DPX-250 spectrometers, operating at proton Lamour frequency of 400 and 250 MHz, respectively. Their peak frequencies were referenced against the respective solvents, benzene-d_6 at 7.15 ppm and chloroform-d at 7.24 ppm. IR spectra were recorded on a Perkin–Elmer Spectrum GX FT IR System.

2.1. Synthesis of 3,5-di-tert-butylcatecholate aluminum chloride dimer, $[C_{14}O_2H_{20}AlCl]_2 \cdot 4THF$ (1)

The ligand 3,5-di-*tert*-butylcatechol (1.11 g, 5.0 mmol) was dissolved in 20 ml of THF. A solution of Et_2AlCl (1.0 M in heptane, 5 ml, 5 mmol) was diluted in 5 ml of THF and added dropwise to the ligand at −78 °C (dry ice/acetone bath). The solution was warmed to r.t. and left stirring overnight, after which time, the volatile components were evaporated under vacuum. After washing with hexanes (3 × 30 ml) a white solid was obtained. Yield: 0.95 g, 90%. Recrystallization was done in THF at −20 °C to give crystals suitable for

X-ray diffraction.^{1}H NMR (C_6D_6): 7.33 (d, aromatic), 7.26 (d, aromatic), 3.96 (s, THF), 1.70 (s, $C(CH_3)_3$), 1.42 (s, $C(CH_3)_3$), 1.21 (s, THF). ^{13}C NMR (C_6D_6): 148.7, 145.5, 138.6, 135.1, 116.1, 109.9 (s, aromatic), 71.4 (s, THF), 35.2 (s, $\mathit{C}(CH_3)_3$), 34.7 (s, $\mathit{C}(CH_3)_3$), 32.2 (s, $C(\mathit{CH_3})_3$), 30.0 (s, $C(\mathit{CH_3})_3$), 25.1 (s, THF). IR (KBr, cm^{-1}): 2962, 1574, 1424, 1360, 1256, 1110, 976, 838, 763.5, 670, 547, 500. EA: Calc. C, 61.45; H, 8.25. Found: C, 60.57; H, 8.28% (for $Al_2Cl_2C_{28}H_{40}O_4 \cdot 3THF$).

2.2. *Addition of protio THF to **1***

A drop of protio THF was added to an NMR tube containing **1** in C_6D_6. By ^{1}H NMR evidence of exchange between coordinated and free THF was seen. ^{1}H NMR (C_6D_6): 7.63 (d, aromatic), 7.26 (d, aromatic), 3.60 (s, THF), 1.70 (s, $C(CH_3)_3$), 1.42 (s, $C(CH_3)_3$), 1.35 (s, THF).

2.3. *Polymerization of propylene oxide with **1***

Two ml of PO were mixed with **1** (0.015 g, 29 mmol). The solution was left stirring for 3 days at r.t., after which time, the excess PO monomer was evaporated under vacuum. Yield: 5%. The polymer obtained was analyzed by ^{1}H and ^{13}C NMR spectroscopy, which revealed a regioirregular polymer [3d]. ^{1}H NMR (C_6D_6): 3.58, 3.55, 3.40, 3.32 (m, $CH+CH_2$ PPO), 1.20 (m, CH_3 PPO).

2.4. *Reaction of dimethylmagnesium and 3,5-di-tert-butylcatechol (**2**)*

$MgMe_2 \cdot 3/8THF$ (0.405 g, 5 mmol) was dissolved in toluene. The ligand (1.11 g, 5 mmol) was dissolved in toluene and added to the solution of $MgMe_2$ slowly at −20 °C. When the temperature was 0 °C, the solution started to turn cloudy. After 4 h, the volatile components were evaporated under vacuum to give a white solid that was insoluble in common solvents such as toluene, benzene, methylene chloride and THF. The product was analyzed by IR and EA. IR (KBr, cm^{-1}): 2953, 1589, 1418, 1361, 1313, 1260, 1201, 1157, 1108, 1071, 1032, 987, 970, 860, 747, 676, 612. EA: Calc. C, 61.34; H, 7.99. Found: C, 63.08; H, 8.75% (for $Mg_2O_3C_{16}H_{25}$, ($LMg_2(O)Et$)).

2.5. *Reaction of dimethylzinc and 3,5-di-tert-butylcatechol (**3**)*

The ligand (1.11 g, 5 mmol) was dissolved in THF. $ZnMe_2$ (2 M in toluene, 2.5 ml, 5 mmol) was dissolved in 10 ml of THF and added slowly to the solution containing the ligand, at −60 °C. The reaction was warmed to r.t. and left stirring overnight, after which time, a white precipitate formed. The solid was filtered off from the gray solution. The product was found to be insoluble in hexanes, benzene, toluene, methylene chloride, THF. The product was analyzed by EA and IR. IR (KBr, cm^{-1}): 2958, 2362, 1587, 1416, 1362, 1306, 1260, 1253, 1109, 1034, 972, 913, 827, 735, 663, 588, 530. EA: Calc. C, 66.46; H, 7.97. Found: C, 64.67; H, 8.57% (for $ZnO_4C_{28}H_{40}$, (ZnL_2)).

2.6. *Attempted polymerization reactions of PO with **2**, **3** and **4***

The same procedure as described for **1** was used. Compounds **2** and **3** were inactive towards polymerization of PO.

2.7. *Attempted reactions*

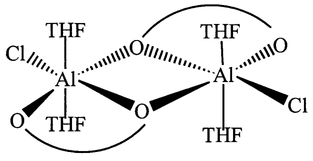
One equiv. of ligand was reacted with 1 equiv. of $[Zn(NSiMe_3)_2]_2$, $Al(NMe_2)_3$, $Al(O^iPr)_3$, $AlMe_3$, using THF, benzene or hexanes as solvent. After stirring overnight, solvent was evaporated under vacuum. In all cases, mixtures or decomposition products were obtained and we were unable to isolate any discrete compound.

3. Results and discussion

3.1. *Reactions*

Robson's zinc complex shown in **I** failed to react with PO at room temperature and even with heating to 60 °C. The complex is not soluble in neat PO, so the reaction was also carried out in the presence of added 2-propanol, but still no reaction was observed. This contrasts with the Inoue (TPP)AlCl, which too is not soluble in PO but reacts and goes into solution as the polyether forms [5]. We must conclude that the zinc(II) complex is insufficiently electrophilic to initiate ring-opening. Thus, the consideration of geometric preference outlined in Scheme 1 was not successfully tested. Because of this we turned to the use of the catecholate ligand with Al(III) which bears a higher positive charge and should be more electrophilic.

The reaction between Et_2AlCl and catechol (1 equiv.) in tetrahydrofuran, THF, leads to the formation of the dimeric compound $Al_2Cl_2(O\cdots O)_2 \cdot 4THF$ where $O\cdots O$ represents the catecholate(2−) ligand. The structure of this compound is described in detail later but has the desired structural motif as shown in **II** below.



II

In the solid state, the Al–Cl bonds lie in the equatorial plane but in solution the THF ligands are labile to dissociation (see later). This would afford reactions between the adjacent metal centers of the type depicted in Scheme 1, where PO replaces the THF and subsequent initiation by Cl^- ion produces the active RO ligand.

In reality, $Al_2Cl_2(O\cdots O)_2\cdot 4THF$ is very poor at initiating the ring-opening of PO and does not sustain ROP. In fact, it is even less effective than the binolate aluminum chloride compounds of the type $(O\cdots O)Al(Cl)THF$ described previously [3].

The reactions between catechol and $ZnMe_2$ gave only white materials, insoluble in all common organic solvents, which have the approximate composition $Zn(O\cdots O)$ and are presumed to be polymeric. These too failed to initiate polymerization of PO. This is perhaps not surprising, if the zinc compound is polymeric but it is worthy of note that pyrogallol, 1,2,3-trihydroxybenzene, and $ZnEt_2$ do form an active catalyst for the ROP of PO. This catalyst and zinc glutarate are completely insoluble in PO and THF but are active catalysts for ROP of PO and the co-polymerization of PO and CO_2 [7].

3.2. Molecular structure of $Al_2Cl_2(O\cdots O)_2\cdot 4THF$

An ORTEP drawing of the molecular structure found in the solid-state is given in Fig. 2 and selected bond distances and angles are given in Table 1. A summary of crystallographic data is given in Table 2.

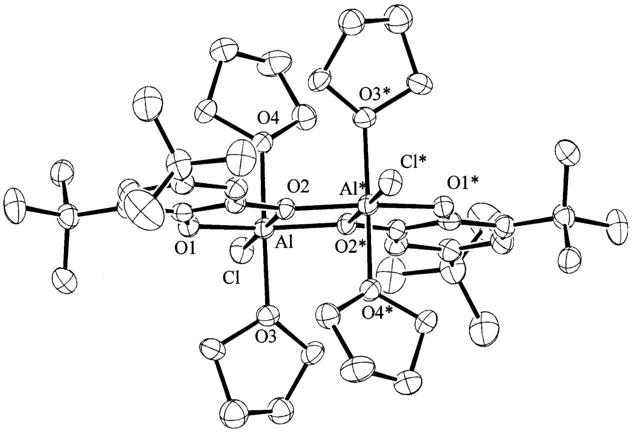


Fig. 2. ORTEP drawing of $Al_2Cl_2(O\cdots O)_2\cdot 4THF$.

Table 1
Selected bond distances (Å) and angles (°) for compound $Al_2Cl_2(O\cdots O)_2\cdot 4THF$

Bond distances	
Al–Cl	2.2541(12)
Al–O(1)	1.806(2)
Al–O(2)*	1.875(2)
Al–O(2)	1.956(2)
Al–O(4)	1.986(2)
Al–O(3)	2.001(2)
Bond angles	
O(1)–Al–O(2)*	159.34(11)
O(1)–Al–O(2)	84.58(9)
O(2)*–Al–O(2)	74.77(10)
O(1)–Al–O(4)	91.74(10)
O(2)*–Al–O(4)	88.79(9)
O(2)–Al–O(4)	91.03(10)
O(1)–Al–O(3)	90.79(10)
O(2)–Al–O(3)	93.18(10)
O(2)*–Al–O(3)	90.25(10)
O(4)–Al–O(3)	175.28(10)
O(1)–Al–Cl	96.75(8)
O(2)*–Al–Cl	103.91(8)
O(2)–Al–Cl	178.67(8)
O(4)–Al–Cl	88.81(8)
O(3)–Al–Cl	86.93(8)

Each aluminum is octahedrally coordinated. The catecholate ligands bridge the two metal atoms in a μ, η^1, η^2 manner. The Al–Cl bonds are trans to the μ-Al–O bonds and together form a $Al_2Cl_2O_4$ equatorial plane. The four THF molecules are axial and mutually trans at each Al center.

The Al–O bond distances to THF, approximately 2.0 Å, are, as expected, notably larger than those to the catecholate ligand. It is, however, interesting to note that the Al–O distances of the bridging oxygen atoms

Table 2
Summary of crystallographic data for compound $Al_2Cl_2(O\cdots O)_2\cdot 4THF$

	Compound **1**
Empirical formula	$C_{44}H_{72}Al_2Cl_2O_8\cdot 2(C_4H_8O_1)$
Formula weight (fw)	998.14
Space group	*Pccn*
a (Å)	30.0223(4)
b (Å)	9.8753(1)
c (Å)	18.7070(2)
α (°)	90.00(0)
β (°)	90.00(0)
γ (°)	90.00(0)
Temperature (K)	150
Z	4
V (Å)	5546.24(11)
D_{calc} (g cm^{-3})	1.195
λ (Å)	0.71073
μ (mm^{-1})	0.201
R (F)	0.0653
R_w (F)	0.0919

are notably different. The Al–O distance trans to the Al–Cl bond is 1.806(2) Å whereas that trans to the terminal Al–O bond of the catecholate is 1.875(2) Å. This presumably reflects the higher trans influence of the Al–O bond relative to the Al–Cl bond.

3.3. NMR solution behavior

The ^{1}H NMR spectrum of $Al_2Cl_2(O\cdots O)_2\cdot 4THF$ is consistent with the maintenance of the dimeric structure found in the solid-state. Specifically, there are two ^{t}Bu singlets along with the 2 inequiv. aromatic signals. At room temperature, the THF signals are somewhat broadened and upon addition of THF show rapid exchange on the ^{1}H NMR time-scale.

When a sample of $Al_2Cl_2(O\cdots O)_2\cdot 4THF$ is heated under a dynamic vacuum some THF is lost and the ^{1}H NMR spectrum corresponds to the presence of three THF molecules per [Al_2] complex. However, unlike the previous work with biphenoxides, we have not been able to isolate complexes of the form $Al_2Cl_2(O\cdots O)_2$ involving tetrahedrally coordinated Al(III) ions [3d].

4. Concluding remarks

The lack of success of these compounds to initiate ROP of PO suggests that this template geometry (Scheme 1) is ineffective. This may well be due to geometric factors, since zinc(2+) alkoxide clusters are known to be effective—even though heating is often required. The structure of the reported Al catecholate is interesting in relationship to the biphenoxide structures reported recently. The poorer reactivity in the ring-opening of PO may well indicate that a low coordinate aluminum(III) ion is more electrophilic. Based on these results, we shall direct our future work towards higher nuclearity alkoxide aggregates of zinc(II) and aluminum(III) that contain four- and five-coordinate metal atoms.

5. Supplementary materials

CCDC 178039 contains 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 Center, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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