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Aluminum(III) complexes containing O,O chelating ligand

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The stoichiometric reactions of trimethylaluminum with 2,6-$(MeOCH_2)_2C_6H_3OH$ (LH) revealed compounds L_3Al (1) and L_2AlMe (2). On the other hand reaction of 1 equiv. of LH with trimethylaluminum did not lead to the formation of complex $LAlMe_2$ (3), rather 2 together with Me_3Al were observed as a result of a disproportionation of 3. Compounds 1 and 2 were characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy and in the case of 1 by X-ray diffraction. Derivative 2 underwent transmetalation with Ph_3SnOH, giving $LSnPh_3$ (4) as the result of a migration of ligand L from the aluminum to the tin atom. The identity of 4 was established by elemental analysis, ^1H, ^{13}C and ^{119}Sn NMR spectroscopy and ^1H, ^{119}Sn HMBC experiments. The system 2 and $B(C_6F_5)_3$ in a 1:1 molar ratio was shown to be active in the polymerization of propylene oxide and ε-caprolactone. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: aluminum; tin; chelating ligands; transmetalation; polymerization

INTRODUCTION

The reactivity of organoaluminum alkyls towards alcohols yielding organoaluminum alkoxides/aryloxides $R_{3-n}Al(OR'_3)_n$ has been extensively investigated, in reference to their wide use in organic synthesis.[1–6] In particular, monomeric aluminum phenolates with bulky *ortho*-substituents (Ph, ^{t}Bu) have found applications in the stereo- and regioselective activation of carbonyl groups,[7–11] the reduction of benzophenone[12] and transfer of alkyl groups from aluminum to main group chlorides.[13] The function of these bulky substituents is a prevention of self-association that is typical for less sterically demanding aluminum phenolate complexes.[14–16] The aluminum centers in such compounds have a free coordination site available, although sterically restricted, which enables them to act as Lewis acids.[17–19]

The use of phenolates with potentially intramolecularly coordinating *ortho*-substituents provides attractive alternatives to steric bulk around the phenolic center. Many works dealing with the possibility of intramolecular coordination in aluminum phenolates using various types of bidentate ligands [Fig. 1(A, B)[20–25]], potentially tridentate ligands [Fig. 1(C)[26–28]] or the special class of so called Salen ligands [Fig. 1(D)[29–36]], have emerged recently. While the majority of these complexes contain nitrogen as a neutral donor atom, the utilization of ethereal oxygen atoms in intramolecular coordination of aluminum phenolates is quite scarce [Fig. 1(E)[37,38]].

Some of these intramolecularly coordinated aluminum complexes allow the isolation of organoaluminum cations that exhibit interesting activities in propylene oxide (PPO) polymerization.[39–43]

Here we report on the reactions of potentially O,O,O chelating ligand [2,6-$(MeOCH_2)_2C_6H_3OH$, LH; Fig. 1(F)] with Me_3Al. The reaction of the resulting complex, L_2AlMe, with Ph_3SnOH gives the product of migration of the ligand $LSnPh_3$. The investigation of the activity of the L_2AlMe–$B(C_6F_5)$

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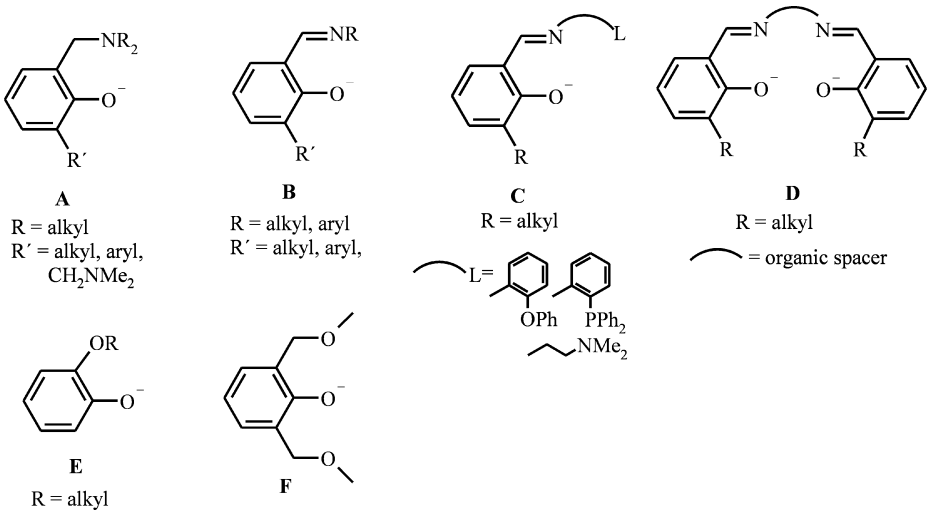


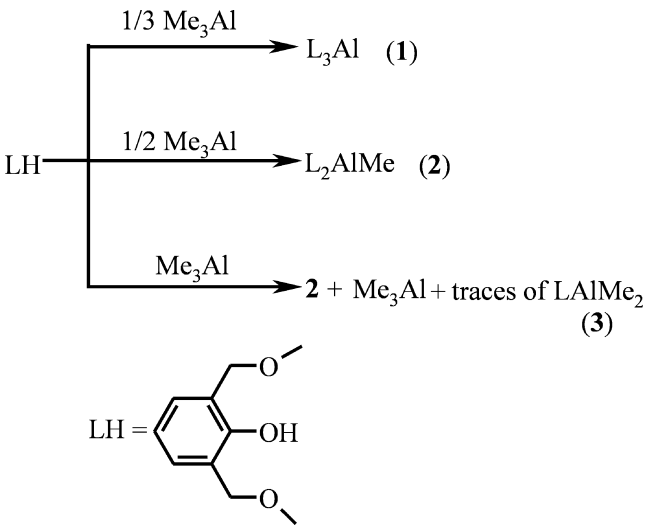
Figure 1. Chelating ligands used in aluminum chemistry.

system in PPO and ε-caprolactone (CLO) polymerization is also included.

RESULTS AND DISCUSSION

Reactions of Me_3Al with 2,6-$(MeOCH_2)_2C_6H_3OH$

The reaction of trimethylaluminum with 3 or 2 equiv. of 2,6-$(MeOCH_2)_2C_6H_3OH$ (LH) resulted in the formation of two aluminum complexes via methane evolution, L_3Al (**1**) and L_2AlMe (**2**), in good or excellent yield (Scheme 1). Derivative **1** was isolated as a pale yellow powder and compound **2** as a yellow oil rather than a crystalline solid; both are air- and moisture-sensitive. Compounds **1** and **2** are readily soluble in ether, aromatics and in the case of **2** also in aliphatic hydrocarbons.



Scheme 1. Synthesis of studied compounds.

The structure of **1** was determined by X-ray diffraction and is shown together with selected structural parameters in Fig. 2. Compound **1** is monomeric in the solid state and the central aluminum atom is surrounded by three L ligands bonded through phenolic oxygen atoms. Two of the L ligands also coordinate via one alkoxy group, but the third remains monodentate. The geometry about the aluminum atom is best described as distorted trigonal bipyramidal, where the three more tightly bound phenolic oxygen atoms O11, O21 and O31 form the equatorial plane [Σ angles O–Al–O = 359.86(5)°]. Ethereal donor atoms O13 and O23 occupy apical positions defining an angle of 179.75(5)° for O13–Al–O23. The observed geometry around aluminum is general for 5-coordinated aluminum complexes containing three covalent and two dative bonds.[44] The $Al–O_{phenolic}$ distances range from 1.7214(12) to 1.7565(12) Å, in the range normally found in aluminum phenolates. The $Al–O_{ether}$ bond lengths suggest strong intramolecular coordination as their values are considerably shorter than analogous bonds found in complexes containing structurally related ligands, i.e. $(2\text{-}MeOC_6H_4O)AlMe_2$ 2.198(3) Å and $(2\text{-}MeOC_6H_4CH_2O)AlMe_2$ 2.572(2) Å.[37] However, shorter dative Al–O bonds were detected in complexes containing 2-tetrahydrofurturyl alcohol [$(2\text{-}C_4H_8O)CH_2OH$] as the ancillary ligand.[45,46]

As a result of fluxional processes, the room temperature ^1H and ^{13}C NMR spectra of **1** contain one set of very broad signals for both CH_2O and OCH_3 groups. The variable temperature ^1H NMR measurement revealed three equally intense signals for the OCH_3 groups, indicating their non-equivalence at 260 K and most probably a structure for **1** similar to the one found in the solid state.

One set of relatively sharp signals for CH_2O and OCH_3 groups was detected in ^1H and ^{13}C NMR spectra of compound

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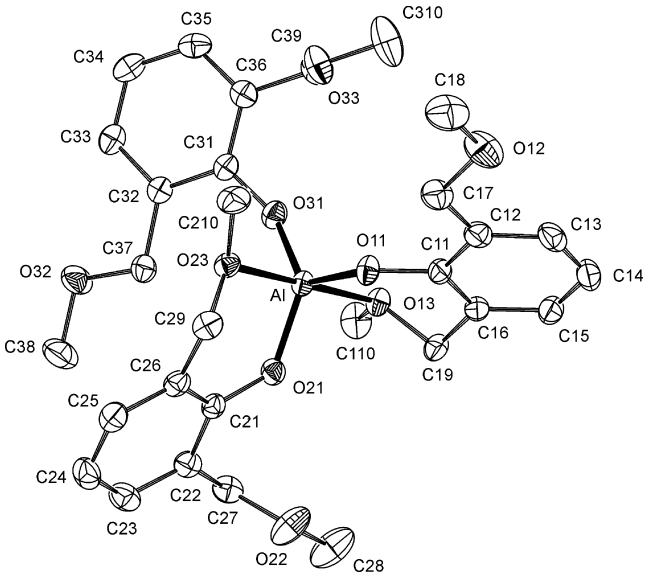

Figure 2. ORTEP drawing (50% probablity displacement ellipsoids) of [2, 6-$(MeOCH_2)_2C_6H_2O]_2Al$ (1). Hydrogen atoms have been omitted for clarity. Selected structural parameters [bond lengths (Å), bond angles (deg): Al–O11, 1.7515(11); Al–O13, 1.9806(11); Al–O21, 1.7563(11); Al–O23, 1.9805(11); Al–O31, 1.7214(11); O11–Al–O13, 90.10(5); O11–Al–O21, 115.52(5); O11–Al–O23, 89.69(5); O11–Al–O31, 121.62(6); O13–Al–O21, 89.04(5); O13–Al–O23, 179.75(5); O13–Al–O31, 87.24(5); O21–Al–O23, 90.94(5); O21–Al–O31, 122.71 (5) and O23–Al–O31, 92.98(5).

2. The presence of a signal at higher field [$\delta(^1H) = -0.56$ ppm] is assignable to the Al–Me group and it proves the identity of **2**. In the ^1H NMR spectrum at 235 K the signal of the CH_2O group was split into one AB pattern and one singlet in a 1 : 1 ratio. Two singlets of equal intensity for the OCH_3 group were detected; the signal of the Al–Me group remaining unchanged. This resonance pattern indicates that only one of the donor oxygen atoms of each ligand is coordinated to aluminum at low temperature and the coordination number of the central aluminum is 5. The resulting structure at low temperature is trigonal bipyramidal, most probably resembling the one found for **1** in the solid state. This means that the ligand bonded in monodentate fashion in **1** is replaced by methyl group in the structure of **2** (Fig. 2).

The reaction of Me_3Al with 1 equiv. LH in *n*-hexane did not lead to the expected product, $LAlMe_2$ (**3**) (Scheme 1). This derivative could be detected only as by-product (10% by ^1H NMR), besides the main products **2** and Me_3Al. The ^1H NMR spectrum of this reaction revealed after 10 min three signals in the region for Al–Me resonances [$\delta(^1H) = -0.54$ ppm for **3**, -0.56 ppm for **2** and -0.36 ppm for Me_3Al] and two signals both for OCH_3 and CH_2O groups (Fig. 3). After an additional 20 min only **2** and Me_3Al in a 1 : 1 ratio were detected. If this reaction was performed in THF, **3** could not be detected by ^1H NMR spectroscopy. This is the result of a fast Lewis-based induced disproportionation of **3**,[18] similarly to the results obtained in the reaction of Me_3Al with 2,6-$(Me_2NCH_2)_2C_6H_3OH$.[20] It is interesting, that no such disproportionation was observed in the reaction of Me_3Al with 2,4,6-$(Me_2NCH_2)_3C_6H_3OH$.[25]

Reactions of compound 2 with Ph_3SnOH

We have recently discovered a migration of O,C,O chelating ligand from aluminum to tin by the reaction of 2,6-$(ROCH_2)_2C_6H_3Al^iBu_2$ with Ph_3SnOH.[47] To prove the ability of the discussed aluminum complexes to follow a similar reaction path, the reaction of **2** (monophenolic complex **3** is unstable, see above) with Ph_3SnOH was studied. This reaction proceeds in a similar fashion and 2,6-$(MeOCH_2)_2C_6H_3OSnPh_3$ (**4**) was observed in reasonable yield 78% (based on Ph_3SnOH) as a product of transmetalation after extraction with hexane. The identity of **4** was established by elemental analysis, ^1H, ^{13}C and ^{119}Sn NMR spectroscopy. ^1H, ^{13}C NMR spectra contained only signals of appropriate integral intensity and multiplicity. Only one signal was detected in ^{119}Sn NMR [$\delta(^{119}Sn) = -109$ ppm], that resembles those found for other triaryltin oxides $Ph_3SnOSnPh_3$ [$\delta(^{119}Sn) = -80.6$ ppm[48]] and $Ph_3SnOSiPh_3$ [$\delta(^{119}Sn) = -103$ ppm].[49] Moreover, the ^1H, ^{119}Sn HMBC experiments confirmed the structure of **4**, because cross-peaks of the signal [$\delta(^{119}Sn) = -109$ ppm] to the CH_2O group and aromatic protons were clearly visible (Fig. 4).

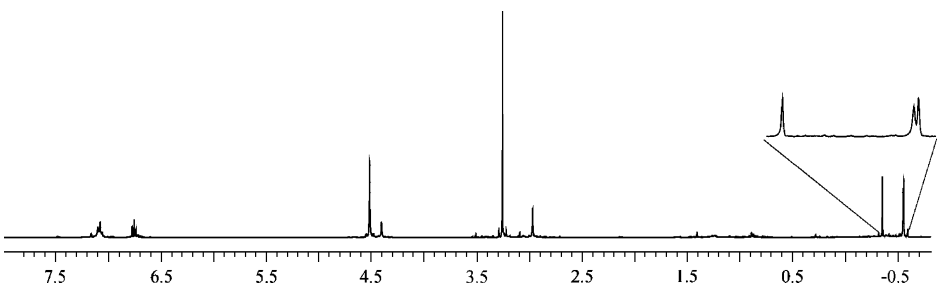

Figure 3. ^1H NMR spectrum of reaction between Me_3Al and LH (10 min).

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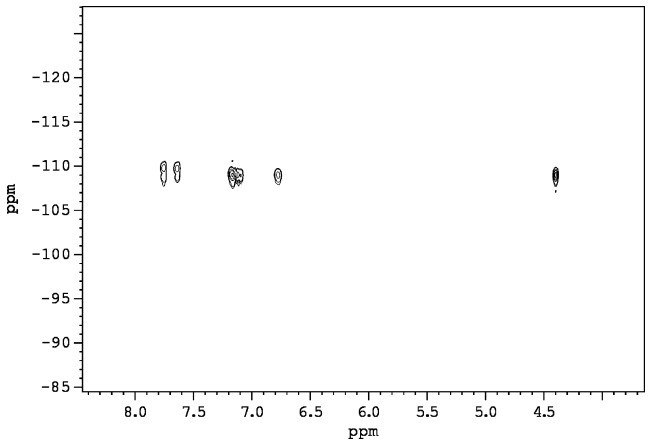

Figure 4. $^{1}H-^{119}Sn$ HMBC spectrum of compound **4**.

Polymerization of PPO by 2–B(C_6F_5)$_3$ (1 : 1)

The attempt of methyl abstraction from **2** via the reaction with one equivalent of B(C_6F_5)$_3$ should result in an aluminum cation stabilized by two ligands with [MeB(C_6F_5)$_3$]$^-$ co-anion (**5**). After the addition of B(C_6F_5)$_3$ to the pale yellow solution of **2** in CH_2Cl_2, the mixture turned green-yellow and the evaporation of the solvent gave a yellow powder soluble only in CH_2Cl_2 and THF. The presence of presumed anion in CD_2Cl_2 solution was clearly established by typical signals in ^{1}H NMR [$\delta(^{1}H) = 0.47$ ppm] and ^{11}B NMR spectra [$\delta(^{11}B) = -11.9$ ppm].[23,26,27] However the ^{1}H and ^{13}C NMR spectra of the corresponding organoaluminum cation were rather strange and no conclusions about its structure can be made. Unfortunately, attempts to grow single crystals were unsuccessful. Nevertheless, this *in situ* prepared system [**2**–B(C_6F_5)$_3$] was active in PPO and CLO polymerization. The initial stage of PPO polymerization was very fast and exothermic, thus polymerization was initiated at −40 °C by addition of PPO (3600 equiv. to **2**) to a CH_2Cl_2 solution of **2**–B(C_6F_5)$_3$ to avoid overheating the reaction mixture. To ensure a maximum monomer conversion, the polymerization mixture was allowed to warm up to room temperature and mixed overnight. Almost complete monomer conversion (95%) was achieved. The resulting poly(propyleneoxide) (pPPO) is a low-molar mass oily product with $M_n = 1640$ g mol^{-1} and $M_w/M_n = 1.22$ as determined by SEC. A large discrepancy between measured M_n and the value calculated from the monomer : initiator ratio excluded the living character of polymerization, despite the very narrow molar mass distribution. The variation of the PPO–**2**–B(C_6F_5)$_3$ ratio from 400 to 16 000 did not lead to significant changes in pPPO molar mass, which remained below 2000 g mol^{-1}, indicating the substantial extent of transfer reactions.

Furthermore the polymerization behavior of **2**–B(C_6F_5)$_3$ was tested in the polymerization of CLO at a monomer: initiator ratio of 1000. Monomer conversion was lower than in the case of PPO, reaching 13% after 24 h at room temperature. In contrast, the molar mass of poly(ε-caprolactone) (M_n = 6100 g mol^{-1}, $M_w/M_n = 1.25$) was higher than that of pPPO.

EXPERIMENTAL SECTION

General comments

All manipulations were carried out under argon atmosphere using the standard Schlenk technique. All solvents were dried by standard procedures and distilled prior to use. The synthesis of the starting ligand, 2,6-bis(methoxymethylen)fenol, was performed analogously to the literature.[50,51] ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker AMX360 or Bruker500 Avance spectrometers, using 5 mm tuneable broadband probes. Appropriate chemical shifts (in ppm) in ^{1}H and ^{13}C NMR spectra were calibrated on the residual signals of the solvents [benzene-d_6: $\delta(^{1}H) = 7.16$ ppm and $\delta(^{13}C) = 128.39$ ppm; toluene-d_8: $\delta(^{1}H) = 2.09$ ppm and $\delta(^{13}C) = 20.40$ ppm]. ^{11}B and ^{119}Sn NMR chemical shifts were related according to the external standards, $BF_3 \cdot Et_2O$ and Me_4Sn.

X-ray diffraction

Single crystals of **1** were obtained by crystallization from a saturated toluene solution held at −30 °C. $C_{30}H_{39}AlO_9$, M = 570.59, monoclinic, $P2_1/n$, $a = 15.3030(3)$ Å, $b = 8.73900(10)$ Å, $c = 21.8320(3)$ Å, $\beta = 93.6780(8)°$, $V = 2913.64(8)$ Å^3, $Z = 4$, $D_x = 1.301$ Mg m^{-3}. Data for a colorless air-sensitive crystal of dimensions 0.12 × 0.35 × 0.60 mm was measured on a Nonius Kappa CCD using monochromatized Mo$K\alpha$ radiation at 150 K. Absorption was neglected ($\mu = 0.122$ mm^{-1}). A total of 51 758 diffractions were measured ($\theta_{max} = 27.5°$), from which 6694 were unique ($R_{int} = 0.046$) and 4935 observed according to the $I > 2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92) and refined by full-matrix least squares based on F^2 (SHELXL97). The refinement converged to $R = 0.042$ for observed reflections and $wR^2 = 0.113$ (all data). Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 634620 for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Synthesis

*Synthesis of [2,6-(MeOCH$_2$)$_2$C$_6$H$_3$O]$_3$Al (**1**)*

2,6-(MeOCH$_2$)$_2$C$_6$H$_3$OH 1 g (5.49 mmol) was dissolved in 20 ml hexane and added to a stirred solution of 0.91 ml 2 M Me_3Al (1.82 mmol) in hexane 20 ml at 0 °C. The reaction mixture was allowed to reach room temperature and stirred under reflux for an additional 48 h. The solvent was removed *in vacuo* and the resulting pale yellow powder was washed with 10 ml of pentane to yield **1**, 0.81 g, 78%. M.p. 89–91 °C. Anal. calcd for $C_{30}H_{39}AlO_9$ (570.62) C, 63.15; H 6.89. Found: C, 63.36; H 6.99. ^{1}H NMR (benzene-*d6*, 300K): $\delta = 3.23$ [s(br),

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18H, OCH_3], 4.54 [s(br), 12H, CH_2O], 6.78 (t, 3H, *H4*-Ar), 7.13 (d, 6H, *H*3,5-Ar). ^{13}C NMR (benzene-*d6*, 300 K): $\delta = 59.0$ (br, OCH_3); 71.1 (br, CH_2O); 118.1, 123.65, 128.4 (br, *C*−Ar); 157.0 (br, C−O).

*Synthesis of [2,6-(MeOCH$_2$)$_2$C$_6$H$_3$O]$_2$AlMe (**2**)*

2,6-(MeOCH$_2$)$_2$C$_6$H$_3$OH 1 g (5.49 mmol) was dissolved in hexane 20 ml and added to the stirred solution of 1.37 ml 2 M Me_3Al (2.74 mmol) in hexane 20 ml at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for an additional 12 h. The solvent was removed *in vacuo* and compound **2** was observed as a yellow oil in almost quantitative yield, 1.09 g, 98%. Anal. calcd for $C_{21}H_{29}AlO_6$ (404.44) C, 62.37; H 7.23. Found: C, 62.60; H 7.42. ^{1}H NMR (benzene-*d6*, 300K): $\delta = -0.56$ (s, 3H, AlCH_3), 3.28 (s, 12H, OCH_3), 4.48 (s, 8H, CH_2O), 6.72 (t, 2H, *H4*-Ar), 7.10 (d, 4H, *H*3,5-Ar). ^{13}C NMR (benzene-*d6*, 300 K): $\delta = 58.9$ (OCH_3), 73.3 (CH_2O), 117.6, 126.3, 129.2 (*C*−Ar), 158.30 (*C*−O).

*Attempt of synthesis of [2,6-(MeOCH$_2$)$_2$C$_6$H$_3$O]AlMe$_2$ (**3**)*

Method A: 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$OH 1 g (5.49 mmol) was dissolved in hexane 20 ml and added to the stirred solution of 2.74 ml 2 M Me_3Al (5.49 mmol) in hexane 20 ml at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for an additional 10 min and the solvent was removed *in vacuo*. The mixture of **2**, Me_3Al and **3** (approximately in 1 : 1 : 0.10 ratio) was obtained. ^{1}H NMR (benzene-*d6*, 300 K): $\delta = -0.56$ (s, 3H, AlCH_3, **2**), −0.54 (s, 6H, Al(CH_3)$_2$, **3**), −0.36 [s, 9H, Al(CH_3)$_3$, Me_3Al], 3.09 (s, 6H, OCH_3, **3**), 3.28 (s, 12H, OCH_3, **2**), 4.40 (s, 4H, CH_2O, **3**), 4.48 (s, 4H, CH_2O, **2**), 6.73–7.09 (*H*-Ar, **2** and **3**).

Method B: 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$OH 1 g (5.49 mmol) was dissolved in THF 20 ml and added to the stirred solution of 2.74 ml 1 M Me_3Al (5.49 mmol) in THF 20 ml at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for an additional 10 min and the solvent was removed *in vacuo*. The mixture of Me_3Al and **3** (in 1 : 1 ratio) was obtained. ^{1}H NMR (benzene-*d6*, 300 K): $\delta = -0.56$ (s, 3H, AlCH_3, **2**), −0.36 [s, 9H, Al(CH_3)$_3$, Me_3Al], 3.28 (s, 12H, OCH_3, **2**), 4.48 (s, 4H, CH_2O, **2**), 6.72 (t, 2H, *H4*-Ar), 7.10 (d, 4H, *H*3,5-Ar).

*Synthesis of [2,6-(MeOCH$_2$)$_2$C$_6$H$_3$O]SnPh$_3$ (**4**)*

Ph_3SnOH 0.67 g (1.82 mmol) was added to a solution of **2** 0.74 g (1.82 mmol) in toluene at 0 °C and then stirred for additional 12 h at room temperature. The solvent was removed *in vacuo* and the residue extracted with 2 × 20 ml of hexane. Evaporating of the hexane gave **4** as a white powder, 0.76 g, 78% (related to starting Ph_3SnOH). Anal. calcd for $C_{28}H_{28}SnO_3$ (531.22) C, 63.31; H 5.31. Found: C, 63.22; H 5.51. ^{1}H NMR (toluene-*d8*, 300 K): $\delta = 2.66$ (s, 6H, OCH_3), 4.40 (s, 4H, CH_2O), 6.76 (t, 1H, *H4*-Ar-ligand), 7.10–7.15 (m, 11H, *H*3,5-Ar-ligand, *H*3,4,5-Ph-Sn), 7.68 (d, 6H, *H2,6*-Ph-Sn).^{13}C NMR (toluene-*d8*, 300 K): $\delta = 57.8$ (OCH_3); 73.7 (CH_2O); 118.9, 128.9, 129.6, 129.9, 130.4, 136.9, 140.3 (*C*−Ar); 159.9 (*C*−O). ^{119}Sn NMR (toluene-*d8*, 300 K): −109.

Polymerization of PPO by 2–B(C$_6$F$_5$)$_3$ (1 : 1)

To the stirred solution of **2**–B(C$_6$F$_5$)$_3$ (29 mg, 32 μmol in 20 ml of CH_2Cl_2) cooled to −40 °C 8.0 ml (114 mmol) of PPO was added. The flask was placed on ice and mixed for 7 h, allowed to warm up to room temperature and mixed overnight. The solvent was evaporated and the yellow oily product was dried in the vacuum of a rotary pump for 24 h. Yield of polymer 6.28 g, 95%. $M_n = 1640$ g mol^{-1}, $M_w/M_n = 1.22$, determined by SEC in THF against PS standards.

Polymerization of CLO by 2– B(C$_6$F$_5$)$_3$ (1 : 1)

To the stirred solution of **2**–B(C$_6$F$_5$)$_3$ (33 mg, 36 μmol in 20 ml of CH_2Cl_2) cooled to −40 °C 4.0 ml (36 mmol) of CLO was added. The reaction mixture was allowed to warm up to room temperature and mixed overnight. The polymer was precipitated in cold methanol, filtered and dried in the vacuum of a rotary pump for 24 h. Yield of polymer 0.543 g, 13%. $M_n = 6100$ g mol^{-1}, $M_w/M_n = 1.25$, determined by SEC in THF against PS standards.

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