



Sterically crowded dimeric diisobutylaluminum aryloxides: Synthesis, characteristics, and application as activators in homo- and copolymerization of olefins

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ABSTRACT

A row of dimeric diisobutylaluminum aryloxides bearing different sterically crowded substituents in ortho-positions of the aryl ligand [(ArO)AlⁱBu₂]₂ (ArO = 2-ⁱBu-C₆H₄O (**Al_{ITBP}**), 2-Me,6-ⁱBu-C₆H₃O (**Al_{MTBP}**), 2,6-ⁱPr₂-C₆H₃O (**Al_{DIPP}**), 2-Ph-C₆H₄O (**Al_{PP}**), 2,6-Ph₂-C₆H₃O (**Al_{DPP}**), 1-C₁₀H₇O (**Al_{N-1}**)) was synthesized. The Molecular structures of **Al_{MTBP}**, **Al_{DIPP}**, **Al_{PP}**, **Al_{DPP}**, and **Al_{N-1}** have been determined by X-ray crystallography. All dimeric diisobutylaluminum aryloxides were tested as activators of *rac*-Et (2-MeInd)₂ZrMe₂ in homopolymerization of ethylene, propylene, copolymerization of ethylene with propylene and terpolymerization of ethylene/propylene/5-ethylidene-2-norbornene. It was shown that only **Al_{MTBP}** and **Al_{DPP}** work as effective activators in all polymerization processes, with activity of **Al_{MTBP}** system being significantly higher than that of **Al_{DPP}**. The evaluation of dimerization energies of synthesized aryloxides by means of DFT calculations have shown **Al_{MTBP}** and **Al_{DPP}** to form the least stable dimers. The activation of *rac*-Et (2-MeInd)₂ZrMe₂ was modeled as bonding of diisobutylaluminum aryloxide with zirconocene followed by the first insertion of ethylene into Zr⁺-Me bond. As per that model, DFT calculations demonstrated the process to be the most favorable for **Al_{MTBP}** and **Al_{DPP}** which well corresponds to experimental observations.

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1. Introduction

An activator (or cocatalyst) is a major component of homogeneous single-site catalytic systems for olefin polymerization [1–9]. Traditional and commercially available activator is methylaluminumoxane (MAO) [1–3]. In order to improve solubility in aliphatic hydrocarbons and to increase the effectiveness of the activator, the modified versions of MAO (MMAO) were synthesized [3,10]. Although MAO and MMAO yield very high catalytic activities they have several drawbacks associated with high cost of the reagents at the need for large molar excess to precatalyst (Al/Mt) for obtaining acceptable polymerization activities.

A series of articles [11–20] shows the possibility to activate a number of metallocene complexes with higher β-branched aluminumoxanes, such as tetraisobutyl aluminumoxane (TIBAO) [11,12],

tetraisoctyl aluminumoxane [11,12,14], ethylisobutyl aluminumoxane [14–16], polyisoctyl aluminumoxane [14], isobutyl aluminumoxane [18–20]. The aluminumoxanes are obtained by hydrolysis of parent aluminum alkyls or their mixture. Some of these systems are more active in ethylene and propylene polymerization at low Al/Mt molar ratio [13–19] than the catalysts with MAO as an activator.

Promising activators are aluminumoxanes and aluminum trialkyls (alkyl = ⁱOct, ⁱBu) modified with phenols with sterically hindered or electron-accepting substituents [17,21–28]. It has been found that such activators exhibit higher activation ability towards organometallic component than unmodified ones. Modification of MAO with phenol can be used to remove free trimethylaluminum (TMA) from MAO thus preventing the formation of Me-bridged dinuclear species which are believed to be catalytically inactive [3,29,30]. ¹³C NMR study of the system Cp*₂ZrCl₂/AlⁱOct₃/C₆F₅OH allowed to identify the formation of alkyl cationic complexes Cp*₂Zr(ⁱOct)^{δ+}ClA^{δ-} (A – activator) that are catalytically active in ethylene polymerization [17]. According to the authors, the activator in these

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systems is $C_6F_5OAl^iOct_2$ formed in the reaction of trialkyl aluminum with phenol. However, it should be noted that tri-coordinated aluminum compounds are prone to the association. In particular, the work [31] shows that pentafluorophenoxides $R_2AlOC_6F_5$ ($R = Me, Et, ^iBu$) exist as dimers. Probably, more sterically crowded isooctyl groups prevent or significantly diminish the dimerization process thus providing the presence of 3-coordinated Al species responsible for activation.

Previously we have shown [32] that isobutylaluminum aryloxides bearing two tertbutyl groups in ortho-positions of the aryl moiety have MAO-level activating ability towards zirconocene *rac*-Et (2-MeInd)₂ZrMe₂ in homo- and copolymerization of ethylene with propylene and terpolymerization of ethylene, propylene and 5-ethylidene-2-norbornene at low molar ratio (Al/Mt $\approx 10^2$ mol/mol). These new activators are individual monomeric compounds of 3-coordinated Al [33,34]. In addition these compounds may also serve as moisture scavenging agents with formation of corresponding phenol as hydrolysis product [35,36].

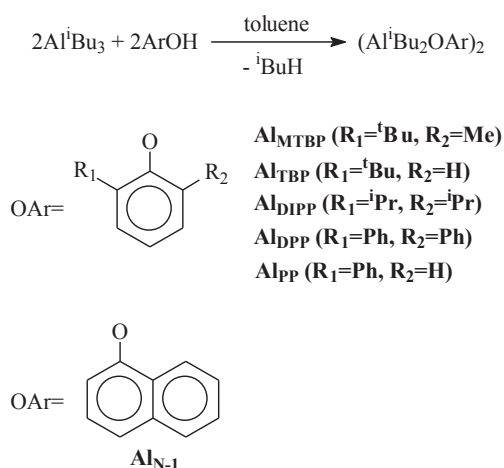
The question remains whether the presence of *tert*-butyl substituents in ortho-positions of aryl rings is principal factor for the preservation of the monomeric structure and activating properties of isobutylaluminum aryloxides. In this work, we have synthesized new isobutylaluminum aryloxides with different substituents in ortho-position of the aryloxy groups, investigated the influence of different combinations of ortho-substituents on the structure of isobutylaluminum aryloxides and their properties as activators in homo- and copolymerization of ethylene and propylene, and terpolymerization of ethylene/propylene/5-ethylidene-2-norbornene. Zirconocene Et (2-MeInd)₂ZrMe₂ was used as a pre-catalyst.

2. Results and discussion

2.1. Synthesis and molecular structure of diisobutylaluminum aryloxides

Synthesis of diisobutylaluminum aryloxides was carried out in toluene through the reaction of triisobutylaluminum with phenols, which contain various combinations of alkyl and aromatic substituents in ortho-positions of the phenyl ring (Scheme 1). All synthesized compounds unlike previously described Al_{DTBP} ($R_1, R_2 = ^iBu$) [33] are prone to dimerization. The crystals of dimeric compounds were grown from saturated toluene solutions.

Molecular structures of diisobutylaluminum aryloxides Al_{MTBP} , Al_{DPP} , Al_{N-1} , Al_{DIPP} , and Al_{PP} were determined by X-ray



Scheme 1.

crystallography. Additionally, for comparison the same structures were optimized using quantum-chemical method (DFT) with solvent (toluene) accounted for according to SCRf model. X-ray molecular structures are presented in Figs. 1–5. Selected bond lengths and bond angles are summarized in Tables 1–5. Al_{MTBP} (Fig. 1), Al_{N-1} (Fig. 2), Al_{DPP} (Fig. 3) and Al_{DIPP} (Fig. 4) are crystallized in monoclinic system and determined in $P2_1/c$ (Al_{MTBP} , Al_{N-1} , Al_{DPP}) and $C2/c$ (Al_{DIPP}) space groups. Al_{PP} (Fig. 5) is crystallized in the triclinic system, crystalline structure is described by the space group P-1. The asymmetric part of the crystalline structures of Al_{MTBP} and Al_{N-1} contains half of the dimeric molecule localized near the inversion center. The crystalline structure of Al_{DPP} includes three dimeric molecules of diisobutylaluminum aryloxides. The molecular structure of Al_{DIPP} consists of independent whole molecule and a half of a molecule of diisobutylaluminum aryloxides. The asymmetric part of Al_{PP} molecular structure includes two halves from diisobutylaluminum aryloxide molecules located near the center of inversion.

The crystals of Al_{TBP} have been also obtained, but the crystal structure was not determined. We proposed that the crystals of Al_{TBP} are twins, including blocks formed by *cis*- and *trans*-isomers. The presence of *cis*- and *trans*-isomers in proportion 1 to 5 was reported earlier on the base of ¹H NMR spectrum of this compound in toluene [35]. DFT calculation of *cis* to *trans* isomerisation of Al_{TBP} in standard conditions has given the values of $\Delta G = -0.85$ kcal/mol and equilibrium constant $K = 4.2$ (*trans*-isomer is prevalent). Similar calculations show that for other dimeric aryloxides, where *cis*-*trans* isomerisation is possible, *cis*-isomer is virtually nonexistent in solution (Supporting Information), which explains feasibility of determining their molecular structures.

The molecular structures determined by X-ray crystallography were compared with DFT optimized (DFT) ones. As a starting point for optimization the X-ray data were used. Features that distinguish DFT optimized and X-ray structures (Table 6), are the differences of angles (α) between planes of the aryl rings and triangles Al-O-Al (tetragon Al_2O_2), as well as the magnitude of dihedral angle O-Al-Al-O (β) (Scheme 2).

The angles between planes (α) and dihedral angles (β) in the synthesized dimeric isobutylaluminum aryloxides are in the range

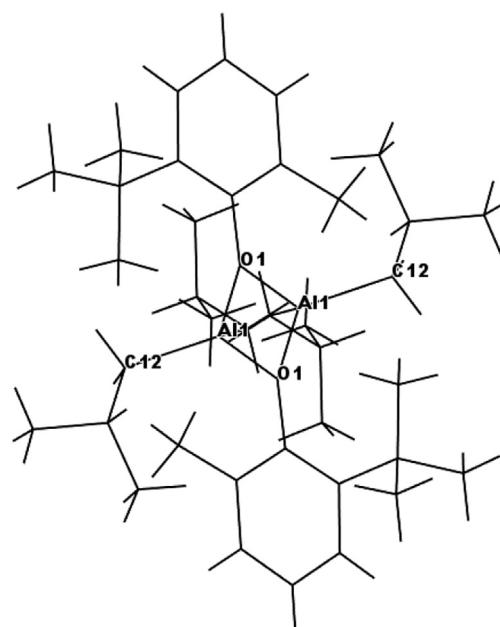


Fig. 1. Molecular structure of [(2-Me,6-^tBu-C₆H₃O)AlⁱBu₂]₂ (Al_{MTBP}).

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