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Catalyst Systems for Alkene Polymerization Based on Metallocene Complexes and Sterically Hindered Organoaluminates

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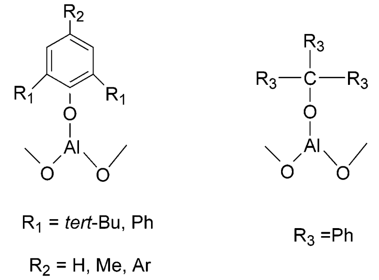
ABSTRACT: The article describes two types of organoaluminate compounds which can serve as cocatalysts for metallocene complexes in alkene polymerization reactions: (a) sterically hindered arylaluminates, oligomeric compounds containing [Al(OPh)−O] units where Ph are aryl groups substituted in the second and the sixth positions with bulky alkyl or aryl groups; and (b) alkylaluminates, compounds containing [Al(OR)−O] units where OR is a heavily sterically hindered alkoxy group. The most effective substituents Ph in the arylaluminates are phenyl groups with two ortho-positioned *tert*-butyl or phenyl groups. The most effective substituent R in the alkylaluminates is CPh_3. These cocatalysts can be produced via two alternative routes: (1) a reaction between an alkylalumoxane and a sterically hindered phenol or an alcohol or (b) two consecutive reactions: first, a reaction between a trialkylaluminum compound and a sterically hindered phenol or an alcohol and, second, a reaction between the product of the first step and water. Oligomeric cocatalyst compositions containing units of two types, organoaluminate and alkylalumoxane, also can serve as cocatalysts for metallocene complexes.

Introduction

Methylalumoxane $[Al(Me){-}O]_n$ (MAO) is widely used as a cocatalyst in polymerization reactions of various alkenes and styrenes with metallocene complexes (see ref 1). It is conventionally synthesized by controlled hydrolysis of $AlMe_3$,[2−5] by reacting $AlMe_3$ either with water[1,4−7] or with hydrates of inorganic salts.[5,7,8] NMR data[5,9−13] show that virtually all aluminum atoms in MAO solutions are four-coordinated and all oxygen atoms are three-coordinated. It is generally accepted that MAO is a mixture of oligomeric compounds with n ranging from 4 to 30.[5,6,14−17] Most oligomers form three-dimensional cage structures composed of hexagonal and square faces,[14,15,17,18] similar to *tert*-butylalumoxane, which cage structure was determined experimentally by Barron.[10,19] DFT calculations suggest that MAO species may exist as an equilibrium between several cage structures with the hexagonal-faced $[-Al(Me){-}O-]_{12}$ being the most abundant at room temperature.[14,15] Other alkylalumoxanes $[-Al(R){-}O-]_n$ either are much less effective cocatalysts for metallocene complexes (when R is iso-Bu or n-Oct) or are practically inactive (R = Et). Recently, two alternative approaches to the synthesis of alkylalumoxanes were described: reactions of AlR_3 and organotin compounds containing Sn−O bonds[20,21] and thermal decomposition of Me_2AlOR' compounds with sterically crowded alkyl R′ groups.[22]

Numerous attempts were undertaken in the past to find alternative cocatalysts for metallocene complexes: (1) The oldest known cocatalysts for metallocene complexes are organoaluminum compounds, AlR_2Cl and AlR_3. AlR_2Cl work well with titanocenes[23,24] whereas some AlR_3 compounds can activate zirconocenes.[25] (2) A combination of $AlMe_3$ and AlR_2F.[26] (3) Compounds or salts generating noncoordinative anions for metallocenium cations, such as $[R_3NH]^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$, $[CPh_3]^+[B(C_6F_5)_4]^-$, etc.[27−33] (4) Combinations of MgR_2 and AlR_2Cl.[34]

Scheme 1



I **II**

This article describes a family of organoaluminates (compounds containing AlO_3 moieties with an organic group attached to one of the oxygen atoms) that can serve as alternative cocatalysts for metallocene complexes in alkene polymerization reactions. Two types of organoaluminates can be used (Scheme 1): (a) sterically hindered arylaluminates **I**, oligomeric compounds containing [Al(OPh)−O] units where Ph is an aryl group substituted in the second and the sixth positions with bulky alkyl or aryl groups; (b) sterically hindered alkylaluminates **II**, compounds containing [Al(OR)−O] units where R is a sterically hindered alkyl group.

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Cocatalyst compositions containing units of two types, organoaluminate and alkylalumoxane, also can be used as the cocatalysts.

The original idea for a possibility of replacing alkyl groups in alkylalumoxanes with sterically hindered phenoxy groups came from the results of Goodall.[35] He found that dialkylaluminum phenoxides R_2AlOPh, where Ph is a 2,6-R_2-disubstituted phenyl group (R = Et and *i*-Bu), as well as their reaction products with $AlEt_2Cl$ and $AlEtCl_2$ are effective catalysts for $TiCl_3$ in alkene polymerization reactions whereas their unsubstituted analogue Et_2AlOPh is ineffective as a cocatalyst.[36] (As can be seen from the data below, these phenoxides are ineffective as cocatalysts for metallocene complexes.)

The organoaluminate cocatalysts described in this paper can be produced via two alternative routes: (1) a reaction between an alkylalumoxane $[-AlR-O-]_n$ and a sterically hindered phenol or an alcohol; (2) two consecutive reactions: first, a reaction between AlR_3 and a sterically hindered phenol or an alcohol and, second, a reaction between the product of the first step and water.

The use of such cocatalysts for activating metallocene complexes was earlier briefly described in a patent by Marks et al.[37] and in our patents.[38,39]

Experimental Section

Reagents. Commercial MAO sample was supplied by Schering Berlin Polymers Co. as solution in toluene: $[Al]_{total}$ = 5.23 wt %; MAO concentration ~10 wt %, free $AlMe_3$ ~30% of the total Al content. Heptane-soluble MAO containing ~15% of Al−iso-Bu bonds (MMAO), isobutylalumoxane (IBAO), and all alkylaluminum compounds were supplied by Akzo Nobel Chemicals Co.

The following phenols and alcohols were used for synthesis of organoaluminates: Mono-phenols: 2,6-di-*tert*-butylphenol (DBP), 2,6-diphenylphenol (DPP), 2,6-di-*tert*-butyl-4-methylphenol (DBMP), 4-methylphenol. Bis-phenols: 2,2-methylene-bis(6-*tert*-butyl-4-methylphenol) (MBBM), 1,1′-bis-2-naphthol. Tris-phenol: 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene (TDBHB). Alcohols: triphenylmethanol (Ph_3COH), benzyl alcohol, fenchyl alcohol (1,3,3-trimethyl-2-norbornanol), *tert*-butyl alcohol, triphenylsilanol (Ph_3SiOH).

Two porous materials were used for the synthesis of supported catalysts: Davison-Grace 655-grade silica calcined at 600 °C and spherical polystyrene particles with an average diameter of 30 μm and a pore volume of 1.9 g/cm^3 manufactured by Advanced Polymer Systems Co.

Polymerization Reactions. Polymerization reactions of ethylene and copolymerization reactions of ethylene and 1-hexene were carried out in a 0.5 L Autoclave Engineers reactor equipped with a magnet-driven stirrer, a thermocouple, an electric heating jacket, and several ports for adding reaction components.[40,41] Prior to polymerization, the reactor was purged with nitrogen at 105−110 °C for 1 h. All reactions were carried out in *n*-heptane. In most experiments, $AlMe_3$ or Al*i*-Bu_3 was added to the solvent as an impurity scavenger. Polymerization of neat 4-methyl-1-pentene was carried out in a 30 cm^3 glass vial sealed with a rubber septum.

Spectroscopic Analysis. ^1H and ^{13}C NMR spectra of the cocatalysts (toluene solutions) were recorded with a JEOL GX400 NMR spectrometer. IR spectra were recorded with a Perkin-Elmer 1600 FTIR spectrophotometer. Samples of cocatalysts were either deposited from toluene solution onto a KBr window and sealed between two windows or were prepared as mulls in dry Nujol and also sealed between two KBr windows.

Polymer Characterization. Melt indices I_2 of the polymers were measured at 190 °C with a Kayeness extrusion plastometer according to the ASTM Standard D 1238, condition E. Molecular weights of the polymers were estimated from their melt indices using an M_w(GPC)−I_2 correlation for a series of ethylene/1-hexene copolymers prepared with metallocene complexes activated with MAO. Copolymer compositions were measured by IR. DSC data were recorded with a DuPont 9900 thermal analyzer. DSC samples were crystallized by cooling from 140 to 40 °C at a rate of 0.5 °C/min. Melting curves of the crystallized samples were recorded from 30 to 140 °C at a rate of 2 °C/min. Samples of isotactic poly(4-methyl-1-pentene) were melted at a rate of 10 °C/min from 30 to 300 °C.

Experimental Results

The first proposed route to organoaluminates, a reaction of an alkylalumoxane $[AlR-O]_n$ with a sterically hindered phenol or an alcohol, appears to be the most straightforward. However, all commercial samples of alkylalumoxanes, including MAO, contain from 10 to 30% of their Al atoms as AlR_3, and one has to expect that Al−R bonds both in the alkylalumoxanes and in AlR_3 will react with the phenols or alcohols in parallel, thus making discrimination between the effects of the respective reaction products difficult. For this reason, the data on the two-step reaction of organoaluminate synthesis are presented first.

Part 1. Arylaluminates: Two-Step Synthesis from Trialkylaluminum Compounds, Phenols, and Water. *Synthesis.* In the first step, a sterically hindered phenol PhOH with two bulky substituents in the second and the sixth position is reacted with AlR_3. Four AlR_3 compounds were tested: $AlMe_3$, $AlEt_3$, Al-*i*-Bu_3, and Al-*n*-Oct_3. The reaction can be carried out in either aromatic or aliphatic solvents, usually at room temperature. Under typical conditions, a small amount of PhOH, from 0.3 to 1 g, is dissolved in 5−10 cm^3 of toluene in a glass vial capped with a rubber septum; the solution is thoroughly flushed with nitrogen and added with a syringe to a vial with AlR_3 solution. The reactions proceed vigorously with the formation of alkylaluminum phenoxides and an alkane:

$$AlR_3 + PhOH \rightarrow AlR_2OPh + RH \qquad (1)$$

$$AlR_3 + 2PhOH \rightarrow AlR(OPh)_2 + 2RH \qquad (2)$$

These reactions were thoroughly described earlier.[22,35,43] The ratio between AlR_2OPh and $AlR(OPh)_2$ in the products depends mostly on the ratio between PhOH and AlR_3. Taking into account the well-known reactivity pattern of organoaluminum compounds in reations with OH-containing compounds, AlR_3 >AlR_2OR' > $AlR(OR')_2$,[43] one can expect that when the [PhOH]:[AlR_3] molar ratio is close to 1, the dominant reaction product is AlR_2OPh.

NMR data for several types of AlR_2OPh were published earlier.[22,35] Our NMR analysis of the reaction product of $AlMe_3$ and DBMP, $Me_2Al-O-(4\text{-}Me\text{-}2,6\text{-}{}^tBu_2-C_6H_2)$, gave the following results. The signal of the $CH_3(Al)$ carbon atoms in its ^{13}C NMR spectrum is at −9.0 ppm; compare to −7.3 ppm for $AlMe_3$ and −10.3 ppm for $Me_2Al-O-(4\text{-}{}^tBu-C_6H_4)$[22] (see Supporting Information). Most signals in the $4\text{-}Me\text{-}2,6\text{-}{}^tBu_2-C_6H_2-O-$ moiety in AlR_2OPh show high-field shifts compared to those in the phenol: the CH_3 signal of ^{t}Bu groups by 1.8 ppm, the $C(Me_3)$ signal of these groups by 0.8 ppm, the $C_{arom}(O)$ atom signal by 0.8 ppm, other C_{arom} signals from 1.5 to 2.8 ppm. The signal of the $(Al)CH_3$ protons in the ^1H NMR spectrum of $Me_2Al-O-(4\text{-}Me\text{-}2,6\text{-}{}^tBu_2-C_6H_2)$ is at −0.20 ppm vs −0.15 ppm for $AlMe_3$ and −0.20 ppm for $Me_2Al-O-(4\text{-}{}^tBu\text{-}C_6H_4)$.[22]

Table 1. Preparation of Sterically Hindered Al Phenoxides (Reactions 1 and 2) and Phenylaluminates (Reaction 3)

cocat.	PhOH	Al source	[PhOH]/[AlR_3]	[H_2O]/[Al]	expected main product[a]
I-A	DBMP	$AlMe_3$	1:1	0	$Me_2Al-OPh$
I-B	DBMP	$AlMe_3$	2:1	0	$MeAl(OPh)_2$
I-C	DBP	$AlMe_3$	1:1	0.8:1	$(PhO)(Me)Al-[O-Al(OPh)]_n-O-Al(Me)(OPh)$
I-D	DBP	$AlMe_3$	2:1[b]	0.5:1[c]	$(PhO)_2Al-O-Al(OPh)_2$
I-E	DBP	$AlMe_3$	1:1	0.5:1[c]	$(PhO)(Me)Al-O-Al(Me)(OPh)$
I-F	DBP	$AlMe_3$	1:1	0.9:1[d]	$(PhO)(Me)Al-[O-Al(OPh)]_n-O-Al(Me)(OPh)$
I-G	DBP	$AlMe_3$	1:1	1:1[e]	$(PhO)(Me)Al-[O-Al(OPh)]_n-O-Al(Me)(OPh)$
I-H	DBP	$AlEt_3$	1:1	0.9:1[d]	$(PhO)(Et)Al-[O-Al(OPh)]_n-O-Al(Et)(OPh)$
I-I	DBP	Al-*i*-Bu_3	1:1	0.9:1[d]	$(PhO)(i\text{-}Bu)Al-[O-Al(OPh)]_n-O-Al(i\text{-}Bu)(OPh)$
I-J	DBP	Al-*n*-Oct_3	1:1	0.9:1[d]	$(PhO)(n\text{-}Oct)Al-[O-Al(OPh)]_n-O-Al(n\text{-}Oct)(OPh)$
I-K	DPP	$AlMe_3$	1:1[b]	0.6:1[c]	$(PhO)(CH_3)Al-O-Al(CH_3)(OPh)$
I-L	MBBM	$AlMe_3$	0.9:1[b,f]	0.5:1[c]	LAl−O−AlL[f]
I-M	phenol	$AlMe_3$	1:1	0.9:1[d]	$(C_6H_5O)(Me)Al-[OAl(OC_6H_5)]_n-O-Al(Me)(OC_6H_5)$

[a] Ph groups are 4-Me-2,6-$^tBu_2$-C_6H_2 in products I-A and I-B, 2,6-$^tBu_2$-C_6H_3 in products I-C−I-J, and 2,6-Ph_2-C_6H_3 in product I-K. [b] To bring the reaction to completion, the solution was kept at 70 °C for 30 min. [c] Sluggish reactions, lasted ~20−30 min. [d] H_2O was added in two steps, first at [H_2O]:[Al] of 0.5 and then 0.4. [e] H_2O added in two steps, both at [H_2O]:[Al] of 0.5. [f] The first stage produces mostly CH_3−Al(L), where L is the bidentate ligand derived from MBBM.

In the second stage of the arylaluminate synthesis, AlR_2OPh is contacted with water:

$$AlR_2OPh + H_2O \rightarrow [Al(OPh)-O]_n + 2RH \qquad (3)$$

This stage of the synthesis is also carried out under moderate conditions, usually at room temperature, in contrast to the syntheses of alkylalumoxanes from AlR_3 and water which have to be carried out at low temperatures under carefully controlled conditions to avoid overheating.[1,4−7] Reactions 3 are relatively slow and usually require from 15 to 60 min to come to completion. They are monitored by observing slow disappearance of drops of water from the bottom of the reaction vessel. The total required amount of water could be added in one or in several steps. Generally speaking, these reactions produce mixed "co-oligomers" $Ph-[O-Al(OPh)]_x-[O-Al(R)]_y-O-Al(R)-OPh$ in which the x:y ratio depends on the ratio between AlR_3 and PhOH in the first stage of the synthesis. If the [PhOH]:[AlR_3] ratio in reactions 1 and 2 is slightly higher than 1 and the [H_2O]:[Al] ratio in reaction 3 is ~1, the products of reaction 3 and the catalyst compositions based on them are air-stable, in contrast to alkylalumoxanes.

The following example describes a typical synthesis procedure for an arylaluminate (cocatalyst I-C in Table 1). DBP (2.7 mmol) was dissolved in 3 cm^3 of toluene; the solution was flushed with nitrogen and slowly added to a 25 cm^3 glass vial containing an equimolar amount of $AlMe_3$ in 5 cm^3 of toluene. A rapid reaction ensued resulting in methane evolution; the gas was released through a syringe needle. The reaction products, mostly 2,6-$^tBu_2-C_6H_3-O-AlMe_2$, remained dissolved in toluene. Next, neat water (2.16 mmol) was added to the vial at room temperature to bring the [H_2O]:[Al] ratio to 0.8. Water droplets gradually reacted with $Me_2Al-OPh$ with methane evolution and produced a toluene-soluble product of light pink color with the general structure $Ph-O-Al(Me)-[O-Al(OPh)]_x-O-Al(Me)-OPh$. A number of arylaluminates of different compositions were prepared in a similar way. They are listed in Table 1. The numbers in the designations of the cocatalysts and catalyst compositions in Tables 1 and 4 refer to the numbers of respective tables, e.g., catalyst IV-C is described in Table 4, etc.

Polymerization Reactions. Copolymerization reactions of ethylene and α-olefins are a convenient means of testing viability of the new cocatalysts for metallocene complexes. Ethylene homopolymerization reactions produce polymers with very high molecular weights which are difficult to measure whereas the molecular weights of the copolymers are much lower and can be easily evaluated. Analysis of melting points of the copolymers vs their composition provides an approximate estimation of uniformity of active centers in the catalysts with respect to their copolymerization ability.[1]

Table 2. Polymerization Reactions with Metallocene Complexes and Reaction Products of Sterically Hindered Phenols, Alkylaluminum Compounds, and Water[a]

run[b]	cocatalyst (Table 1)	[Al], mmol	[Al]:[Zr]	productivity, kg/(mmol of Zr h)	C_H,[c] mol %
II-r1	I-A	1.9	1300	~0	
II-r2	I-B	1.9	1300	~0	
II-r3	I-C	2.7	1800	3.3	1.6
II-r4	I-D	2.7	1800	1.9	1.5
II-r5	I-E	2.7	1800	3.3	1.5
II-r6	I-F	2.7	1800	33.8	1.5
II-r7	I-G	2.7	6100	9.8	1.7
II-r8	I-H	2.7	1800	2.4	1.8
II-r9	I-I	2.7	1800	11.0	1.3
II-r10	I-J	2.7	1800	8.2	1.4
II-r11	I-K	2.7	1800	3.9	1.8
II-r12	I-L	2.7	1800	5.1	1.4
II-r13	I-M	2.7	1800	~1.0	3.1

[a] Cocatalyst compositions are given in Table 1. [b] Reaction conditions: 80 °C, [1-hexene] = 0.64 M, P_{total} ~ 1.24 MPa, [ethylene] = ~0.7 M. [c] 1-Hexene content in copolymer.

All arylaluminates and alkylaluminum phenoxides listed in Table 1 were tested in ethylene/1-hexene copolymerization reactions using $C_2H_4(Ind)_2ZrCl_2$ and Cp_2ZrCl_2 as catalysts. Catalyst productivities and copolymer compositions are given in Table 2. The first number in the designation of the polymerization experiments (such as run II-r1 in Table 2) refers to the number of the respective table, and the second number refers to the run number. $AlMe_3$ or Al*i*-Bu_3 was added to the mixtures of the solvent and 1-hexene as an impurity scavenger and as an alkylating agent for a metallocene complex. The data in Table 2 demonstrate that all arylaluminates with sterically hindered aryl groups are effective cocatalysts for metallocene complexes in the polymerization reactions and that they produce ethylene/1-hexene copolymers of approximately the same composition. Both dimethylaluminum phenoxides Me_2AlOPh with 2,6-disubstituted phenyl groups (I-A and I-B) were inactive as cocatalysts. These examples show that arylaluminates themselves, rather than possible admixtures of alkylaluminum phenoxides (due to incomplete conversion in reaction 3), are the true cocatalysts for metallocene complexes. All these polymerization reactions were quite stable: after a short acceleration period, 10−15 min, the reaction rates reached a steady level, and the reactions continued at this level for 2−3 h. Molecular weights of the copolymers prepared with different arylaluminates were all in a range of 50 000−80 000.

Part 2. Arylaluminates: Synthesis from Alkylalumoxanes. *Synthesis*. The second method of arylaluminate synthesis involves reacting an alkylalumoxane $[Al(R)-O]_n$ (such as MAO) with a sterically hindered phenol PhOH. PhOH is dissolved in toluene, the solution is flushed with nitrogen, and then a required amount of MAO solution in toluene (or solution of another alkylalumoxane) is added to the PhOH solution. The reactions are relatively vigorous although they proceed at much lower rates than similar reactions of MAO with alcohols. The reactions involving MAO produce a large volume of methane (it is vented from the vial through a syringe needle) and leave transparent slightly yellow solutions:

$$[Al(Me)-O]_n + PhOH \rightarrow [Al(OPh)-O]_n + CH_4 \quad (4)$$

The products of reaction 4 usually contain both −Al(Me)−O− and −Al(OPh)−O− groups. Their ratio is determined by the ratio between MAO and the phenol.

All commercial MAO samples contains from 10 to 30% of its Al atoms as $AlMe_3$. This fact significantly complicates investigation of reaction 4:

1. $AlMe_3$ readily reacts with PhOH with the formation of either Me_2AlOPh or $MeAl(OPh)_2$ (reactions 1 and 2). A priori, these reactions should proceed at higher rates than reaction 4. Although the products of reactions 1 and 2 are not effective cocatalysts (see Table 2), their formation complicates estimations of conversion in reaction 4.

2. Dialkylaluminum phenoxides formed in reaction 1 are stable in a broad temperature range. However, they can undergo a disproportionation reaction in the presence of zirconocene complexes, when the cocatalysts are used in polymerization reactions:[35]

$$2AlR_2OPh \xrightarrow{\text{(zirconocene)}} AlR(OPh)_2 + AlR_3 \quad (5)$$

Reaction products formed in the DBMP−MAO mixture prepared in toluene at an [Al]:[PhOH] molar ratio of 1:1 were studied spectroscopically. DBMP has a strong O−H stretching mode band at 3640 cm^{-1} in its IR spectrum (see Supporting Information), indicating that the OH group in this molecule is strongly shielded and does not form the H-bond, in contrast to cresol [ν(OH) at 3224 cm^{-1}]. Addition of MAO greatly reduces the absorbances of both the ν(OH) band (only ∼15% of unreacted DBMP remains in the mixture) and that of the ν(CO) band at 1157 cm^{-1}. The ν(OH) band position in the spectrum of the reaction products does not shift; i.e., the OH group in the remaining DBMP does not form the H-bond with the oxygen atoms of the arylaluminate as well. Subsequent addition of TMA to this mixture in an amount of ∼0.5 mol/mol DBMP results in complete conversion of the phenol. The IR spectrum of the DBMP−MAO mixture also shows new ν[C−O(Al)] bands at 1234 and 1247 cm^{-1} and the ν[Al−O(C)] band[42] at 802 cm^{-1}. The (O)H proton signal in the ^1H NMR spectrum of the 1:1 DBMP−MAO mixture is reduced by ∼90% compared to the spectrum of the phenol itself. ^{13}C NMR signals of the 4-Me-2,6-$^tBu_2-C_6H_2-O-$ moiety in the mixture belong to two species, the unreacted phenol (10−15%) and the same group attached to an Al atom, both in the alkoxide AlR_2OPh (with high-field shifts by 0.8−2.8 ppm compared to the phenol; see the previous section) and in the arylaluminate group −O−Al(OPh)−O−. The presence of weak broad resonances of the remaining $-Al(CH_3)-O-$ units in the NMR spectra of the mixture (∼−5 ppm in the ^{13}C spectrum, ∼0 ppm in the ^1H spectrum) indicates incomplete conversion in reaction 4.

Polymerization Reactions. From the viewpoint of polymerization catalysis, it was necessary to ensure that a sufficient quantity of a sterically hindered phenol PhOH was used to convert all admixture of $AlMe_3$ in an MAO aliquot into phenoxides (reactions 1 and 2) and to convert most −Al(Me)O− groups of MAO into −Al(OPh)O− groups but that no free phenol remains. Therefore, most syntheses were carried out in two steps. First, reaction 4 was carried out at a ∼1.2:1 excess of the phenol. The products of these reactions do not contain Al−C bonds in any significant amount; they are air-stable and do not react with alcohols. They were heated to 70 °C for 30 min to bring reaction 4 to completion; the solutions were cooled to 20 °C and then, to remove a possible excess of the phenol, were treated with a small quantity of fresh $AlMe_3$.

Table 3 gives the results of ethylene/1-hexene copolymerization reactions with $C_2H_4(Ind)_2ZrCl_2$ and sterically hindered phenylaluminates formed in reaction 4 between MAO and DBMP. As before, $AlMe_3$ or Al*i*-Bu_3 (1.35 mmol) was added to the reactor as an impurity scavenger and as the alkylating agent for the metallocene complex. All the arylaluminates with sterically hindered aryl groups were quite effective cocatalysts, independent of the ratio between Al−Me and Al−OPh groups. All copolymers in Table 3, judging by their low melting points, have uniform branching distributions typical of ethylene/1-hexene copolymers prepared with the same metallocene complex activated with MAO.

A series of experiments were carried out to demonstrate the essential role of shielding of oxygen atoms in arylaluminates as a prerequisite for their usefulness as cocatalysts for metallocene complexes. Several parallel reactions were carried out between MAO (1.9 mmol) and different phenols, DBMP, 4-methylphenol, 4-$CF_3-C_6H_4$-OH, and 1,1′-bis-2-naphthol, at [phenol]:[MAO] ratios of 0.9:1 and 0.5:1. These products were used in combination with $C_2H_4(Ind)_2ZrCl_2$ in ethylene/1-hexene copolymerization reactions at 80 °C. The first reaction (run III-r4) produced an ethylene/1-hexene copolymer (productivity 130 kg/mmol of Zr) containing 2.4 mol % of 1-hexene. On the other hand, the products of the MAO reactions with 4-methylphenol, 4-$CF_3-C_6H_4OH$, and the bis-naphthol prepared at sufficiently high [phenol]:[Al] ratios were essentially inactive as cocatalysts (runs III-r12−III-r14).

The products of reaction 4 are quite stable and can be used after several days of storage. They also can be precontacted with solutions of metallocene complexes in toluene, and the combined solutions can be later used as single-component polymerization catalysts. Several examples of such premixed catalyst systems are given in Table 4, and the polymerization results with these catalysts are shown in Table 5. All preformed catalyst systems derived both from MAO and MMAO exhibited good activity in ethylene/1-hexene copolymerization

Table 3. Copolymerization Reactions of Ethylene and 1-Hexene with $C_2H_4(Ind)_2ZrCl_2$ and Sterically Hindered Phenylaluminates Formed in Reaction between MAO and Phenols

run	PhOH	[PhOH]/[Al]	[Al], mmol	[Zr], mmol	[Al]:[Zr]	1-hexene, M	ethylene, MPa	temp, °C	productivity, kg/(mmol of Zr h)	C_{Hex}[a], mol %	T_m[b], °C
III-r1	DBMP	0.3	4.75	2.9×10^{-4}	16 400	1.63	1.04	90	205.6	6.3	
III-r2	DBMP	0.9	4.75	2.9×10^{-4}	16 400	1.63	0.69	85	322.8	5.9	84.9
III-r3	DBMP	0.9	0.95	2.9×10^{-4}	3300	1.63	0.69	80	18.5	5.9	85.1
III-r4	DBMP	0.9	1.90	1.5×10^{-4}	12 700	0.64	0.69	80	142.6	2.4	109.7
III-r5[c,d]	DBMP	1.2	1.90	5.8×10^{-4}	3300	0.96	0.69	80	30.3	4.3	97.7
III-r6[c,e]	DBMP	1.2	1.90	6.5×10^{-4}	2900	0.64	0.69	80	31.5	2.7	109.7
III-r7		0	2.16	2.9×10^{-4}	7400	0.64	1.21	80	139.1	1.5	121.5
III-r8	DBP	0.3	4.75	7.4×10^{-5}	64 200	0.64	1.04	80	91.9	2.4	
III-r9		0	4.75	7.4×10^{-5}	64 200	0.64	1.04	80	129.0	2.5	
III-r10	DPP	0.5	4.75	2.9×10^{-4}	7400	0.64	1.04	80	91.9	2.4	
III-r11	4-MePhOH	0.1	4.75	2.9×10^{-4}	16 400	0.64	0.69	80	13.8		
III-r12	4-MePhOH	0.9	4.75	2.9×10^{-4}	16 400	0.64	0.69	80	~0.8		
III-r13	4-CF_3PhOH	0.5	2.41	1.5×10^{-3}	1600	0.64	1.21	80	~0		
III-r14	bis−naphthol	0.9	2.16	5.8×10^{-4}	3300	0.64	1.21	80	1.2		

[a] 1-Hexene content in copolymer. [b] Melting point of copolymer. [c] Excess of DBMP was removed from the cocatalyst by treating it with $AlMe_3$, as described in the text. [d] $AlMe_3$ was used as an alkylating agent for metallocene complex and impurity scavenger. [e] Al-*i*-Bu_3 was used as an alkylating agent for metallocene complex and impurity scavenger.

Table 4. Compositions of Single-Component Polymerization Catalysts Containing Sterically Hindered Phenylaluminates

catalyst	PhOH	Al source	[PhOH]/[Al]	[Al], mmol	metallocene complex	[Zr], mmol	[Al]:[Zr]
IV-A	DBMP	MAO	0.9	1.9	$C_2H_4(Ind)_2ZrCl_2$	1.45×10^{-4}	13000
IV-B	DBMP	MAO	0.5	3.9	$C_2H_4(Ind)_2ZrCl_2$	3.92×10^{-3}	1000
IV-C	DBMP	MAO	1.0	2.0	$C_2H_4(Ind)_2ZrCl_2$	1.90×10^{-3}	1000
IV-D	DBMP	MMAO[a]	0.5	3.6	$C_2H_4(Ind)_2ZrCl_2$	4.35×10^{-4}	8300
IV-E	DBMP	MMAO[a]	1.0	1.8	$C_2H_4(Ind)_2ZrCl_2$	2.17×10^{-4}	8300
IV-F	DBMP	MAO	0.9	2.4	$(n\text{-Bu-Cp})_2ZrCl_2$	1.20×10^{-2}	200
IV-G	DBMP	MAO	1.2[b]	2.4	$(n\text{-Bu-Cp})_2ZrCl_2$	1.20×10^{-2}	200
IV-H	DBMP	MAO	0.9	2.4	Cp_2HfCl_2	2.37×10^{-2}	115
IV-I	MBBM	MAO	0.9[c]	1.9	$C_2H_4(Ind)_2ZrCl_2$	5.82×10^{-4}	3300
IV-J	TDBHB	MAO	1.0	2.4	$C_2H_4(Ind)_2ZrCl_2$	1.45×10^{-3}	1600
IV-K	DBMP	IBAO[d]	0.9	1.9	$C_2H_4(Ind)_2ZrCl_2$	1.53×10^{-4}	1000

[a] Modified, heptane-soluble MAO containing ca. 15% of Al−*i*-Bu bonds. [b] Excess of DBMP was removed from the cocatalyst by treating it with $AlMe_3$. [c] [OH]:[Al] molar ratio. [d] Excess of DBMP was removed from the cocatalyst by treating it with Al-*i*-Bu_3.

Table 5. Copolymerization Reactions of Ethylene and 1-Hexene with Single-Component Catalysts Containing Sterically Hindered Phenylaluminates as Cocatalysts (Table 4)

run[a]	catalyst	temp, °C	productivity, kg/(mmol of Zr h)	C_{Hex},[b] mol %	M_w
V-r1	IV-A	80	42.0	2.4	
V-r2	IV-B[c]	80	46.7	3.3	72 000
V-r3	IV-C[d]	80	25.0	1.8	67 000
V-r4	IV-D	80	67.0	3.4	75 000
V-r5	IV-E	80	77.0	2.8	67 000
V-r6	IV-F	120	16.8	2.2	~10 000
V-r7	IV-G	80	0.7	1.3	101 000
V-r8	IV-H	80	~0.2	5.5	
V-r9	IV-I	80	21.2	2.9	
V-r10	IV-J	80	4.5	2.4	
V-r11	IV-K	80	16.9	3.0	
V-r12	IBAO	80	3.3		

[a] All reactions at [1-hexene] = 1.63 M and $P_E = 0.69$ MPa. [b] 1-Hexene content in copolymer. [c] 14 vol % of catalyst IV-B was used in polymerization. [d] 18 vol % of catalyst IV-C was used in polymerization.

reactions. Arylaluminates produced in reaction 4, when used together with bridged metallocene complexes, also catalyze stereospecific polymerization reactions of 1-alkenes. The catalyst containing $C_2H_4(Ind)_2ZrCl_2$ and the phenylaluminate derived from MAO and DBMP was tested in polymerization of 4-methyl-1-pentene. A glass vial with a magnetic stirrer was filled with 10 cm^3 of neat dry 4-methyl-1-pentene. The monomer was treated with $AlMe_3$ (0.68 mmol), and then the preformed catalyst solution IV-D containing 1.62×10^{-3} mmol of $C_2H_4(Ind)_2ZrCl_2$ was added to it. The reaction mixture was stirred at 20 °C for 20 h and produced 2.9 g (44% yield) of isotactic poly(4-methyl-1-pentene) with a melting point of 224 °C.

Supported Catalysts. Stability of solutions containing metallocene complexes and sterically hindered arylaluminates makes them convenient candidates for the synthesis of supported metallocene catalysts. Two such catalysts were prepared. In the first example, DBP (1.185 mmol) was dissolved in toluene and combined with 2.38 mmol of MAO solution. The solution was heated at 70 °C for 60 min and then combined with solution of 1.18×10^{-2} mmol of $C_2H_4(Ind)_2ZrCl_2$ in toluene. In a separate vial, 0.5 g of porous 600 °C-calcined silica containing ~0.72 mmol of OH group/g of silica was slurried in *n*-heptane and was treated at 60 °C with 0.31 mmol of $AlMe_3$ for 30 min to convert Si−OH groups in the silica into Si−O−$AlMe_2$ groups. After that, the solution containing the metallocene complex and the phenylaluminate was added to the vial with the silica/*n*-heptane slurry, and then all solvents were removed from the vial in a nitrogen flow at 60 °C for 2.5 h, yielding 0.58 g of dry catalyst. This supported catalyst, in an amount of ~0.01 g, was used in an ethylene/1-hexene copolymerization reaction at 80 °C and $P_E = 1.24$ MPa. The catalyst was quite active: it produced an ethylene/1-hexene copolymer (productivity 1.16×10^4 g/mmol of Zr in 3 h) with M_w of 43 500 containing 3.8 mol % of 1-hexene.

In the second example, solid DBP (4.75 mmol) was reacted with MAO at an [Al]:[PhOH] ratio of 1:1. A vigorous reaction with methane evolution was completed in ~1 min and resulted in the formation of a concentrated viscous phenylaluminate solution in toluene. Because this compound is air-stable, all subsequent steps were carried out in air. 2.38×10^{-2} mmol of $C_2H_4(Ind)_2ZrCl_2$ was dissolved in the phenylaluminate solution, providing an [Al]:[Zr] ratio of 200. The solution was mixed with 1.3 g of an inert porous support, spherical 30 μm polystyrene particles with a pore volume of 1.9 g/cm^3. The supported catalyst was dried at 60 °C for 6 h; the yield of dry catalyst was 2.43 g. This catalyst was tested in ethylene/1-hexene copolymerization reaction under the same conditions as in the above experiment. Its productivity over a 3 h period was 1.63×10^4 g/mmol of Zr; it produced a copolymer with M_w of 54 800 containing 2.9 mol % of 1-hexene.

Part 3: Alkylaluminates: Synthesis and Use as Cocatalysts. The second type of the new cocatalysts for metallocene complexes is oligomeric alkylaluminate $[Al(OR)-O]_n$ (**II** in Scheme 1), where R is a strongly sterically hindered alkyl group. Similar to arylaluminates, these cocatalysts are produced either by reacting a trialkylaluminum compound, in sequence, with ROH and with water or by reacting MAO with ROH. The alcohol most suitable for the cocatalyst synthesis is triphenylmethanol.

The first method for producing sterically hindered alkylaluminates consists of two stages. First, ROH is reacted with AlR_3, usually at room temperature. The reaction produces alkylaluminum alkoxides:

$$AlMe_3 + ROH \rightarrow Me_2Al-OR + CH_4 \qquad (6)$$

$$AlMe_3 + 2ROH \rightarrow MeAl(OR)_2 + 2CH_4 \qquad (7)$$

These reactions were described in detail in the literature.[43] Next, the products of reactions 6 and 7 are reacted with water. This reaction is relatively slow and requires, depending on temperature (usually from 20 to 70 °C), from 15 to 60 min to come to completion:

$$Me_2Al-OR + H_2O \rightarrow [Al(OR)-O]_n + 2CH_4 \qquad (8)$$

Depending on the ratio between AlR_3 and ROH in reactions 6 and 7 and a ratio between the alkylaluminum alkoxide and water, this method produces "co-oligomers" $[Al(OR)-O]_x-[Al(R)-O]_y$, where the x:y ratio can approach ~1:0. To test this route to alkylalumoxanes, 2.7 mmol of Ph_3COH was dissolved in toluene and was reacted with 2.7 mmol of $AlMe_3$ for 30 min to produce $Me_2Al(OCPh_3)$. Then neat water was added to the solution in two steps, first at $[H_2O]:[Al] = 0.5$ for 30 min and, second, in the amount sufficient to reach the total $[H_2O]:[Al]$ ratio of 0.9, thus producing an alkylaluminate containing predominantly $[Al(OCPh_3)-O]$ units. This product was tested in combination with $C_2H_4Ind_2ZrCl_2$ (1.47×10^{-3} mmol, $[Al]:[Zr] = 1860$) in an ethylene/1-hexene copolymerization reaction at 80 °C, $P_E = 1.24$ MPa, and [1-hexene] = 0.64 M. The alkylaluminate was quite effective as a cocatalyst: the polymerization reaction produced an ethylene/1-hexene copolymer (productivity ~10 kg/mmol of Zr over 2 h) containing 2.6 mol % of 1-hexene.

When the products of reaction 6 are used as intermediates in the synthesis of the alkylaluminate cocatalysts, there exists one complicating circumstance that should be taken into account. Recently, Barron et al.[22] have described in detail thermal decomposition of several Me_2AlOR compounds, where R are sterically crowded alkyl groups such as CPh_3. The reaction produces MAO:

$$Me_2Al-OCPh_3 \xrightarrow{\text{(temp)}} [Al(Me)-O]_n + CPh_3Me \qquad (9)$$

This reaction usually proceeds at high temperatures, above 80 °C, and it is strongly autocatalytic; MAO serves as the most effective catalyst. Because of this, the induction period in conversion of $Me_2AlOCPh_3$ to MAO in reaction 9 lasts ~2−3 h even at 90 °C.[22] (With respect to the possibility of a similar reaction involving dialkylaluminum phenoxides $Me_2Al-OPh$ described in the previous sections, Barron did not observe such a reaction when a dimethylaluminum phenoxide was used instead of alkoxides.[22] Our NMR analysis of an AlR_2-OPh compound produced in reaction 1, cocatalyst I-A, also found no evidence of a reaction similar to reaction 9, such as the formation of an aromatic compound with the 1-Me-2,6-^{t}Bu$_2$ substitution pattern.)

Several experimental facts allow us to exclude formation of MAO in reaction 9 as the reason for catalytic activity of the products of reaction 8: (a) reactions 6−7 were carried out at much lower temperatures than those required for reaction 9; (b) when the final product of reaction 8 was used as a cocatalyst for a metallocene complex in a polymerization reaction, the reaction rate was steady for 2 h and did not exhibit any acceleration associated with reaction 9. A control experiment was also carried out to demonstrate that the aluminum alkoxide with a sterically hindered alkyl group is not a cocatalyst for metallocene complexes. A product of reaction 7 was prepared at an $[Ph_3COH]:[Al]$ ratio of 2.0 in toluene solution; it was tested in combination with $C_2H_4Ind_2ZrCl_2$ (1.45×10^{-3} mmol, $[Al]:[Zr] = 1860$) in an ethylene/1-hexene copolymerization reaction under conditions of run VI-r1 (see below) and was found inactive.

The second method for the synthesis of sterically hindered alkylaluminates is the reaction between an alkylalumoxane and the alcohol*R*OH. It proceeds vigorously, e.g.

$$[Al(Me)-O] + ROH \rightarrow [Al(OR)-O] + CH_4 \qquad (10)$$

When excess of ROH is used (to account for the presence of $AlMe_3$ in MAO), it should be neutralized in a subsequent reaction with an additional aliquot of $AlMe_3$. Table 6 shows three examples of reaction products between MAO and Ph_3COH and their use as cocatalysts for $C_2H_4(Ind)_2ZrCl_2$ in ethylene/1-hexene copolymerization reactions. Another sterically crowded alcohol, fenchyl alcohol, can also be used for the preparation of a modestly active alkylaluminate (run VI-r4). Control experiments were carried out to demonstrate that only highly sterically hindered alcohols produce catalytically active alkylaluminates. The results for *tert*-butyl alcohol and benzyl alcohol (runs VI-r5 and VI-r6, respectively) show that these alkylaluminates are inefficient as cocatalysts. Triphenylsilanol cannot replace Ph_3COH in producing an active cocatalyst either (run VI-r7).

Discussion

When the relative efficiency of various cocatalysts for metallocene complexes, such as alkylalumoxanes and the cocatalysts described in this paper, is estimated from productivity of respective catalyst systems in alkene polymerization reactions under a particular set of

Table 6. Copolymerization Reactions of Ethylene and 1-Hexene with $C_2H_4(Ind)_2ZrCl_2$ and Alkylaluminates Formed in Reaction Between MAO and Different Alcohols[a]

run	ROH	[ROH]:[Al], mol/mol	[Al], mmol	[Zr], mmol	[Al]:[Zr]	productivity, kg/(mmol of Zr h)	C_{Hex},[b] mol %	M_w
VI-r1	Ph_3COH	0.5	1.90	2.9×10^{-4}	6500	184.2	4.2	53 000
VI-r2	Ph_3COH	0.8	1.90	2.9×10^{-4}	6500	79.0	4.1	52 500
VI-r3	Ph_3COH	0.5	1.27	9.8×10^{-4}	1290	11.5		
VI-r4	fenchyl alcohol	0.5	2.40	1.5×10^{-3}	1610	~1.9	2.4	41 000
VI-r5	^tBuOH	0.9	2.85	4.4×10^{-4}	6500	~0.5		
VI-r6	$PhCH_2OH$	0.5	2.85	1.5×10^{-3}	1840	~0.7		
VI-r7	Ph_3SiOH	0.5	4.75	2.9×10^{-4}	16200	5.4		

[a] Conditions: 80 °C, [1-hexene] = 0.64 M, $P_E = 0.69$ MPa in runs VI-r1–VI-r3, VI-r5, and VI-r6 and 1.24 MPa in run VI-r4. $AlMe_3$ was used as an alkylating agent for metallocene complex and impurity scavenger. [b] 1-Hexene content in copolymer.

reaction conditions, one should take into account that these catalyst systems usually exhibit very high catalytic activity (which requires the use of very low zirconocene concentrations) and that precise measurement of the reactivity is difficult. Even under best circumstances, the reactivity levels are usually estimated within ±25%. In addition, the reactivity of such catalytic systems strongly depends on a ratio between a cocatalyst and a metallocene complex. These ratios are usually very high, from several hundreds to many thousands, but no leveling-off of the dependence between reactivity and the [cocatalyst]:[Zr] ratio was observed even at the very high ratios.[1,3]

The main finding of this work is that two types of oligomeric organoaluminates with sterically hindered organic substituents, arylaluminates **I** and alkylaluminates **II** (Scheme 1), can be used as cocatalysts for metallocene complexes in alkene polymerization and copolymerization reactions. Both mono-phenols and poly-phenols can be used for the synthesis of the arylaluminates (DBP, DPP, DBMP, MBBM, TDBMB; see polymerization results in Tables 2, 3, and 5). Mixed oligomers containing two types of groups, organoaluminate, −Al(OR)−O−, and alkylalumoxane, −Al(R)−O−, are also effective cocatalysts. The most plausible mechanism for the formation of active centers with these cocatalysts is the same as in the case of MAO: a zirconocene complex Cp_2ZrCl_2 is alkylated by a trialkylaluminum compound AlR_3 (which is always present in the polymerization reactions) to a dialkyl derivative Cp_2ZrR_2, and the organoaluminate abstracts one of the alkyl groups R as an anion, leaving a catalytically active zirconocenium species Cp_2ZrR^+. Apparently, adducts of sterically hindered organoaluminates and R^- form voluminous anions with broadly distributed negative charges, similar to MAO. The catalyst systems utilizing these cocatalysts are, essentially, single-center systems: they produce ethylene/1-alkene copolymers with uniform compositional distributions, judging by low melting points of the copolymers (Table 3).

Determining a possible role of alkylaluminum aryloxides R_2AlOPh and $RAl(OPh)_2$ and alkoxides R_2AlOR and $RAl(OR)_2$ in polymerization catalysis is an important prerequisite in discussing the function of the organoaluminates. There are two potential sources of these products. When the organoaluminates are produced from AlR_3, sterically hindered phenols or alcohols, and water, alkylaluminum aryloxides, and alkoxides are semiproducts in the synthesis, they are formed in reactions 1, 2 or 6, 7 and can be partially preserved if the subsequent reactions with water (reactions 3 and 8) are not exhaustive. When the organoaluminates are produced from alkylalumoxanes (reactions 4 and 10), alkylaluminum aryloxides and alkoxides are produced in parallel with organoaluminates from admixtures of AlR_3 in the alumoxanes. These alkylaluminum aryloxides and alkoxides, by themselves, are not effective cocatalysts for metallocene complexes; see runs II-r1 and II-r2 and the data for $MeAl(OCPh_3)_2$ in part 3. On the other hand, these compounds do not interfere with the organoaluminates or alkylalumoxanes in their function as cocatalysts. Polymerization runs III-r1 and III-r8 were carried out at such low [PhOH]:[MAO] ratios that the cocatalysts in these experiments are, essentially, the mixtures of the original MAO and Me_2AlOPh. Judging by productivities of respective catalyst systems in comparison with MAO/zirconocene catalysts (runs III-r7 and III-r9, respectively), the presence of Me_2AlOPh does not affect efficiency of MAO. In contrast, the presence in MAO of even a small quantity of dimethylaluminum phenoxide with a nonhindered phenyl group reduces the efficiency of MAO by 1 order of magnitude (run III-r11 vs run III-r7).

Obviously, the efficacy of arylaluminates as cocatalysts hinges on strong steric protection of the oxygen atom in the Ph−O−Al group. The reaction product of $AlMe_3$, a nonhindered phenol, and water (cocatalyst I-M) produced an inferior cocatalyst (run II-r13). Reaction products of MAO and sterically nonhindered or partially hindered phenols were also ineffective as cocatalysts (runs III-r12−III-r14). The same conclusion is valid in the case of alkylaluminates: the products of the reaction of MAO and Ph_3COH (runs VI-r1 and VI-r2) are much more effective cocatalysts than the products of similar reactions with fenchyl alcohol (only a partially protected OH group), *tert*-butyl alcohol, or benzyl alcohol (runs VI-r4, VI-r5, and VI-r6).

Table 2 compares cocatalyst efficiency of arylaluminates prepared using the same technique (interaction of AlR_3 and PhOH followed by reaction with water) but derived from different alkylaluminum compounds and produced at different [PhOH]:[AlR_3] and [H_2O]:[Al] ratios. The main conclusions from the comparison can be formulated as follows: (1) The most effective cocatalysts (cocatalysts I-F and I-G, tested in runs II-r6 and II-r7) are oligomeric arylaluminates formed at [PhOH]:[AlR_3] and [H_2O]:[Al] ratios close to 1:1 when most compounds formed in reaction 1 are Me_2AlOPh and when nearly all $Al-CH_3$ bonds in the latter are consumed in the reaction with water (reaction 3). (2) To be an effective cocatalyst, the arylaluminate should have a significant molecular weight. Both studied "dialuminates" derived from $AlMe_3$ and DBP (cocatalysts I-D and I-E) exhibit lower activities (runs II-r4 and II-r5). (3) A comparison of polymerization results for arylaluminates derived from different AlR_3 shows that they all are active cocatalysts and that arylaluminates generated from Al-*i*-Bu_3 and Al-*n*-Oct_3 (products I-I and I-J, tested in runs II-r9 and II-r10, respectively) have activities of the same order of magnitude as the products of the same composition derived from $AlMe_3$ (runs II-r6 and II-r7). (4) Comparison of two dialuminates, one derived from DBP and another from DPP (compositions I-E and I-K, tested in runs II-r5 and II-r11, respectively), shows that the steric protection provided by the *tert*-butyl group and the phenyl group in the second and the sixth positions of the phenol moiety is similar.

Table 3 compares cocatalyst efficiency of arylaluminates prepared from MAO and PhOH at similar [PhOH]:[MAO] ratios, from 0.9 to 1.2, and tested at different [Al]:[Zr] ratios. Overall, the efficiency of these cocatalysts (runs III-r2 to III-r6) is similar to that of MAO (run III-r7). A single-component catalyst of the same composition (product IV-A) also has a similar reactivity (run V-r1).

The reaction products of MAO and sterically hindered phenols (reaction 4) are, in effect, co-oligomers containing both −Al(OPh)−O− and −Al(Me)−O− groups. Their ratio is determined by the ratio between the phenol and MAO. The results in Tables 4 and 5 show that the ratio between PhOH and MAO (all other conditions being approximately equal) has a relatively small effect on the activity of single-component catalysts: compare run V-r2 vs V-r3 for MAO-based compositions and run V-r4 vs V-r5 for MMAO-based compositions.

The results produced with IBAO and with the phenylaluminate derived from it are especially demonstrative with respect to the significance of sterically hindered phenyl groups in aryl aluminates. Pure IBAO was tested as a cocatalyst for $C_2H_4(Ind)_2ZrCl_2$ (run V-r12) in parallel with the catalyst IV-K derived from IBAO and DBMP. The former polymerization reaction was very sluggish: only ca. 0.9 g of polymer was produced after 110 min. On the other hand, the phenylaluminate derived from IBAO and DBMP (product IV-K) resulted in a catalyst system with a 5 times higher activity (run V-r11). This comparison supports the conclusion that the phenylaluminate groups, rather than the remaining alkylalumoxane groups, are the prerequisite for producing effective cocatalysts in this case.

Broadly speaking, the two processes for the synthesis of arylaluminates, one from PhOH, $AlMe_3$, and water and another from PhOH and MAO, give comparable results in terms of cocatalyst efficiency when polymerization experiments at the same [Al]:[Zr] ratios are compared: the productivity in the range of 10−35 kg/(mmol of Zr h) in runs II-r6, II-r7, and II-r9 vs the productivity in the range of 18−32 kg/(mmol of Zr h) in runs III-r2, III-r5, and III-r6. On the other hand, when efficiencies of phenylaluminates prepared from MAO and IBAO using the same phenol, DBMP, are compared (runs V-r3 and V-r11), the former obviously makes a more effective cocatalyst. These differences in reactivity can be apparently attributed to differences in the molecular weights and the cage structures of their alumoxane sources.[10,14,15,17−19]

As cocatalysts for metallocene complexes, sterically hindered organoaluminates exhibit some features characteristic of MAO,[1] such as a higher reactivity of zirconocene complexes compared to that of their Hf analogues, a higher 1-alkene copolymerization efficiency of hafnocenes compared to that of zirconocenes (catalyst IV-H vs IV-G, runs V-r7 and V-r8), strong reduction of the molecular weight with temperature (run V-r6 vs V-r7), etc.

Both in the case of MAO[1,3] and the arylaluminates in the present study, the [Al]:[Zr] ratio is an important factor determining reactivity of the catalysts. The experiments performed at higher [Al]:[Zr] ratios always resulted in a much higher catalyst productivity than the experiments with the same cocatalysts carried out at lower [Al]:[Zr] ratios: compare a decreasing level of activities in runs III-r2, III-r4, III-r3, III-r5, and III-r6; run V-r1 vs run V-r3 and run VI-r1 vs run VI-r3.

The use of arylaluminates with sterically hindered phenyl groups as cocatalysts has one practical disadvantage: when polymers prepared with them are exposed to air, they gradually acquire bright coloration due to oxidation of the phenolic moieties with the formation of quinoid structures. Alkylaluminates derived from sterically hindered alcohols do not exhibit this feature.

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Supporting Information Available: ^{13}C NMR spectra of $AlMe_3$ and $Me_2Al-O(4\text{-}Me\text{-}2,6\text{-}{}^tBu_2\text{-}C_6H_2)$ and IR spectra of DBMP, $4\text{-}Me\text{-}2,6\text{-}{}^tBu_2\text{-}C_6H_2\text{-}OH$, and its 1:1 reaction product with MAO. This material is available free of charge via the Internet at http://pubs.acs.org.

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