NMR investigations of the reactivity between zirconocenes and β-alkyl-substituted aluminoxanes

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Abstract

^{1}H and ^{13}C NMR studies of the reactions between two β-alkyl-substituted aluminoxanes obtained from the in situ reaction between Al(i-Bu)$_3$, Al(i-Oct)$_3$ and H$_2$O with two metallocenes Cp$_2$ZrCl$_2$ and Cp$_2^*$ZrCl$_2$ (Cp = cyclopentadienyl, and Cp* = pentamethylcyclopentadienyl) have been performed. The β-branched aluminoxanes were obtained from the in situ reaction between Al(i-R)$_3$ and H$_2$O at Al/H$_2$O molar ratio of 2 (R = i-Bu (TIBAO), R = i-Oct (TIOAO)). A comparison of the Cp$_2$ZrCl$_2$ and Cp$_2^*$ZrCl$_2$ reactivity with MAO, as the reference point for aluminoxanes, as well as with their parent aluminum alkyls AlMe$_3$ (TMA), Al(i-Bu)$_3$ (TIBA), and Al(i-Oct)$_3$ (TIOA) has been made. Cp$_2^*$ZrCl$_2$, because of steric hindrance, is less reactive than Cp$_2$ZrCl$_2$ towards all aluminium compounds considered. The Cp$_2^*$Zr-i-BuCl and Cp$_2^*$Zr-i-OctCl produced appear to be more stable than Cp$_2$Zr-i-BuCl and Cp$_2$Zr-i-OctCl due to the Cp* steric hindrance, which inhibits β-hydrogen eliminations. The lower reactivity of Cp$_2^*$ZrCl$_2$ along with the higher stability of the zirconium alkyls produced has allowed us to produce evidence of the greater capacity of TIOAO with respect to TIBAO for yielding alkylated ion pairs. These results explain the polymerization activities yielded by metallocenes when combined with the above aluminoxanes, that is, the Cp$_2$ZrCl$_2$ activity only with MAO, and the high polymerization activities of substituted metallocenes when β-alkyl-substituted aluminoxanes are used as cocatalysts. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminoxanes (RAlO)$_n$ with R different from methyl are of practical interest as substitutes for methylaluminoxane (MeAlO)$_n$ in the catalysis for olefin polymerization. Superior linear alkylaluminoxanes do not have suitable catalytic activities. Studies aimed at substituting methylaluminoxane (MAO), with less risky and more readily available Al cocatalysts, showed that water had some activating effect when added to AlR$_3$ different from trimethylaluminum and from linear aluminum alkyls [1]. Recent results indicated that branched β-alkyl-substituted aluminoxanes, prepared in situ from hydrolysis of the parent aluminum alkyls, are alternatives to MAO of variable effectiveness as cocatalysts depending on the metallocenes they are combined with [2–4]. We became interested in un-

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derstanding the way in which the changes in the alkyl group, which is bonded to aluminum and the changes in the kind of cyclopentadienyl ligands of metallocenes affect the cocatalytic ability of aluminoxanes. Our strategy for addressing this problem consists in studying by low-temperature ^{1}H and ^{13}C NMR spectroscopy the reactions between two β-alkyl-substituted aluminoxanes TIBAO and TIOAO with two metallocenes Cp_2ZrCl_2 and $Cp_2^*ZrCl_2$ (Cp = cyclopentadienyl, and Cp^* = pentamethylcyclopentadienyl). The β-branched aluminoxanes were obtained from the in situ reaction between $Al(i\text{-R})_3$ and H_2O at Al/H_2O molar ratio of 2 (R = i-Bu (TIBAO), R = i-Oct (TIOAO)). We chose two simple, symmetrical and nonbridged metallocenes, which greatly differ in their ster-

ics as well as in their electronics. They have been reacted with MAO, as the reference point for aluminoxanes, as well as with their parent aluminum alkyls $AlMe_3$ (TMA), $Al(i\text{-Bu})_3$ (TIBA), and $Al(i\text{-Oct})_3$ (TIOA). The MAO used has been freed from residual TMA by vacuum distillation. The TIBAO and TIOAO cocatalysts were prepared in situ at the Al/H_2O ratio of 2 (the mole ratio at which they give the highest catalytic activity) [2–5]. TIBAO and TIOAO, the reaction products obtained at $Al/H_2O = 2$ (Eq. 1), are represented as dimers, although they are probably mixtures of aluminium alkyls and different oligomers, associated in more complex structures. TIOAO is reported to have the advantage with respect to TIBAO of giving more stable solutions, over a period of time.

Eq. 1

(1)
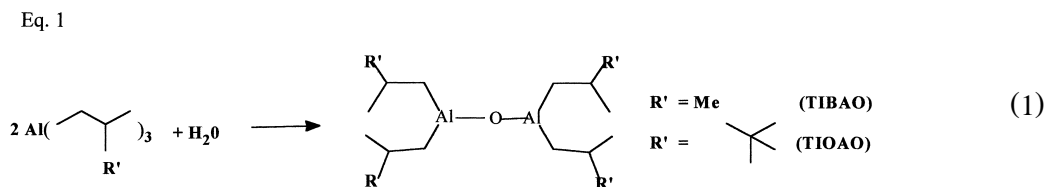
2. Experimental

All manipulations were performed under dry nitrogen atmosphere by using a glove-box or Standard Schlenk technique. Materials: MAO, $Al(i\text{-Bu})_3$, were all purchased from WITCO. $Al(i\text{-Oct})_3$, TIBAO and TIOAO were synthesized as already reported [5]. For the NMR studies, 30% solutions of MAO in toluene (WITCO) were used after removing all volatiles and drying the resulting powder in vacuum (12 h, room temperature, 0.1 mm Hg). Cp_2ZrCl_2 and $(Me_5Cp)_2ZrCl_2$ were purchased from Aldrich. *rac*-Ethylenebis-(indenyl)$ZrCl_2$ (*rac*-EBIZrCl$_2$) was purchased from WITCO. *rac*-Ethylenebis-(4,7-dimethyl-indenyl)$ZrCl_2$ (*rac*-EBDMIZrCl$_2$) was synthesized following the method reported in the literature [6]. Toluene-d$_8$

was distilled under nitrogen from sodium benzophenone ketyl.

2.1. NMR analysis

All the ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM-270 spectrometer operating at 270 MHz (^{1}H) and at 67.89 MHz (^{13}C) in the PFT mode. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H NMR signals and to ^{13}C NMR signals of the deuterated toluene-d$_8$ solvent, respectively. NMR probe temperatures were measured using an anhydrous methanol sample $\Delta\nu$ (MeOH).

In all ^{1}H NMR spectra, the pulse width was 4.0 μs. Pulse repetition time was 11.72 s. Dwell time of 105 μs was used with 16 K of computer memory for the interferogram. In all ^{13}C NMR

spectra, the pulse width was 5.0 μs. CPD was used to remove $^{13}C–^{1}H$ couplings, the pulse angle was 90°C, the pulse repetition time was 10.46 s. Dwell time of 28 μs was used with 16 K of computer memory for the interferogram.

In a drybox under a nitrogen atmosphere, a 5-mm NMR tube was charged with approximately 0.5 mmol of zirconocene complex and 0.5 ml toluene-d_8. The tube was then capped with a septum rubber cap, removed from the drybox, and cooled to a given temperature. A known amount of aluminum derivative as toluene-d_8 solution was syringed into the cooled NMR tube via a gas-tight microsyringe and the septum wrapped with parafilm. The tube was shaken briefly and transferred to the precooled NMR probe and the spectra were obtained.

2.2. Polymerization

Ethylene polymerization was performed in a 2.3-l stainless-steel autoclave purged with ethylene. A total of 1.0 l of *n*-hexane and 9.6 bar of ethylene were introduced, and the temperature was increased to 80°C. The cocatalyst and the metallocene in toluene solution (0.1–0.5 mg in 5 ml), were introduced in a 10-ml Schlenk tube; stirred for 5 min and injected into the autoclave

through a stainless steel vial with ethylene over-pressure. The total pressure was maintained constant by continuously feeding ethylene. After 1-h polymerization at 80°C, the reactor was degassed, the polymer was recovered by filtration and dried in vacuum at 70°C. Intrinsic viscosity of polymers was measured in tetrahydronaphthalene at 135°C.

3. Results and discussion

3.1. Ethylene polymerization with different cocatalysts

The reactivity for ethylene polymerization of unbridged methyl-substituted zirconocenes, as well as of a great number of bridged metallocenes, with a broad range of symmetries and substitution degrees, has been tested for polymerization by using different AlR_3/H_2O mixtures as cocatalysts [2–5]. The comparison of the catalytic activity of a selection of metallocenes, which differ greatly with regard to the electronic density on the metal, is reported in Fig. 1.

The simplest Cp_2ZrCl_2, as was already known, is highly active only with MAO and
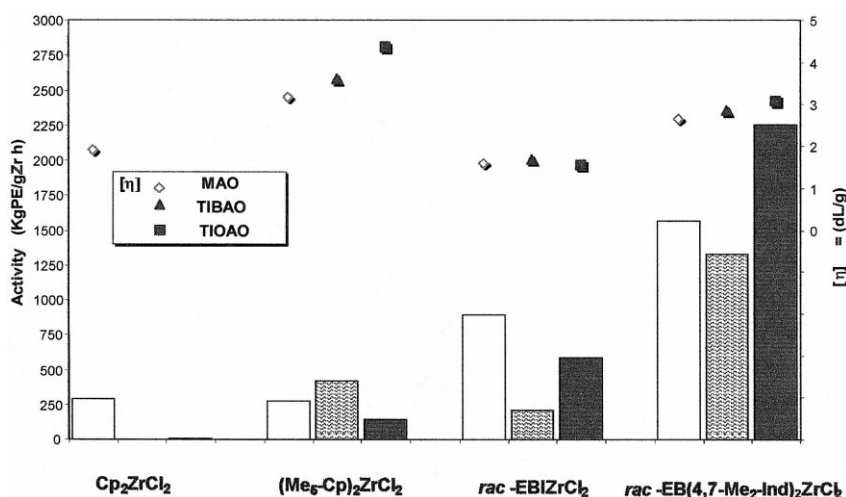

Fig. 1. Polymerization conditions: 2.3-l stainless-steel reactor; Hexane, 1 l; $pP_E = 9.6$ bar; $T = 80°C$; [Zr] = 0.5–3.4 × 10^{-6} M; [Al]:[Zr] = 5000 mol/mol, $t = 60$ min.

AlMe$_3$/H$_2$O mixtures; only TIOAO, among the β-alkyl-substituted aluminum derivatives, shows a little activity. Cp$_2^*$ZrCl$_2$ yields remarkable polymerization activity with β-branched aluminum alkyl–water mixtures also.

As to the catalytic performances in the presence of the two C$_2$ ethane bridged zirconocenes *rac*-ethylenebis-1-indenyl zirconium dichloride (*rac*-EBIZrCl$_2$) and *rac*-ethylenebis(4,7-dimethyl-1-indenyl)zirconium dichloride (*rac*-EBDMIZrCl$_2$) with different aluminoxanes the classical *rac*-EBIZrCl$_2$ yields very high activity when TIOAO is used. This activity is greater than that of TIBAO, although the highest polymerization activity is obtained when MAO is used as cocatalyst. The *rac*-EBDMIZrCl$_2$ has excellent polymerization activity with almost all the aluminoxanes considered here, due to the presence of two electron-releasing methyl substituents in 4 and 7 positions. Worth of note is that TIOAO gives polymerization activity notably higher than that yielded by MAO.

This comparison clearly demonstrates the strong differences in polymerization activity given by different cocatalysts, which do not seem to sensibly affect polymer molecular weights. The presence of electron-releasing groups on Cp ligands, which increase electron density at the metal center surely contributes to their more or less great catalytic activity [6,7], however, it does not explain the impressive variations in their catalytic activity when substituting MAO for TIBAO and TIOAO.

3.2. NMR studies of reaction equilibria between metallocenes and cocatalysts

Our strategy for understanding the way in which the nature of the alkyl group bonded to aluminum and the type of ancillary π ligands of metallocenes affect the cocatalytic ability of aluminoxanes consists in studying the reactions between metallocenes and aluminoxanes by low-temperature ^{1}H and ^{13}C NMR spectroscopy. The role of MAO cocatalyst in metallocene-based polymerization consists in alkylat-

ing the metallocene, and in generating and stabilizing the ion pair active for polymerization. During our previous NMR studies of the reactions between very simple titanocenes and zirconocenes and MAO, we have got direct evidence of the alkylation reaction as well as of the ion pair formation [8–10].

We have undertaken a study to elucidate the nature of the species produced from the reactions between two metallocenes (Cp$_2$ZrCl$_2$ and Cp$_2^*$ZrCl$_2$) and two β-alkyl-substituted aluminoxanes TIBAO and TIOAO, prepared in situ according to Eq. 1, by variable temperature ^{1}H and ^{13}C NMR spectroscopy. The reactions with MAO, taken as the reference point for aluminoxanes, and the aluminum alkyls, from which aluminoxanes derive, have been studied as well.

The reaction equilibria were studied at temperatures ranging from 203 to 313 K. Al/Zr ratios were varied from 1 to 60. The reaction products have been assigned by comparing their Cp chemical shifts with those of the species assigned in previous ^{13}C NMR studies of isotopically enriched Cp$_2$Zr^{13}CH$_3$Cl and MAO catalytic systems [11]. We report only results obtained at Al/Zr mole ratio of 10 and at two temperatures.

The chemical shifts and the related amounts of reaction products obtained by reacting Cp$_2$ZrCl$_2$ with all the aluminoxanes and aluminum alkyls considered for the present study at 256 K and at the Al/Zr mole ratio of 10 are compared in Table 1. TIBA and TIBAO reaction products have chemical shifts, which are similar to the MAO non-ionized complex and which are very similar to each other. While in the presence of TIOAO, we observe two Cp resonances, which are shifted downfield with respect to those of the alkylated complex obtained with TIOA, which indicates that there is a partial positive charge on the zirconium.

The reactions with TIBA, TIBAO, TIOA and TIOAO are rather more complex than those with MAO and TMA. In general, in the presence of β-alkyl-substituted aluminum compounds, no starting zirconocene remains unre-

Table 1
Cp_2ZrCl_2 reaction products at 256 K[a]

Cocatalyst	^{13}C NMR (δ)[b] (Cp)	Zirconocene complex[c]	mol%
TMA	113.07	$Cp_2ZrMeCl \cdot A$	69
	116.06	Cp_2ZrCl_2	31
MAO	113.19	$Cp_2ZrMeCl \cdot A$	40
	114.57	$Cp_2ZrMe^+ Cl \cdot A^-$	31
	116.31	Cp_2ZrCl_2	17
TIBA	113.20	$Cp_2Zr(i\text{-}Bu)Cl \cdot A$	19
TIBAO	113.28	$Cp_2Zr(i\text{-}Bu)Cl \cdot A$	62
TIOA	112.98	$Cp_2Zr(i\text{-}Oct)Cl \cdot A$	6
TIOAO	113.24	$Cp_2Zr(i\text{-}Oct)^{\delta+} Cl \cdot A^{\delta-}$	10
	113.41		9

[a] Solvent: toluene-d_8; [Zr] = 0.07 M; [Al]:[Zr] = 10.

[b] ^{13}C NMR spectra were recorded in toluene-d_8 on a Bruker AM 270 spectrometer. Chemical shifts are referenced to ^{13}C NMR signal (δ = 20.52) of the deuterated toluene-d_8 solvent.

[c] A = cocatalyst.

acted. Soon after the alkylated species is formed, it starts to decompose. In all of them, we observe the formation of several types of decomposition products of the alkylated zirconocenes, and for this reason, the total amount of the relative mole percentage of the reported reaction products does not reach 100%. On raising the temperature and the Al/Zr ratio, they tend to be transformed into a single species in both the two β-alkyl-substituted systems. Worthy of note is that the decomposition process of the alkylated species is less favored in the presence of aluminoxanes, than in the presence of aluminumalkyls. Irreversible decomposition has been recently observed in the reactions between TIBA and Cp_2ZrCl_2 [12].

At a temperature as high as 313 K both β-alkyl-substituted aluminum alkyls TIBA and TIOA react completely with Cp_2ZrCl_2 and the Zr-alkyls formed undergo decomposition probably through β-hydrogen elimination to yield 100% of one decomposition product (^{13}C NMR: Cp ∼ 104 ppm). On the basis of the ^{1}H NMR data, this compound seems to be a neutral dihydride, of the type characterized by Shoer and Gell [13], which should be inactive for polymerization. Not even in the presence of TIBAO do any alkylated species remain. Of the two

β-alkyl-substituted aluminoxanes, TIOAO is the only aluminoxane, which allows 16% of the alkylated species to remain.

Differences in Cp_2ZrCl_2 reactivity toward MAO and β-alkyl-substituted aluminoxanes are summarized in Scheme 1. TIOAO behavior, besides some quantitative difference, is similar to that of TIBAO.

The results obtained from the present NMR study of Cp_2ZrCl_2 reactivity can be summarized as following:

1. The ion pair active for polymerization is present only in the presence of MAO as cocatalyst.
2. All the β-alkyl-substituted Al-compounds prevailingly yield decomposition products, which derive from the alkylated zirconocenes and which are inactive for polymerizations.
3. TIOAO, unlike TIBAO, allows a small amount of the alkylated species not to decompose.

The reactivity of per-methylated $Cp_2^*ZrCl_2$ with TMA and MAO, TIBA and TIBAO, TIOA and TIOAO has been studied also. In Table 2, ^{13}C NMR data and tentative assignments of mono-alkylated products and ion pairs obtained by reacting at 256 and 313 K the permethylated
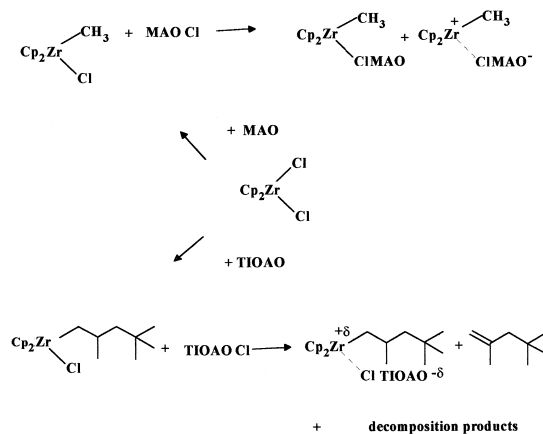
Scheme 1.

Table 2
$Cp_2^* ZrCl_2$ reaction products at 256 and 313 K[a]

Cocatalyst	Zirconocene complex[b]	^{13}C NMR $(\delta)^c$ (Cp^*)		mol%	
		256 K	313 K	256 K	313 K
/	$Cp_2^* ZrCl_2$	123.66			
TMA	$Cp_2^* ZrMeCl \cdot A$	120.33	120.51	19	20
	$Cp_2^* ZrCl_2$	123.66	123.92	81	80
MAO	$Cp_2^* ZrMe^+ Cl^- A^-$	120.60	121.07	19	29
	$Cp_2^* ZrCl_2$	123.70	124.40	81	71
TIBA	$Cp_2^* ZrCl^+ ClA^-$	125.14	124.90	100	100
TIBAO	$Cp_2^* Zr(i\text{-}Bu)^{\delta+} Cl \cdot A^{\delta-}$	121.24	120.93	2	14
		121.47	121.22	2	8
	$Cp_2^* ZrCl^+ ClA^-$	125.11	124.57	96	78
TIOA	$Cp_2^* Zr(i\text{-}Oct)^{\delta+} ClA^{\cdot\delta-}$	120.89	120.72	8	16
	$Cp_2^* ZrCl^+ ClA^-$	124.85	124.69	92	84
TIOAO	$Cp_2^* Zr(i\text{-}Oct)^{\delta+} Cl \cdot A^{\delta-}$	120.92	120.29	30	11
			120.58		30
	$Cp_2^* ZrCl^+ ClA^-$	124.69	124.69	70	59

[a] Solvent: toluene-d_8; [Zr] = 0.07 M; [Al]:[Zr] = 10.

[b] A = cocatalyst.

[c] ^{13}C NMR spectra were recorded in toluene-d_8 on a Bruker AM 270 spectrometer. Chemical shifts are referenced to ^{13}C NMR signal (20.52) of the deuterated toluene-d_8 solvent.

$Cp_2^* ZrCl_2$ with all the aluminium alkyls and aluminoxanes are listed.

Chemical shifts of methyl substituents on Cp are not greatly influenced by the presence of cocatalysts, and they have not been reported here. Differences in Cp chemical shifts of related species obtained either in the presence of an aluminoxane or of its parent aluminum alkyl are rather small and they are smaller than differences we observed in $Cp_2 ZrCl_2$ reaction products.

The downfield shifts of $Cp_2^* ZrCl_2$ resonances observed in the presence of TIBA and TIBAO, TIOA and TIOAO with respect to the starting $Cp_2^* ZrCl_2$ indicate that there is a positive charge on zirconium, and that it is ionized. This seems to indicate that β-substituted aluminium alkyls and related aluminoxanes have a greater capability of abstracting a chlorine with respect to MAO. Moreover, the Cp^* permethylation causes steric hindrance, which partially reduces the alkylation reactions with respect to the unsubstituted Cp. Electronic effects also reduce $Cp_2^* ZrCl_2$ reactivity. 81% of the starting complex is not alkylated at 256 K, either with TMA or with MAO. In contrast only 31% and

17% of $Cp_2 ZrCl_2$, respectively, did not undergo alkylation reaction under the same conditions (Table 1). These results are in accordance with the lower reactivity of $Cp_2^* ZrCl_2$ towards TMA reported by Beck and Brintzinger [12]. The authors explained their findings on the basis of the increased electron density at the Zr center caused by the presence of methyl groups of the Cp ligands. 100% of $Cp_2^* ZrCl_2$ in the presence of TIBA and 96% in the presence of TIBAO is not alkylated, although as we have already pointed out, it is ionized. What is worth noting is that, of all the aluminoxanes, TIOAO produces the greatest amount of alkylated ion pairs. TIOAO seems to have the greatest capacity for stabilizing the ion pair. No decomposition reactions are observed here.

At 313 K, the reactivity is analogous to that observed at lower temperature (Table 2). However, TIOAO yields two alkylated ion pairs, one of them has a chemical shift similar to the alkylated species produced by TIOA. Furthermore, differences in reactivity between TIBAO and TIOAO tend to diminish. In this range of temperatures, TIBAO reactivity increases four times while the increase in TIOAO reactivity is

Scheme 2.
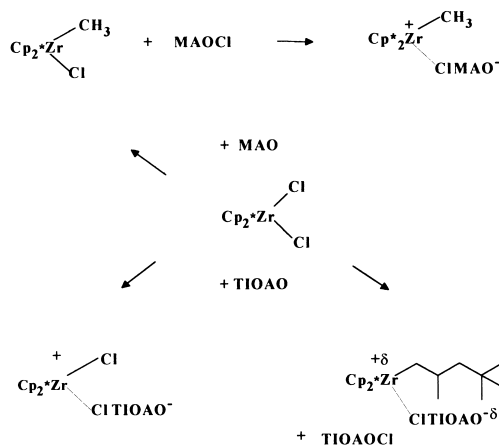
only 0.25. In addition, almost no decomposition of the alkylated species is observed at 313 K.

The Cp^* steric hindrance, which inhibits β-hydrogen elimination during olefin polymerization probably inhibits β-hydrogen elimination and decomposition of alkylated zirconocene ion pairs. The results obtained from the present NMR study of $Cp_2^* ZrCl_2$ reactivity, represented in Scheme 2, can be summarized as following:

1. Decomposition of alkylated products are not observed.
2. All the aluminoxanes have a better alkylating capacity with respect to related β-alkyl-substituted Al-alkyls.
3. Cl^- abstraction from $Cp_2^* ZrCl_2$ decreases in the following order: TIOAO ≈ TIBAO > MAO.
4. Aluminoxane capacity for producing the alkylated ion pair decreases in the following order: TIOAO > MAO > TIBAO.

4. Conclusions

Our NMR investigations of the reactivity between $Cp_2 ZrCl_2$ and $Cp_2^* ZrCl_2$ and β-branched aluminoxanes allowed us to identify the species formed and to find a rationale for the polymerization activities exhibited by the different cocatalysts. Our data show that the incapacity of isobutylaluminoxane in activating $Cp_2 ZrCl_2$ is due to the instability of the alkylated species such as $Cp_2 Zr$-i-BuCl, which tend to decompose and to form inactive neutral dihydrides. The lower reactivity of $Cp_2^* ZrCl_2$ along with the fact that Cp^* steric hindrance inhibits β-hydrogen elimination and decomposition of zirconium alkyls has allowed us to produce evidence of the greater capacity of isooctylaluminoxane with respect to isobutylaluminxane of yielding the alkylated ion pairs, which may be responsible for polymerization activity. In addition, TIBAO and TIOAO are Lewis acids strong enough to abstract Cl^- ions from $Cp_2^* ZrCl_2$.

In conclusion, the changes in the alkyl group bonded to aluminum of aluminoxanes affect the cocatalytic ability of aluminoxanes by influencing the active species formation, that is, the alkylating power and the capability of stabilizing the ion pairs. Changes in the metallocene ligands affect the reactivity towards the aluminoxanes and the stability of the alkylated species. Moreover, the reactivity of each metallocene–aluminoxane catalytic pair is differently affected by temperature.

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