

The negative role of chloride counter-anion in the activation process of zirconocene dichloride by methylaluminoxane

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Abstract

The different elementary steps in the *rac*Et(Ind)₂ZrCl₂ activation process by commercial methylaluminoxane (MAO) are studied by UV–VIS spectroscopy technique and correlated with hexene polymerization kinetics. After monomethylation of the zirconocene dichloride ($\lambda = 396$ nm), abstraction of Cl ligand by MAO at low Al:Zr ratios (Al:Zr = 150) yields tight ion pairs, [racEt(Ind)₂ZrMe]⁺, [MAOCl][−] with an absorption band centered at $\lambda = 440$ nm, inactive towards hexene polymerization. Addition of MAO in large excess (Al:Zr = 2000) is therefore required to form active species identified as TMA separated ion pairs, [racEt(Ind)₂Zr⁺(μ -Me)₂AlMe₂], [MAO-Cl][−] ($\lambda = 470$ nm). The activation of *rac*Et(Ind)₂ZrMe₂ by MAO reveals much easier and is complete at low Al:Zr ratios (Al:Zr = 150), yielding directly active ion pairs [racEt(Ind)₂ZrMe]⁺, [MAOMe][−], absorbing at $\lambda = 439$ nm. These data underline the negative role of [MAOCl][−] as a counter-anion in the activation process of zirconocene dichloride precursor for olefin polymerization. In the same conditions, the use of TMA-depleted MAO allows the direct formation, at low Al:Zr ratio, of active tight ion pairs ($\lambda = 440$ nm). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocene; Zirconocene dichloride; Methylaluminoxane; Trimethylaluminium; UV–VIS spectroscopy

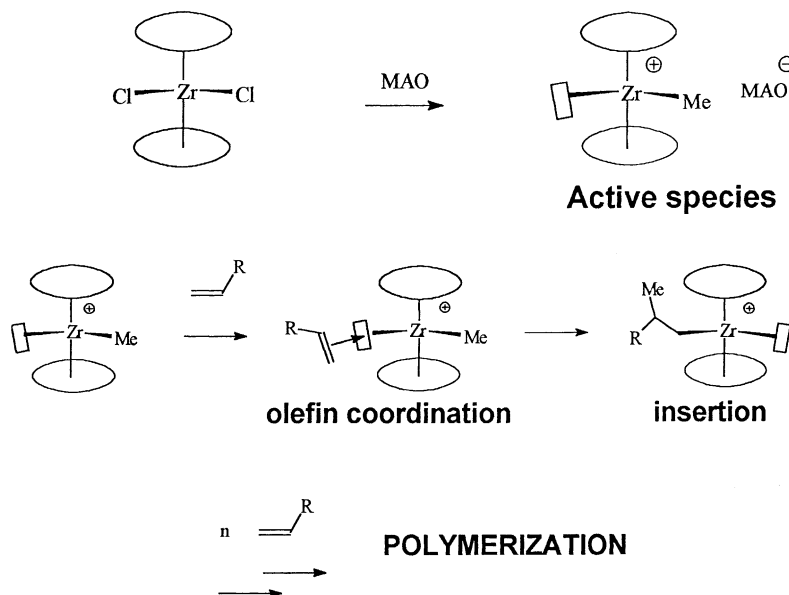
1. Introduction

The activation pathway of metallocenes by methylaluminoxane (MAO) is still a question that puzzles the scientific community involved in olefin polymerization. Although the main elementary steps yielding “cationic” metallocene active species upon addition of MAO onto metallocene derivatives are now quite well-established (Scheme 1), several pending questions remain: the need of large amounts of MAO (generally Al:Met \geq 2000) to obtain high polymerization activity, the exact nature of the species (ion pairs, sol-

vated ion pairs, loose ion pairs, free ions, etc.) including the nature and role of the [MAO][−] counter anion that may compete with the incoming monomer during polymerization, are important aspects of the activation process still under debate.

A series of spectroscopic studies have already been performed to further understand the activation mechanism of zirconocene derivatives by MAO but it has to be admitted that a present limitation to the understanding still comes from the high amount and complex structure of MAO making quite difficult to precisely characterize the active catalytic species. NMR spectroscopy was found a useful technique to investigate these systems. Tritto and co-workers were able to detect by ¹³C NMR several intermediate species formed by the reaction of Cp₂ZrMe₂ with MAO. However,

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Scheme 1. General activation mechanism of dichlorozirconocene by MAO.

the necessity to use relatively high zirconium concentrations ($[\text{Zr}] > 0.01 \text{ M}$) and low MAO:Zr ratios ($\text{Al:Zr} \leq 40$) [1] makes that the observed species are not representative of those present in highly active systems. The high concentration of MAO required to form such polymerization active species remains a strong limitation for their direct characterization by NMR and evidences for the generally admitted cation-like alkyl zirconocene structure have been obtained mainly from analogies found with boron-type activator/metallocene systems that work at stoichiometric ratio [2–4]. Recently, limits of the NMR technique could be shifted to lower zirconium concentrations ($[\text{Zr}] \geq 4.5 \times 10^{-4} \text{ M}$) and higher Al:Zr ratios ($\text{Al:Zr} = 4000$) close to those used for highly active polymerization systems [5]. This was achieved at very low temperature ($\leq -25^\circ\text{C}$) by using Cp_2ZrMe_2 with ^{13}C -labeled methyl groups. Interestingly, the formation of a hetero-bimetallic complex between Cp_2ZrMe_2 and TMA has been identified as the active species in such catalytic system.

UV–VIS spectroscopy was found to be a very useful and complementary technique, since it is possible to follow the different transformation steps of metallocene species at very low zirconium concentration ($\approx 10^{-5} \text{ M}$) and high Al:Met ratio (up to 5000), much

closer to the polymerization conditions [6–9]. Indeed, aromatic ligands directly linked to the transition metal yield to the formation of absorption bands in the range 300–800 nm, characteristics of ligands to metal charge transfer (LMCT) and which express the electronic change on the metal. In the meantime, MAO does not show any absorption in this domain and is totally transparent allowing direct zirconocene observation even at very high Al:Zr ratios. We already reported a series of UV–VIS investigations focused on the activation process of zirconocene dichloride by MAO [6–8]. Depending on the Al:Zr ratio, the formation of several species could be readily shown by the UV–VIS absorption band changes. However, the exact reason for the need of very large amount of MAO to get the final polymerization active species could not be clearly elucidated.

In this paper, we report our last understandings on the MAO activation process of zirconocene dichloride with a special focus on the role of the extracted chlorine ligands and of TMA; spectroscopic and kinetic observations lead to evidences for their direct influence on the retarded formation of active species, and on the necessary huge amount of MAO required for activation.

2. Experimental

2.1. Materials

racEt(Ind)₂ZrCl₂ and trimethylaluminium (TMA) (97% or 2 M in toluene) were purchased from Sigma Aldrich Chimie, Saint Quentin Fallavier, France. B(C₆F₅)₃ (minimum 97%) and [C₆H₅N(CH₃)₂H]⁺ [B(C₆F₅)₄]⁻ were purchased from Strem Chemicals, Inc., Bischheim, France. All zirconocenes and boron derivatives were kept in a glove box under nitrogen. MAO (10% w/w in toluene, containing 30–35% TMA, CK Witco GmbH, Bergkam, Germany) and TMA were used as received, following conventional safety procedures.

Toluene (Mallinckrodt Baker B.V., Deventer, Holland) was first dried over calcium hydride and distilled. Then a small amount of styrene (99%, Sigma Aldrich Chimie) and *sec*-BuLi (1.3 M in cyclohexane, Fluka from Sigma Aldrich Chimie) were added to the toluene and stirred until the characteristic red color of polystyryl anion was obtained, meaning that all moistures have been consumed. The desired volume of toluene was finally distilled just before use. For zirconocene synthesis, a last distillation over sodium mirror was done.

Ether (Baker) was dried over Na/benzophenone and distilled under vacuum. All solvents were stored in glass apparatus fitted with PTFE stopcocks.

racEt(Ind)₂ZrMe₂ was synthesized following literature procedure [10]. About 0.7 ml of MeLi (1.6 M, Fluka from Sigma Aldrich Chimie) was added at -78°C to 0.205 g of *racEt(Ind)₂ZrCl₂* in ether solution. After stirring 30 min, the medium was raised to room temperature and stirred for 3 h. After solvent evaporation, the solid residue was dissolved in toluene and the solution was filtered to remove insoluble LiCl. Cooling to -78°C leads to formation of pale yellow crystals of *racEt(Ind)₂ZrMe₂* characterized by NMR; (Me (s, 6H) $\delta = -0.96$ ppm; Et (m, 4H) $\delta = 2.57$ – 2.95 ppm; Cp (d, 2H) $\delta = 5.67$ ppm (d, 2H) $\delta = 6.42$ ppm; Ph (m, 8H) $\delta = 6.82$ – 7.33 ppm).

TMA-depleted MAO was prepared by a thermal treatment of commercial MAO. After solvent removal at room temperature under reduced pressure, residual off-white gel was maintained at 80°C under reduced pressure for several hours to eliminate TMA (present in 30–35 mol% of total aluminum in commercial MAO

solution) yielding a white powder which was kept in a glove box. Estimation of TMA by complexation with PPh₃ followed by ³¹P NMR showed that few amount of TMA still remain (7.2 mol%) even after such radical treatment [11]. Nevertheless, the peak attributed to TMA is no more observed in ¹H NMR spectrum.

2.2. Instrumentation

UV–VIS absorption spectra were recorded on a Varian Cary 3E UV–VIS spectrometer in a quartz cell (0.5 cm path length) attached to the glass reactor fitted with PTFE stopcocks.

2.3. Polymerization

Kinetics were followed by dilatometry recording the volume contraction of the polymerization solution in a 16 ml dilatometer. Reaction temperature was kept constant at 20°C, toluene was used as a solvent, [hexene] = 1 mol l⁻¹.

3. Results and discussion

Activation of *racEt(Ind)₂ZrCl₂* by MAO has been already extensively studied by UV–VIS spectroscopy [6]. The formation of different zirconocene species when varying the Al:Zr ratio was successively observed from the changes in the UV–VIS absorption spectra. Briefly, addition of small amounts of MAO (Al:Zr ratios up to 30) onto *racEt(Ind)₂ZrCl₂* ($\lambda_{\max} = 427$ nm, Fig. 1A, curve a), leads to the formation of a new species with an absorption band located at 396 nm (Fig. 1A, curve e). On the basis of the molecular orbital theory, the hypsochromic shift was interpreted by an increase of the electronic density on the metal atom corresponding to the substitution of one Cl ligand by a methyl group, as discussed later in this paper.

Further addition of MAO, equivalent to ratios 30 < Al:Zr < 150, leads then to a reverse bathochromic shift of the zirconocene main absorption band from 396 to 440 nm (Fig. 1B, curve j) corresponding to an important decrease of the electronic density on the metal, as it could be expected in a cationization process of the metallocene resulting from the abstraction of one of its X ligands. However, it was checked

that the species absorbing at 440 nm were inactive towards hexene polymerization. Indeed, this is after the addition of much larger amounts of MAO (Al:Zr > 2000) that activation towards olefin polymerization takes place. This activation step is correlated to a second bathochromic shift of the metallocene absorption band from 440 to 470 nm (Fig. 1B, curve m). The presence of a second isosbestic point shows that active species are formed in the place of the inactive ones.

To better identify the structure of metallocene species located at 440 and 470 nm and to understand the parameters which govern the activity of the different electron deficient species towards olefin poly-

merization, a series of complementary experiments was carried out varying the metallocene and activator structures. In that respect, activation of dimethylated zirconocenes $racEt(Ind)_2ZrMe_2$ by weakly coordinating boron-type anions was first implemented.

The synthesis of $racEt(Ind)_2ZrMe_2$ was achieved following literature reports by reaction of MeLi onto the dichloride derivative. Insoluble LiCl was removed by careful filtration to avoid the presence of any trace of chloride. Note that dimethylzirconocene is characterized by an absorption band located at 367 nm which is clearly distinct from the one observed for the derivative formed by addition of small amount of MAO onto $racEt(Ind)_2ZrCl_2$ ($\lambda_{max} = 396$ nm). This allows us to attribute the 396 nm band to the monomethylated, monochlorinated derivative. The observed direct bathochromic shift of the 396 nm band upon further addition of MAO therefore supports the direct chloride abstraction from the monomethylated derivative by MAO to yield electron deficient zirconium. It is worth noting that the formation of $racEt(Ind)_2ZrCIME$ is also observed after addition of few equivalents of trimethylaluminium (TMA, Al:Zr = 6). However, in this case, further addition of TMA (Al:Zr = 3000) leads to a second hypsochromic shift of the main band down to $\lambda = 367$ nm in agreement with the formation of the dimethylated compound. The latter signal remains even after addition of large amount of crude TMA, in agreement with the ineffectiveness of TMA to act as ionizing agent for dimethylzirconocene.

The activation process of $racEt(Ind)_2ZrMe_2$ by $[B(C_6F_5)_4]^-$, $[^+NHMe_2Ph]$ was followed in the same way by UV–VIS spectroscopy (Fig. 2). Upon addition of the boron derivative the UV–VIS spectrum of $racEt(Ind)_2ZrMe_2$ shows a direct bathochromic shift of the 367 nm band to 421 nm through formation of an isosbestic point. Conversion is completed after addition of a stoichiometric amount of $[B(C_6F_5)_4]^-$, $[^+NHMe_2Ph]$ with respect to zirconocene as noticed in previous NMR spectroscopic studies [2–4]. The addition of larger amount of boron derivative does not yield any further shift of the absorption band.

It is worth noting that species located at 421 nm are highly active towards hexene polymerization (1×10^6 kg PH mol $_{Zr}^{-1}$ h $^{-1}$), approximatively as active as the ones absorbing at 470 nm in the $racEt(Ind)_2ZrCl_2$ /MAO system for Al:Zr = 2000 (1.3×10^6 kg PH mol $_{Zr}^{-1}$ h $^{-1}$). Accordingly, these

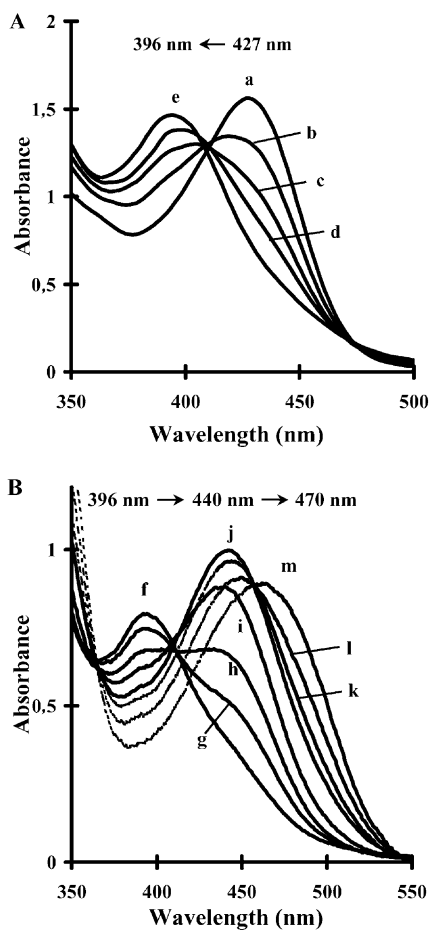


Fig. 1. UV–VIS absorption spectrum of $racEt(Ind)_2ZrCl_2$ in toluene at 20°C in the presence of increasing amounts of MAO. (A) Al:Zr = 0 (a); 4 (b); 6 (c); 8 (d); 15 (e). (B) Al:Zr = 24 (f); 32 (g); 40 (h); 56 (i); 120 (j); 200 (k); 400 (l); 2000 (m).

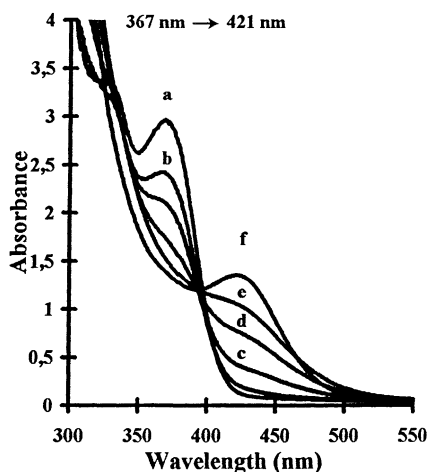


Fig. 2. UV–VIS absorption spectrum of *racEt(Ind)₂ZrMe₂* in toluene at 20°C in the presence of increasing amounts of $[\text{HNMe}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. B:Zr = 0 (a); 0.2 (b); 0.25 (c); 0.5 (d); 0.7 (e); 1 (f).

results lead to the conclusion that species exhibiting an UV–VIS absorption band at 421 nm corresponds to the active “cation-like” alkyl zirconocene species [2,12].

Activation of isolated *racEt(Ind)₂ZrMe₂* by MAO also takes place indicating that MAO can directly abstract a methyl group. Interestingly, cationization is already complete at low Al:Zr ratios (Al:Zr = 150), yielding species absorbing at 439 nm, a value very close to the one obtained in the case of dichlorozirconocene activation. However, contrarily to those issued from *racEt(Ind)₂ZrCl₂/MAO*, these species exhibit high activity towards hexene polymerization ($1.2 \times 10^6 \text{ kg PH mol}_{\text{Zr}}^{-1} \text{ h}^{-1}$). These results suggest a poisoning effect of the extracted chloride ligand in the *racEt(Ind)₂ZrCl₂/MAO* system, at low MAO:Zr ratios.

To further characterize the distinct electron deficient species with an absorption band centered at 440 and 470 nm, the cationization of *racEt(Ind)₂ZrCl₂* was carried out in the presence of a TMA-depleted MAO.¹ The activation steps of *racEt(Ind)₂ZrCl₂* by TMA-depleted MAO were followed by UV–VIS

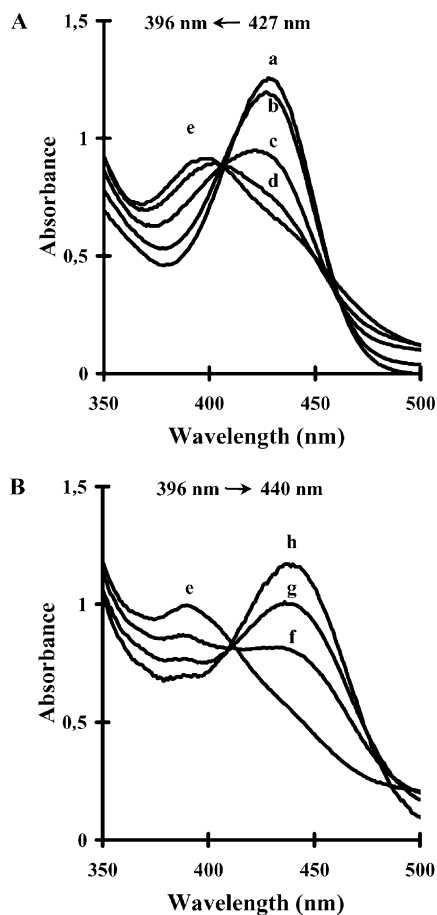


Fig. 3. UV–VIS absorption spectrum of *racEt(Ind)₂ZrCl₂* in toluene at 20°C in the presence of increasing amounts of “TMA-free” MAO. (A) Al:Zr = 0 (a); 4 (b); 8 (c); 12 (d); 15 (e). (B) Al:Zr = 15 (e); 25 (f); 35 (g); 200 (h).

spectroscopy. The formation of different species with increasing the Al:Zr ratio was observed in agreement with our previous data (Fig. 3). Formation of *racEt(Ind)₂ZrClCH₃* is first observed at low Al:Zr ratio as indicated by the band shift from 427 to 396 nm (Fig. 3A, curve e). As expected, the addition of larger amounts of TMA-depleted MAO (Al:Zr = 150–200) leads then to the formation of electron deficient species absorbing at 440 nm (Fig. 3B).

However, contrarily to data obtained from *racEt(Ind)₂ZrCl₂* activated by commercial MAO, species located at 440 nm reveals highly active towards hexene polymerization, stressing the importance of the

¹ After thermal treatment of commercial MAO (see Section 2), the sharp single peak attributed to TMA ($\delta = -0.38 \text{ ppm}$) is no more detected in ^1H NMR spectrum.

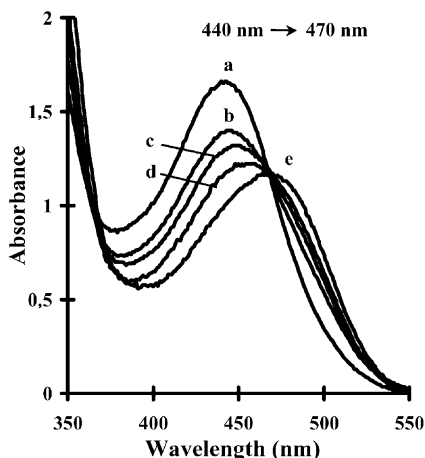
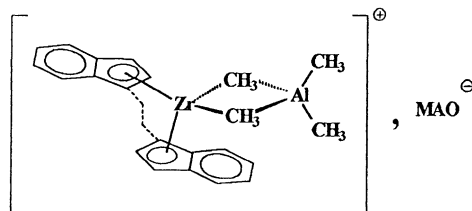


Fig. 4. UV–VIS absorption spectrum of species absorbing at 440 nm resulting from addition of “TMA-free” MAO (Al:Zr = 300) on *rac*Et(Ind)₂ZrCl₂ in toluene at 20°C in the presence of increasing amounts of TMA. TMA:Zr = 0 (a); 90 (b); 360 (c); 780 (d); 1000 (e).

associated activator structure on the activity. Indeed, activity observed at Al:Zr = 200 with TMA-depleted MAO (1.5×10^6 kg PH mol_{Zr}⁻¹ h⁻¹) is equivalent to the one found for Al:Zr = 2000 with commercial MAO. No further bathochromic shift of the metallocene band and no activity change was observed after addition of larger amounts of TMA-depleted MAO (Al:Zr = 3000). These observations point out important changes in MAO structure upon thermal treatment [13], as discussed later in this paper. Finally, TMA addition onto active species located at 440 nm obtained from TMA-depleted MAO was investigated. As shown Fig. 4, the presence of large amount of TMA leads to the formation of new species with a UV–VIS absorption band centered at 470 nm, likely corresponding to active species formed with commercial MAO. In the present case, however, no significant change in catalytic activity was observed between the “TMA-free” system absorbing at 440 nm (1.5×10^6 kg PH mol_{Zr}⁻¹ h⁻¹) and the corresponding one with added TMA at 470 nm (1.3×10^6 kg PH mol_{Zr}⁻¹ h⁻¹).

The results obtained with “TMA-free” systems, i.e. [B(C₆F₅)₄]⁻, [⁺NHMe₂Ph]/*rac*Et(Ind)₂ZrMe₂ and TMA-depleted MAO/*rac*Et(Ind)₂ZrCl₂, are consistent with the formation of “TMA-free” active species absorbing at 420–440 nm, whereas those with an ab-

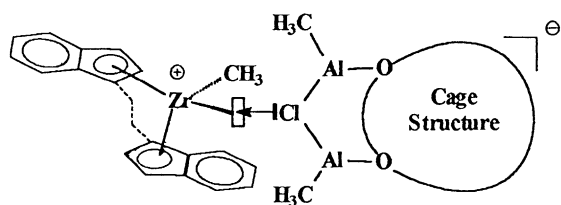


Scheme 2. Hypothetical structure of the species absorbing at 470 nm.

sorption band located at 470 nm, obtained from commercial MAO or upon addition of TMA on a previous system, likely involves TMA complexation on the electron deficient zirconocene. Indeed, the presence of TMA in large amount might lead to the formation of separated ion pairs. This is consistent with the location of the zirconocene main absorption band at a much higher wavelength ($\lambda = 470$ nm), in relation with a charge separation and a decrease of the electronic density on the zirconocenium. In agreement with previous proposals [4,5], a hypothetical structure for such separated ion pairs is shown in Scheme 2.

Besides, possible reasons why zirconocene species issued for commercial MAO/*rac*Et(Ind)₂ZrCl₂ and absorbing at 440 nm are inactive may be found in recent Rytter’s paper [14]. The authors have proposed for MAO a Me_{6m}Al_{4m}O_{3m} ($m = 2-4$) cage-like structure (note the Me_{total}:Al ratio = 1.5) in which only the labile and reactive bridging methyl groups (Me_{bridging}:Me_{total} ≈ 0.2) participate to zirconocene activation. Rapid exchange between these MAO active methyls and chloride ligands of Cp₂ZrCl₂ or of dimethyl aluminum chloride (DMAC) yields chlorinated MAO, “MAO-Cl”, as shown by IR spectroscopy and computational calculation. The resulting “MAO-Cl” revealed inefficient for the activation of metallocene catalysts due to the substitution of methyl bridges by chlorine atoms. On this ground, we may assume that inactive species absorbing at 440 nm, obtained at low Al:Zr ratios, would correspond to tight ion pairs formed between cation-like zirconocenium and [MAO-Cl]⁻ counter ion (Scheme 3).

The addition of large amounts of commercial MAO would finally disrupt the strong interaction between “MAO-Cl” and zirconocenium species and displace the equilibrium towards TMA separated ion pairs (Scheme 2) active for olefin insertion.



Scheme 3. Hypothetical structures of the species absorbing at around 440 nm.

In the case of $racEt(Ind)_2ZrCl_2$ activation by TMA-depleted MAO, it was shown that heating treatment under vacuum of crude MAO leads to important structure modifications of the activator. According to [15], decomplexation of TMA and its consumption through re-condensation between oligomer cage structures would give MAO with much higher average molar mass and would substantially increase the number of reactive bridging methyl groups. This increase of bridging active Me groups eases the trapping of chloride ligands at lower Al:Zr ratios compared to commercial MAO and also enables to keep on the activating power of TMA-depleted MAO. Indeed, we may assume that part of the active bridging methyl groups are still available after chloride abstraction, to yield $[MAO-Me]^-$ counter anions, less nucleophilic than $[MAO-Cl]^-$ allowing olefin coordination.

4. Conclusions

This paper gives clear evidences for the negative role of extracted chloride ligands in the activation process of $racEt(Ind)_2ZrCl_2$ by MAO for olefin polymerization. This is attributed to the formation of a tight ion pair in which strong interaction between chloride

anion and zirconium vacant site still takes place and impedes olefin coordination and insertion.

The replacement of chloride ligands by methyl groups allows a much easier activation of zirconocene derivatives by MAO.

The possibility to substitute chloride ligands by other leaving groups for a better zirconocene activation is under study and will be reported in a forthcoming paper.

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