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Mass spectrometric characterization of methylaluminoxane-activated metallocene complexes

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Mass Spectrometric Characterization of Methylaluminoxane-activated, Metallocene Complexes


Abstract: Electrospray ionization mass spectrometric studies of poly(methylaluminoxane) (MAO) in the presence of Cp₂ZrMe₂, Cp₂Zr(Cl) and Cp₂ZrCl₂ in fluorobenzene (PhF) solution are reported. The results demonstrate that alkylation and ionization are separate events that occur at competitive rates in a polar solvent. Further, there are significant differences in ion pair speciation that result from the use of metallocene dichloride complexes vs. alkylated precursors at otherwise identical Al:Zr ratios. Finally, the counter-conditions may predominate over their persistence of unreactive, homodinuclear ion pairs in the case of Cp₂ZrCl₂ as well as a change in ion-pairing resulting from modification of the anions formed at lower Al:Zr ratios. Models for neutral precursors and anions are examined computationally.

Introduction

Ever since its discovery by Sinn and Kaminsky,[11] MAO has been used extensively as an activator of single-site, olefin polymerization catalysts.[2] MAO is believed to activate single-site catalysts such as metallocene complexes by alkylation and ionization as depicted in equations 1 and 2. Although much is known about the chemistry of the cationic moiety, an alkylmetallocenium ion,[10] much less is known about the structure and composition of the counter-anion.

\[
\text{Cp}_2ZrCl_2 + \text{MAO} \rightarrow \text{Cp}_2ZrCl(\text{Me}) + \text{MAO} \quad (1)
\]

\[
\text{Cp}_2ZrCl(\text{Me}) + \text{MAO} \rightarrow \text{Cp}_2ZrMe + \text{MAO}(\text{Me}) \quad (2)
\]

The basic chemistry summarized in eqns. 1-2 has been studied by a variety of spectroscopic methods. Much of the work has focused on ionization of zirconocene dichlorides and dimethyls using NMR spectroscopy,[14] with reference to Scheme 1, a number of ion-pairs have been detected depending on Al:Zr ratio, and the catalyst precursor employed.

At low Al:Zr ratios contact ion-pairs (e.g. 1) or ion-pairs consisting of homodinuclear cations 2 predominate while at higher Al:Zr ratios more loosely associated ion-pairs 3 are formed. The heterodinuclear Me₃Al adduct 4 predominates at highest Al:Zr ratios with steric unhindered metallocene complexes. The relative amount of the various species present is dependent on zirconocene structure, the use of dimethyl vs. dichloride complexes, the Me₃Al content, and possibly even the source of the MAO used. The basic conclusions of these studies have been corroborated by UV-Vis spectroscopic methods,[5] namely that the ion-pairing is sensitive to the Al:Zr ratio, and that the structure of the ion-pairs formed is also sensitive to this ratio, the presence of Me₃Al, and the structure of the zirconocene complex.

Formation of ion-pairs was originally envisaged to occur by reaction of neutral metallocene complexes with strained aluminoxane cages, believed to be present in MAO, via the process of either methide or halide abstraction.[8] The precedent for this reaction is based on studies of higher aluminoxanes that adopt such structures, and where ring-opening occurs to furnish contact ion-pairs that are competent for insertion.[6] Theoretical studies support this basic mechanism,[26-7] though more recent studies suggest such cages will be a very minor component of MAO relative to much larger strain-free cages.[38]

More recently, attention has been focused on an alternate mechanism for ion-pair formation, namely that MAO functions as a source of the Lewis acidic [Me₂Al]+ moiety in its reactions with neutral donors, including metallocene complexes.[19] Neutral donors such as THF and pyridine readily form 2:1 adducts of this species (ca. 2.5 mol% based on total Al) that can be characterized by ¹H NMR spectroscopy,[15] while metallocene precursors with donor ligands such as Cp₂Zr(OMe)₂ also form.

Scheme 1. Ion-pairs formed on activation of Cp₂ZrX₂ by MAO.

[Scheme 1 diagram]

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adducts such as \([\text{Cp}_2\text{Zr}((\mu-\text{OMe})_2)\text{AlMe}_2][\text{MAO}(X)]\). Compounds featuring donor-stabilized versions of this cation are known to activate metallocene complexes towards olefin polymerization\(^{16}\). Theoretical studies suggest that electrophilic MeAl moieties bonded to MAO are competent for these reactions\(^{16}\) while it has been known for some time that such structures (i.e., Lewis acidic MeAl groups) are present in MAO using ESR spectroscopy in conjunction with the spin label donor TEMPO\(^{13}\).

While the above-referenced work has shed a great deal of light on the activation of metallocene catalysts by MAO, little attention has been focused on the structure of the anions formed in these reactions. When using metallocene dichloride complexes as precursors, or MeAlCl as an additive, it is clear from IR spectroscopy\(^{14}\) that the neutral components of MAO undergo chlorination reactions (e.g., exchange of bound MeAl for MeAlCl\(^{14}\)) and implicit from NMR or other spectroscopic studies that ion-pairs formed at low Al:Zr ratios may feature chlorinated anions (i.e. Scheme 1). Chlorinated aluminoxanes can be prepared by the controlled hydrolysis of MeAlCl; have been structurally characterized, and are competent co-catalysts for olefin polymerization (e.g., TiCl\(_4\)). On the other hand, the ion-pairs formed at low Al:Zr ratios using commercial MAO solutions (containing “free” MeAl), and metallocene dichlorides are largely inactive for hexene polymerization\(^{15,16}\) while fully chlorinated MAO formed by modification of MAO using excess MeAlCl was unable to activate Cp\(_2\)ZrCl\(_2\) for olefin polymerization\(^{14}\).

Recently, we reported the first studies of MAO by the technique of electrospray ionization mass spectrometry (ESI-MS)\(^{17}\) in the presence of a variety of donors, including Cp\(_2\)ZrMe\(_2\) in fluorobenzene (PhF) solvent\(^{18}\). The results of these studies provide strong support for the hypothesis that MAO serves as a source for the electrophilic [MeAl\(^+\)] moiety in its reactions with neutral or anionic donors. Moreover, the number and mass of the anions formed at higher Al:donor ratios were largely invariant to the nature of the additive and whose composition, as partly deduced from MS/MS studies, is consistent with the simple formulae depicted in eqn. 3.

\[
\text{(MeAlO)}_3\text{(AlMe}_3\text{)}_3 + \text{D} \rightarrow \left[\text{MeAl(D)}\right]^+ \left[\text{(MeAlO)}_3\text{(AlMe}_3\text{)}_3\right]^- + \text{Me}\quad \text{(3)}
\]

In this paper we present new studies concerned with the ionization of Cp\(_2\)ZrCl\(_2\), prototypical of the most commonly used catalyst precursors in olefin polymerization, as compared to that of alkylated precursors by MAO. Significant differences in behavior are observed and more importantly are readily interpretable in terms of ion-pair composition. The results are sufficiently compelling that we hope they will provide an impetus for renewed study of this important but elusive activator.

Results – Characterization of Methylaluminoxane by NMR Spectroscopy

In the current study, MAO supplied by Sigma-Aldrich as a 10 wt% solution in toluene was used. No attempt was made to remove “free” MeAl by evaporation or other means though total MeAl content of the MAO was initially monitored by \(^{11}P\) NMR spectroscopy\(^{19}\) and values of 16 and 19 mol% of total Al were obtained for two samples from the same lot (STBC9762V) used during the course of this work.

Three different samples from this lot were subsequently analyzed for both MeAl and [MeAl\(^+\)] content using the \(^1H\) NMR spectroscopic techniques reported by Bochmann and coworkers\(^{10}\). In our hands, the addition of pyridine to these Aldrich samples (ca. 2.1 mol% pyridine:Al) and subsequent analysis by \(^1H\) NMR spectroscopy was not satisfactory – phase separation was observed, leading to very low estimates of [MeAl(py)]\(^+\) content (0.22 and 0.15 mol%) but more consistent values of MeAl content were obtained (14.0 and 15.6 mol% for samples received in September 2013 and January of 2014, respectively).

Use of excess THF (ca. 4.1 mol% pyridine) instead of pyridine, as initially recommended by Imhoff et al.\(^{19}\) was more satisfactory; baseline correction (cubic spline polynomial) was used to subtract the broad peak due to MAO from the sharp peaks of [MeAl(THF)_2]\(^+\) and MeAl(THF)\(^-\); for the same sample of MAO\(^{20}\) values of 18.2 and 0.73 mol% using pyridine can be compared to those obtained using THF of 14.8 and 2.26 mol% for MeAl(THF)\(^-\) and [MeAl(THF)_2]\(^+\), respectively. It is known that pyridine titration often over-estimates MeAl content\(^{19}\) so the latter results are considered more reliable and they show that the pyridine method, at least for MAO obtained from Sigma-Aldrich, underestimates [MeAl\(^+\)] content by about a factor of three.

Finally, analysis of a third sample from lot STBC9762V, purchased in June 2013, using THF provided estimates of 11.5 and 1.2 mol% for MeAl(THF)\(^-\) and [MeAl(THF)_2]\(^+\). Evidently, the MeAl content of MAO purchased from the same lot increased slightly with time (from 11 to ~13 mol%), whereas the [MeAl\(^+\)] content decreased significantly (from 1.2 to ~0.5 mol%). Although all of these samples were refrigerated in a glove-box upon receipt, they were not stored in this manner at Sigma Aldrich and this may account for any differences seen in comparing material from the same batch.

Results – Ionization of Cp\(_2\)ZrMe\(_2\)

These results have been reported elsewhere\(^{18}\) but are reiterated here in greater detail (Figure 1). At Al:Zr ratios of 50:1 or lower, the dominant cation is [([Cp\(_2\)ZrMe\(_2\)]\((\mu-\text{Me})\))\(^+\)] (2\(^+\)) (Figure 1a). At higher Al:Zr ratios, the heterodinuclear cation [Cp\(_2\)Zr(\(\mu-\text{Me})\text{Me}\text{Me})\text{AlMe}_2\]) (4\(^\ast\)) predominates (Figure 1b-c) in agreement with earlier spectroscopic studies.\(^{13,15,16}\) Variable amounts of the parent metallocene ion [Cp\(_2\)ZrMe\(_2\)]\(^+\) with m/z 235 (3\(^\ast\)) are detected. Qualitatively, it would appear that this ion is increasingly favored at sufficiently high Al:Zr ratios, though this behavior is not always observed - (c.f. Figure 1 with Figure 9).

The isotope patterns (see insets to Figure 1) are generally in good agreement with theoretical values (not shown) except for the species at m/z 235 where the M+2 peak is accentuated. M+2 ions are due to hydrolysis (i.e. M+H\(_2\)O-CH\(_3\)) either in solution, or due to an ion-molecule reaction in the source of the mass
A combination of MS/MS studies and chemical m/z 307 m/z 235 energies suggesting at least two technique, is related to the cone voltage (CV) setting. when it leads to ion fragmentation. 

It should be mentioned that the relative amount of $3^+$ with respect to $2^+$ and $4^+$ is sensitive to a number of factors other than the Al:Zr ratio. The most important factor, which is unique to this technique, is related to the cone voltage (CV) setting. Increasing CV leads to increases in sensitivity largely due to an increase in ion transmission through the orifice into the mass spectrometer. However, the ions present have increased kinetic energy as a result of an increased voltage bias and undergo more energetic collisions with neutral molecules (predominantly nitrogen desolvation gas, but also residual solvent) in this region. This process is known as in-source, collision induced dissociation (CID) when it leads to ion fragmentation. As shown in Figure 2, adjusting CV from 8 to 32 V during analysis of the same stock solution (Al:Zr ~ 100:1) leads to essentially complete conversion of $4^+$ to $3^+$ via loss of Me$_2$Al.

Surprisingly, at constant CV, the relative amounts of $3^+$ and $4^+$ appeared insensitive to the Me$_2$Al content of the MAO used. To further clarify this issue, an additional amount of Me$_2$Al (19 mol% with respect to total Al present in MAO for a total of 38 mol%) was deliberately added to MAO prior to catalyst activation. As indicated in Figure 3, the relative amounts of $3^+$ and $4^+$ are essentially unchanged. This result suggests there is already enough “free” Me$_2$Al present in this batch of MAO to completely sequester the metalloccenium ion as the adduct, and that the relative amounts of $3^+$ and $4^+$ are mainly a function of the instrumental conditions used for analysis. The counter-anions that form upon activation of Cp$_2$ZrMe$_2$ have masses in the range 1000-3000 Da. The mass spectra of these anions is largely invariant to Al:Zr ratio and a typical spectrum appears in Figure 4a). The composition of these anions was deduced from a combination of MS/MS studies and chemical intuition and has been discussed in detail elsewhere. The appearance of these spectra is also very sensitive to CV, with the anions able to fragment via loss of 1 or at most 2 Me$_2$Al molecules. Some anions, such as that present at m/z 1811, are resistant to this process, while others such as m/z 1853 readily fragment, suggesting differences in structure (Figure 4b, see also insets to this and Figure 4c).

Earlier MS/MS studies indicated that all of these anions fragment by multiple losses of Me$_2$Al, though the energetics of this process have been studied only in one case. Analysis of the anion at m/z 1853 by energy dependent (ED) ESI-MS/MS revealed a total of 10 losses of Me$_2$Al as the collision energy is systematically increased. As shown in Figure 5, 8 of the 10 losses occur at relatively low energies suggesting at least two different processes that result in fragmentation. In examining the conventional MS/MS spectrum it is seen that loss of the first Me$_2$Al molecule is especially facile, in agreement with the results from changing the CV (in-source CID).
Taken together, the results suggest that these anions have 1 or at most 2 molecules of weakly bound Me₃Al, with the remaining fragmentations resulting from much more strongly bound Me₃Al molecules, or resulting from rearrangement of these anions. It is important to emphasize that the true amount of bound Me₃Al is of importance in correctly formulating these anions and thus their ultimate structure. Other experimental and theoretical work suggests that the amount of bound Me₃Al per neutral molecule of MAO is also variable,\(^{10}\) with perhaps an average of one Me₃Al molecule being bound in this form.

If this is indeed the case for the anions, our original formulæ require modification; for example, if the anion with m/z 1853 and formula \([\text{MeAlO}]_2\text{Me}_3\text{Al}\text{Me}_7\text{Me}\) only contains one molecule of bound Me₃Al, then the remaining 6 molecules dictated by MS/MS studies must result from rearrangement and an alternate formulation is e.g. \([\text{MeAlO}]_2\text{Me}_3\text{Al}\text{Me}_2\text{Me}_2(\text{Me}_9\text{Al})\text{Me}\). In other words, the cage-like anions might be comprised of a mixture of linear and cyclic aluminoxane oligomers. Certainly there is evidence for both of these being present in MAO.\(^{12}\)

**Results - Structures and Mechanisms for Ion-Pair Formation**

One of the lower MW anions that is always present in these mixtures, and appears susceptible to two losses of Me₃Al via in-source CID has m/z 1375 (see Figure 4b and 4c). This can be viewed as forming from a neutral component of MAO and
Cp₂ZrMe₂ by either of two processes. One possible precursor to this anion is (MeAlO)₁₆(Me₂Al)₈ which might react to form the ion-pair [Cp₂Zr(µ- Me)₃ν-AlMe₃][(MeAl(OAlMe)₄Me)₄(Me₂Al)₈Me] via [Me₂Al]⁻ abstraction, or an alternate precursor (MeAlO)₁₆(Me₂Al)₈ could form the ion-pair [Cp₂ZrMe][(MeAl(OAlMe)₄Me)₄(Me₂Al)₈Me] via the process of methide abstraction.

These two processes have been studied in detail for the case of (MeAlO)ₐ₈(Me₂Al)₈ (n = 1, 2) and have been shown to be equivalent in the sense that the contact ion-pair [Cp₂ZrMe][µ- Me(MeAlO)ₐ₈(Me₂Al)] is the global minimum. However, the cage-like precursor featuring two Me₂Al molecules is predicted to be significantly more stable than those having only one or none (ΔG₂₆ = -9.0 or -15.6 kJ mol⁻¹) so the process of [Me₂Al]⁻ abstraction is favored in this case. This appears to be a general result due to the strong tendency of unsaturated MAO molecules to bind additional Me₂Al at equilibrium.

We have elected to study the direct abstraction reaction involving unsaturated precursors as it is computationally simpler for these large molecules.

In prior work, we have studied the structures and formation of aluminoxanes (MeAlO)nₐ₈(Me₂Al)₈ (n = 1-8, a = 0-5) and the energetics of hydrolysis of Me₂Al by computational methods. We have studied the full configurational space until formation of pentameric structures (m = 5). Beyond m = 5 the study of the full configurational space is not practical; that process involved thousands of calculations. For m = 5-8 we employed an approximation, where only the reactions of the lowest energy isomers at each stage of the Me₂Al hydrolysis were followed, thus omitting the (very real) possibility that a higher energy species at one step can lead to a lower energy species at a subsequent step. We checked the validity of this approximation by comparing it to the study involving the full configurational space for m = 1-5, and it turned out notably successful. In 16 out of 20 m/n combinations it produced precisely the same isomer as the study involving the full configurational space. Using these same methods, we studied one pathway of MAO formation by following the reactions of the lowest energy isomer at each stage until reaching (MeAlO)₈ₐ₈(Me₂Al)₈. In terms of elementary species, the overall reaction for its formation is:

\[ 11 \text{Al}_2\text{Me}_6 + 16 \text{H}_2\text{O} \rightarrow (\text{MeAlO})_{16}(\text{Me}_2\text{Al})_8 + 32 \text{CH}_4 \]

The optimized structure of (MeAlO)₈ₐ₈(Me₂Al)₈ that we ended up with (5, Figure 6a) reveals an extended cage structure in accordance with previous findings. The model structure obtained for (MeAlO)₁₆(Me₂Al)₈ is one of the many possible isomers with this composition, with no guarantee of being the global minimum. Nevertheless, it turns out to be notably stable, being thermodynamically favored, as revealed by the calculated Gibbs energy of its formation. With respect to the (MeAlO)₁₂ cage, for example, often used as a reference, it is favored by 8.6 kJ mol⁻¹ per MeAlO unit.

An obvious structural feature is the presence of two Me₂Al molecules bound to Me₂Al end groups, with the former labeled as Al(1) and Al(2) in Figure 6b. The bridging interactions in these two units appears quite strong judging from the optimized Al-C distances; the average distance for binding methyl groups is Al-Me₈ = 2.134(38) Å vs. Al-Me₈ = 1.955(3) Å for the terminal methyl groups in these two units.

On the other hand, at the other end of the cage, there are two quasi-tetrahedral Me₂Al units involved in much weaker bridging interactions with nearby Me groups with Al(3)-Me₈ = 2.2595 and Al(4)-Me₈ = 2.3575 Å, respectively for the dashed lines depicted in Figure 6b. Unlike the dative bound Me₂Al molecules, these Me₂Al units are internally built into the MAO structure and cannot be removed (as neutral molecules) without breaking Al-O bonds. It is self-evident that these strained Me₂Al groups have “latent” Lewis acidity⁴ which might be relieved through methide abstraction from Cp₂ZrMe₂.

Since these sites are inequivalent, there are two possible anions that could be formed via methide or chloride (vide infra).
abstraction reactions. Two of the anions which form by reaction at Al(3) have the general structure shown in Figure 7a and 7b, and in one simplified view can be thought of adducts between Me3Al or Me2AlCl and an anionic aluminoxane cage. These molecules still feature a weak, residual Al-Me interaction with Al(4)-C distances of 2.405 and 2.429 Å, respectively. The two isomeric anions formed by methide or chloride abstraction at the other site [Al(4), Figure 6b] are analogous but feature much more strongly bridged Me groups with Al-Me = 2.177 and 2.0977 Å and Al-Me = 2.0915 and 2.1775 Å (Figure 8a and 8b). As a consequence, these isomers are much lower in energy by -28.0 and -35.6 kJ mol⁻¹, respectively.

Thus, of the two possibilities for abstraction, the Me₂Al site featuring the weakest bridging interaction, Al(4), also gives rise to the most stable anion, though the energy difference is largely due to formation of stronger bridges to the remaining unsaturated Me₂Al group.

Results – Ionization of Cp₂ZrCl₂

In comparison to the studies just described, activation of Cp₂ZrCl₂ by MAO is a more complicated process since two processes are involved in catalyst activation, alkylation and ionization. It is suspected that Me₃Al (free or associated with MAO) is responsible for mono-alkylation of the catalyst and thus the Me₃Al content of the MAO in addition to the Al:Zr ratio is expected to have an impact on the activation process. Also, the by-product of mono-alkylation, namely Me₂AlCl, is known to modify MAO and based on FT-IR studies, it would appear it readily displaces bound Me₃Al in doing so.

At low Al:Zr ratios of 50:1, ESI-MS spectra revealed a somewhat unexpected outcome in comparison to prior work. The dominant cation formed is the analogue of ion-pair 2, namely [(Cp₂ZrMe₂)₂(μ-Cl)]⁺ with m/z 505 (2a⁺, Figure 9c) and a characteristic isotope pattern for this cation is shown in Scheme 2. It should be noted that the titanium analogue of this ion has been detected in NMR studies dealing with MAO activation of titanocene dichlorides, but to our knowledge this complex had
not been implicated in activation of Cp₂ZrCl₅. On the other hand, a more recent study concerned with activation of (2-Ph-ind)₂ZrCl₆ concludes an analogous ion-pair is formed at lower Al:Zr ratios.⁵ We thus suspect this is a general phenomenon. In addition, small quantities of dinuclear cations with m/z 525 and 489 are present (Figure 9c – see also Scheme 2). The former contains one additional Cl atom based on the isotope pattern and is formulated as [(C₅H₅)Zr(Cl)Zr(Cp₂)²⁺], while the latter corresponds to the CH-activation product [C₅H₅Zr(CH₂)(µ-Cl)Zr(Cp₂)]⁺ or an isomer (C₅H₅Zr(Cl)Zr(Me)Cp2)²⁺ (Scheme 2). There is ample precedent for such C-H activation chemistry in related studies using other Group 4 complexes⁶ but, to our knowledge, this is the first time this species has been detected in MAO-activated, zirconocene dichloride complexes.

If dilute solutions of [(C₅H₅)Zr(µ-Cl)]⁺ are allowed to stand at room temperature, the cation with m/z 489 slowly grows in at the expense of cation 2a⁺. If more concentrated solutions are prepared, e.g. by reaction of MAO with solid Cp₂ZrCl₂, not only is [C₅H₅Zr(µ-Cl)](µ-CH₂)Zr(Cp₂)]⁺ prevalent, but a further C-H activation product at m/z 473 is detected, that still contains a single Cl atom (Scheme 2). This ion could be either a fulvalene-bridged, Zr(III) dinuclear cation or its Zr(IV) precursor,⁷ formed by C-H activation of a remaining Cp ring.

![Scheme 2 - Dinuclear cations formed from Cp₂ZrCl₅ and MAO in concentrated toluene solution (i.e. solid Cp₂ZrCl₅ + 10 w/w% toluene solution of MAO) at a 20:1 Al:Zr ratio.](image)

At higher Al:Zr ratios, the dinuclear cation 2a⁺ is remarkably persistent in comparison to the situation for Cp₂ZrMe₂ (c.f. Figure 9b with Figure 1b). At sufficiently high ratios of 500:1, only mononuclear cations with m/z 235 and 307 are detected in these reactions (Figure 9a), along with trace amounts of a species at m/z 255 containing one Cl atom. This ion is reasonably formulated as [C₅H₅ZrCl]⁺ and suggests that ionization of either the catalyst precursor or the monoaalkylated product Cp₂Zr(Me)Cl, formed in situ, can occur upon reaction with MAO.⁸ Also, in this case, ion speciation is sensitive to solvent polarity. When activation is conducted in pure toluene solution vs. a 1:1 mixture of that solvent and PhF, dinuclear cations are disfavored vs. mononuclear cations at otherwise identical Al:Zr ratios and total concentrations (see inset to Figure 9b). Evidently, ionization and alkylation occur at competitive rates, though the rate of the former reaction is understandably more sensitive to solvent polarity.

Having said that, the results are largely counter-intuitive if the mechanism for catalyst activation follows that shown in eqns. 1 and 2. Faster ionization, relative to alkylation, should lead to increased amounts of mononuclear complexes being formed at the expense of dinuclear complexes whereas the opposite effect is seen here.

Even more dramatic changes are evident in the corresponding negative ion spectra. At lower Al:Zr ratios (e.g. 50:1) the spectra (Figure 10c) are barely recognizable compared to those observed upon activation of Cp₂ZrMe₂ (e.g. Figure 4b). In particular, each anion present has undergone extensive chlorination to furnish new anions, with 1, 2, 3 or even 4 chlorine atoms separated in mass from the parent anion by multiples of

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Figure 9. Positive ion ESI-MS of MAO + Cp₂ZrCl₅ in PhF at a) 500:1, b) 100:1 and c) 50:1 Al:Zr ratios. Inset to Figure 9b shows spectrum of a mixture of MAO + Cp₂ZrCl₅ prepared in a 1:1 v:v mixture of toluene and PhF at the same [Al] = 0.75 M and Al:Zr ratio.
As the ratio of Al:Zr increases, the proportion of chlorinated anions decreases and at sufficiently high Al:Zr ratios of 500:1 the spectra resemble those formed from Cp$_2$ZrMe$_2$ and MAO (Figure 10a). Note that the extent of chlorination is not uniform. Anions such as that with m/z 1853, which are able to lose Me$_2$Al readily via CID, are also most prone to chlorination; this is best appreciated by comparing the intensity of m/z 1853 with that of m/z 1811 in Figure 10 as a function of Al:Zr ratio.

It should be noted that the anion chlorination observed is very disproportionate to the amount of Cp$_2$ZrCl$_2$ added with respect to total MAO. In the specific case of the anion at m/z 1853, the intensity of this ion (and its isotopomers), was compared to that of the ions at m/z 1873, 1893 and 1913, containing 1, 2 or 3 Cl atoms respectively as a function of the Al:Zr ratio.

This data is depicted in Figure 11, along with the total chlorination observed (i.e. the weighted sum of the intensities for the three chlorinated ions detected with sufficient intensity). It is evident that at an Al:Zr ratio of 25:1 or an Al:Cl ratio of 12.5:1 (i.e. 8 mol% Cl) that this anion has undergone reaction with at least one equivalent of a chlorinating agent. A similar conclusion applies to the other anions detected but their intensity was insufficient to permit quantitation in this manner.

In earlier work we had noted the formation of chlorinated anions when using MAO and [Bu$_4$N][Cl] as an additive. Qualitatively similar effects had been noted, though the resulting anion distribution was quite different (i.e. chloride is a less discriminating base than Cp$_2$ZrCl$_2$). The spectra were complicated by aggregation effects at high levels of salt, and perhaps as a result, the extent of anion chlorination was reduced at similar additive levels. We had attributed the formation of chlorinated anions as resulting from reaction of the by-product of ion exchange (i.e. Me$_2$AlCl - eqn. 4) with MAO via redistribution reactions involving bound Me$_2$AlCl. Evidently, this process is much more efficient in the case of Cp$_2$ZrCl$_2$.

Finally, we also investigated the use of Cp$_2$Zr(Me)Cl as a precursor, as this complex is known to be the principal product of alkylation of Cp$_2$ZrCl$_2$ by MAO (or Me$_2$Al). At identical Al:Zr ratios, this complex gives a significantly higher proportion of mononuclear cations (c.f. Figures 12 and 9) than does Cp$_2$ZrCl$_2$. Specifially, when compared under identical conditions of concentration and solvent polarity etc. about half as much MAO is needed to activate Cp$_2$Zr(Me)Cl compared to Cp$_2$ZrCl$_2$ - see Figure 13 c) vs. d) where the positive ion spectra are nearly identical.

Also as shown in this figure, at identical Al:Cl ratios this complex is much less effective in forming chlorinated anions than Cp$_2$ZrCl$_2$ (Figure 13a vs. b), despite the fact that a similar amount of Me$_2$AlCl should be formed in both reactions as a by-product. Also, neither the cation with m/z 525 nor 255 is present in significant amounts when using Cp$_2$Zr(Me)Cl, suggesting that this complex ionizes by nearly exclusive formation of [Cp$_2$ZrMe]$^+$ rather than [Cp$_2$ZrCl]$^-$.

We also investigated a 1:1 mixture of Cp$_2$ZrMeCl and Me$_2$AlCl vs. Cp$_2$ZrCl$_2$ and MAO at the same Al:Zr ratio of 50:1. In this case, the extent of anion chlorination was similar in comparing the two spectra while the extent of ion-pair formation also appeared equivalent. Similar results were observed when
Cp₂ZrCl₂ and Me₃Al (excess) were pre-mixed prior to activation with MAO. Unfortunately, the reaction between Me₃Al and Cp₂ZrCl₂ to furnish a mixture of Cp₂ZrMe(Cl) and Me₂AlCl is an equilibrium reaction which can be approached from either direction [29]. Evidently, the Me₂AlCl produced on ionization of (pure) Cp₂Zr(Me)Cl is less effective for chlorination of the anions derived from MAO, whereas the combination of Cp₂ZrCl₂ and Me₃Al or Cp₂ZrMe(Cl) and Me₂AlCl is more effective. A complex between the latter two compounds Cp₂Zr(Me)(μ-Cl)AlMe₂Cl has been detected by IR spectroscopy [29].

Discussion

The need for a large excess of MAO for catalyst activation has been attributed to a number of factors. [2] MAO serves several functions during polymerization catalysis, including catalyst alkylation, ionization and as a scavenger of poisons present in the solvent or monomers used. Under practical conditions, the last of these roles is actually fairly important. The Me₃Al content of MAO in commercially available solutions is variable at around 10-20 mol% (of which ~75% is readily available “free” Me₃Al [10c]), so a larger excess of MAO will be needed compared to simple alkylation compounds to efficiently remove catalyst poisons from solvent and monomer(s). Moreover, a variety of equilibria between dormant and active (e.g. 4 vs. 3), or soluble vs. heterogeneous forms of the catalyst are influenced by changes to absolute catalyst vs. MAO concentration in a reactor that conspire to favor high Al:Zr ratios (or more correctly low [Zr] at fixed [Al]) for maximal activity. These effects have been clearly documented in the case of Cp₂ZrCl₂ [30] but not for the other catalyst precursors studied here. Our studies, and also those involving NMR spectroscopy involving activation of Cp₂ZrMe₂, suggest that catalyst activation is largely complete at much lower Al:Zr ratios – typically 100:1, than those used to activate metalloocene dichloride complexes. It
is known that complexes that are alkylated require much less MAO for high activity in e.g. 1-hexene polymerization. On the other hand, ion-pairing is sensitive to Al/Zr ratio where the limiting dimensions, as measured by e.g. diffusion measurements, reveal aggregation at higher absolute Zr concentration. Indeed, based on the invariance of the anion distribution in these reactions to Al/Zr ratio in the case of Cp₂ZrMe₂, any argument as to the need for very high Al/Zr ratios for catalyst activation must be based on ion-pairing rather than ion-pair identity in the case of Cp₂ZrMe₂.

The current work, involving the activation of Cp₂ZrCl₂ has revealed that the homo-dinuclear complex 2a* is far more persistent than 2*, as a consequence of stronger Cl vs. Me bridging, and suggest that complete activation of the catalyst is not achieved unless significantly higher Al/Zr ratios are employed. Furthermore, this dinuclear complex is unstable in solution, decomposing by sequential C-H activation reactions so that at lower Al/Zr ratios, significant catalyst deactivation is expected.

The extensive chlorination of the anions at lower Al/Zr ratios used is unexpected; it is evident from the Al/Zr ratios used vs. the extent of chlorination, that it is the anions themselves which are especially susceptible to this process rather than any neutral components of MAO. That anion chlorination is highly favored, regardless of the mechanism of this process, is shown by calculations involving both Cp₂ZrCl₂ and Cp₂ZrMe(Cl) as chlorinating agents (eqns. 5-6) using the most stable anions (Figure 8) identified in the case of m/z 1375 and 1395, respectively. Note the significant difference in energy between the first and second process, in agreement with the ESI-MS results; in particular, the monoalkylation of Cp₂ZrCl₂ by an anion (which results in chlorination of the latter) is competitive with conventional alklylation by Me₂Al (eqn. 7).

\[ \Delta E = -28.7 \text{ kJ mol}^{-1} \]
\[ \Delta G_0 = -28.5 \text{ kJ mol}^{-1} \]
\[ \text{Cp}_2\text{ZrCl}_2 \]
\[ \text{[MeAlO]}_{16}(\text{Me}_2\text{Al})_2 \text{Me} \]

As to the mechanism for chlorination, in particular, those anions that most readily lose Me₂Al by CID are also the most susceptible to chlorination (e.g. 1853 vs. 1811). This observation initially suggested that it was Me₂AlCl, the by-product of alklylation, that was the sole agent responsible for these anion modification reactions. Indeed, if Me₂AlCl is added to solutions of MAO (51:1 Al/Cl ratio) and this mixture is used to activate Cp₂ZrMe₂ (100:1 Al/Zr), the anions present are extensively polychlorinated and even new anions are present that are not observed during activation of Cp₂ZrCl₂, while the corresponding positive ion spectrum does not differ significantly (See Supporting Information). The extent of polychlorination is much more advanced in the presence of this additive compared with Cp₂ZrCl₂ at the same Al/Cl ratio. All of these results suggest that alklylation and subsequent ionization of Cp₂ZrCl₂ is not occurring in the simple, sequential manner depicted in eqn. 1-2. In particular, they suggest that ionization and conventional alklylation by Me₂Al may be occurring as competitive processes as suggested in Scheme 3 where the extent of anion chlorination by Me₂AlCl depends upon whether alklylation occurs prior to vs. after ion-pair formation.

Evidently, part of the reason such a large excess of MAO is needed for activation of Cp₂ZrCl₂, reflects the complexity of this activation process, coupled with the instability of any dinuclear complexes formed, and changes to ion-pairing that naturally would result from the presence of different anions at lower Al/Zr ratios. Though it may be coincidental in this case, the amounts of MAO needed to fully activate Cp₂ZrCl₂ while retaining the native anion distribution seen with Cp₂ZrMe₂ are typical of those used in a laboratory setting.

![Scheme 3](image)

**Scheme 3**: Alklyation vs. ionization of Cp₂ZrCl₂ by MAO.

**Conclusions**

Electrospray ionization mass spectrometry offers powerful insight into ion speciation during metallocene catalyst activation by MAO. Specifically, it demonstrates that the anions formed during this process are changing dramatically as a function of the Al/Zr ratio in the case of Cp₂ZrCl₂, whereas in the case of a fully alkylated precursor such as Cp₂ZrMe₂, the anion distribution is largely invariant to changes in this ratio. Therefore, in the former case, ion-pairing is no doubt a very sensitive function of the conditions used for catalyst activation, and ion-pairing effects are known to be decisive in affecting catalyst activity or polymer tacticity in the case of propylene polymerization. Unfortunately, ESI-MS experiments only provide an indirect and incomplete picture of ion-pairing in solution; the most intense ions detected in this experiment are not necessarily the most weakly ion-paired, nor even the most weight and chemical composition. It is reasonable to propose
that the aluminoxane-based anions all have similar compositions and therefore the observed ion intensities are representative of the most abundant ion-pairs present in solution. However, it could well be that the most abundant ion-pairs present are not necessarily the most weakly ion-paired, and therefore reactive towards insertion. Future work will address these issues through the study of how changes to solvent polarity and other experimental variables influence ion speciation during catalyst activation or during polymerization.

**Experimental Section**

MAO (10% w/v in toluene) and Cp₂ZrMe₂ were purchased from Aldrich Chemical Co. and used as received. Different batches of the MAO exhibited somewhat different ESI-MS spectra, depending on supplier or age of the material analyzed; the mass spectra reported herein are for the same lot of MAO, stored in a glove-box freezer and warmed to room temperature and thoroughly stirred to dissolve any precipitated content prior to use. Fluorobenzene (Fluorochem) was refluxed over CaH₂, distilled under N₂, and stored over 4Å molecular sieves in a glove-box prior to use. Cp₂ZrMe₂ was purchased from Strem Chemicals and was purified by recrystallization from hot hexane containing excess AlMe₃ to remove traces of (Cp₂ZrMe₂)₂. Cp₂ZrMe₂(CI) was prepared by a literature method.[36] ¹H or ³¹P NMR spectra of MAO and THF solutions, or MAO and PPh₃ solutions were recorded on a Bruker Avance 500 MHz instrument using 5-10 vol% benzene-de as a lock solvent using procedures reported elsewhere.[30b]

A typical procedure is as follows (all manipulations were carried out inside an LC Technology Solutions Inc. LCBT-1 bench-top glove-box). A stock solution of MAO and the metalocene complex was prepared from a suitable amount of MAO in toluene solution (1.54 M), and a variable amount of a toluene or fluorobenzene solution of the complex (ca. 0.015 M) so as to give the desired Al:Zr ratio (from 10-1000:1). After 15-30 minutes at room temperature an aliquot was removed and diluted with dry PhF so as to give a final solution with [Al] ≤ 0.05 M; the resulting solution was filtered into a clean vial. This solution was injected via syringe pump into a Micrionas QTOF micro spectrometer, with a Z-spray electrospray ionization source, through tubing connected to the source compartment by passing it through a manufacturer-installed feedthrough.[31] Capillary voltage was set at 2900 V, source and desolvol gas temperatures were at 70-90 °C and 140-175 °C, respectively. Desolvation gas flow rate was typically 200-400 L h⁻¹. The Z-spray source was pressurized to slightly above atmospheric pressure (+5 mbar) to avoid ingress of air. Rigorous drying of solvent, filtration of samples prior to analysis, source pressurization, and a good glove-box atmosphere were all critical to obtaining good spectra without blocking of capillaries or resulting in much adventitious hydrolysis and oxidation.

Despite these precautions, and during all of these experiments, the target, sample cone, and other metal parts in the outer source compartment become coated with an electrically insulating deposit of aluminoxane and/or alumina that at some point leads to irreversible loss of signal intensity. We have not found a solution to this problem other than to disassemble the source compartment, clean and dry the individual metal components, and reassemble the source…

Theoretical calculations of neutral and anionic MAO molecules were based on techniques described elsewhere[8,9] or on possible models derived by chemical intuition. Association of Me₃Al into the MAO gives rise to dispersive interactions that complicate theoretical treatment of these molecules. The M06 series of functionals[38] has been recently shown as a cost-effective alternative for correlated ab initio methods in studies involving MAO.[39] The calculations were carried out at M062X/TZVP[40] level of theory using Gaussian 09.[41] The MAO molecules studied were confirmed as true local minima in the potential energy surface by calculation of harmonic vibrational frequencies. Gibbs energies were calculated at $T = 298.15 \text{ K}$ and $p = 1 \text{ atm}$. No scaling factors were applied.

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**Keywords:** Electrospray • ionization • mass spectrometry • metalocene • polymerization

The kinetics and thermodynamics of binding of MesoAl to zirconocene ions has been well studied. See J.M. Camara, R.A. Petros, J.R. Norton, J. Am. Chem. Soc. 2011, 133, 5263-5273 and references therein.


This ion was also detected at high Al/Zr ratios in the case of CpzZrMe2 (figure 1c), and in this case must result from reaction of e.g. 3e or a precursor with a trace chloride contaminant present; these are very difficult to exclude from ESI-MS experiments involving shared instrumentation. For a recent review see L.P.E. Yunker, R.L. Stoddard, J.S. McIndoe, J. Mass Spectrometry 2014, 49, 1-8.


Activation of Cp₂ZrCl₂ by excess methylaluminoxane (MAO) results in extensive anion chlorination at low Al:Zr ratios as revealed by electrospray ionization mass spectrometry. Al:Zr ratios of ≥ 500:1 are required to observe the same anion distribution using Cp₂ZrMe₂ and MAO at lower Al:Zr ratios. Further, less MAO is needed to fully activate an alkylated vs. unalkylated, metallocene catalyst under otherwise identical conditions.

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Mass Spectrometric Characterization of Methylaluminoxane-activated, Metallocene Complexes