Mass Spectrometric Characterization of Methylaluminoxane-Activated Metallocene Complexes


Abstract: Electrospray-ionization mass spectrometric studies of poly(methylaluminoxane) (MAO) in the presence of [Cp₂ZrMe₂], [Cp₂ZrMe(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. Furthermore, there are significant differences in ion-pair speciation that result from the use of metalloocene dichloride complexes in comparison to alkylated precursors at otherwise identical Al/Zr ratios. Finally, the counter anions that form are dependent on the choice of precursor and Al/Zr ratio; halogenated aluminoxane anions [(MeAlO)ₓ(Me₃Al)ᵧ(Me)]⁻ (x = 1, 2, 3…); are observed using metal chloride complexes and under some conditions may predominate over their non-halogenated precursors [(MeAlO)ₓ(Me₃Al)ₓMe]⁻. Specifically, this halogenation process appears selective for the anions that form in comparison to the neutral components of MAO. Only at very high Al/Zr ratios is the same “native” anion distribution observed when using [Cp₂ZrCl₂] when compared with [Cp₂ZrMe₂]. Together, the results suggest that the need for a large excess of MAO when using metalloocene dichloride complexes is a reflection of competitive alkylation vs. ionization, the 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,[1] 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 metalloocene complexes by alkylation and ionization as depicted in Equations (1) and (2). Although much is known about the chemistry of the cationic moiety, an alkylmethylalumoxycenium ion,[3] much less is known about the structure and composition of the counter anion.

The basic chemistry summarized in Equations (1) and (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;[4] with reference to Scheme 1, a number of ion pairs have been detected depending on the Al/Zr ratio and the catalyst precursor employed. At low Al/Zr ratios, contact ion pairs such as 1 (Scheme 1) or ion pairs consisting of homodinuclear cations 2 predominate, whereas at higher Al/Zr ratios more loosely associated ion pairs 3 are formed. The heterodinuclear Me₃Al adduct 4 pre-
dominates at highest Al/Zr ratios with sterically unhindered metalloocene complexes. The relative amount of the various species present is dependent on the 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, 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 metalloocene complexes with strained aluminoxane cages, believed to be present in MAO, via the process of either methide or halide abstraction. 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.

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 metalloocene complexes. 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, while metalloocene precursors with donor ligands, such as [Cp₂Zr(OMe)₂]₂, also form adducts, such as [Cp₂Zr(µ-OMe)₂AlMe₂]₂[MAO(µ-O)]₂. Compounds featuring donor-stabilized versions of this cation are known to activate metalloocene complexes towards olefin polymerization. Theoretical studies suggest that electrophilic Me₃Al moieties bonded to MAO are competent for these reactions, while it has been known for some time that such structures (i.e., Lewis acidic Me₃Al groups) are present in MAO, as evidenced by ESR spectroscopy in conjunction with the spin label donor TEMPO.

Recently, we reported the first studies of MAO by use of electrospray-ionization mass spectrometry (ESI-MS) in the presence of a variety of donors, including [Cp₂ZrMe₂] in fluoro-benzene (PhF) solvent. The results of these studies provide strong support for the hypothesis that MAO serves as a source for the electrophilic [Me₂Al]+ 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 tandem mass spectrometry (MS/MS) studies, is consistent with the simple formulae depicted in Equation (3).

\[ [(\text{MeAlO})₃(\text{AlMe})₂]+ \rightarrow [\text{MeAl}(\text{D})][\text{MeAlO})₄(\text{AlMe})₃]-\text{Me}^+ \]

D = Me₂Si(OSiMe₂)₂Me
D = Cp₂ZrMe₂

Herein we present new studies concerned with the ionization of [Cp₂ZrCl₂], 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” Me₃Al by evacuation or other means, though total Me₃Al content of the MAO was initially monitored by pyridine titration often overestimates Me₃Al content, so the latter results are considered more reliable and they show that the pyridine method, at least for MAO obtained from Sigma-Al,

Use of excess THF (ca. 4:1 THF/Al) instead of pyridine, as initially recommended by Imhoff et al., was more satisfactory; baseline correction (cubic spline polynomial) was used to subtract the broad peak due to MAO from the sharp peaks of [Me₃Al(THF)]+ and [Me₃Al(THF)]⁻ for the same sample of MAO, values of 18.2 and 0.73 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 Me₃Al and [Me₃Al]⁺ content using the ¹H NMR spectroscopic techniques reported by Bochmann and co-workers. In our hands, the addition of pyridine to these samples (ca 2:1 pyridine/Al) in subsequent analysis by ¹H NMR spectroscopy was not satisfactory; phase separation was observed, leading to very low estimates of [Me₃Al(py)]+ content (0.22 and 0.15 mol%), but more consistent values were obtained for Me₃Al content (14.0 and 15.6 mol%) for samples received in September 2013 and January of 2014, respectively.

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rich, underestimates [Me₂Al]⁺ 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 [Me₃Al(THF)]²⁺ and [Me₂Al(THF)₂]⁺. Evidently, the Me₃Al content of MAO purchased from the same lot increased slightly with time (from 11 to ca. 13 mol%), whereas the [Me₂Al]⁺ content decreased significantly (from 1.2 to ca. 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.

Ionization of [Cp₂ZrMe₂]

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 [(Cp₂ZrMe)₂(μ-Me)]⁺ (2⁺) (Figure 1a). At higher Al/Zr ratios, the heterodinuclear cation [Cp₂Zr(μ-Me)₂AlMe₂]⁺ (4⁺) predominates (Figure 1b–c) in agreement with earlier spectroscopic studies.[3–5] Variable amounts of the parent metallocenium ion [Cp₂ZrMe]⁺ with m/z 235 are detected. Qualitatively, it would appear that this ion is increasingly favored at sufficiently high Al/Zr ratios, although this behavior is not always observed (cf. Figure 1 with Figure 9, below).

The isotope patterns (Figure 1, insets) 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 + H₂O → CH₄), either in solution or due to an ion–molecule reaction in the source of the mass spectrometer. The sterically saturated dinuclear ions 2⁺ and 4⁺ are much more resistant to this reaction.

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.[21] Adjusting the 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 AlMe₃ (Figure 2).

Surprisingly, at constant CV, the relative amounts of 3⁺ and 4⁺ appeared insensitive to the Me₃Al content of the MAO used. To further clarify this issue, an additional amount of Me₃Al (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. The relative amounts of 3⁺ and 4⁺ are essentially unchanged (Figure 3). This result suggests there is already enough “free” Me₃Al present in this batch of MAO to completely sequester the metallocenium ion as the adduct,[22] 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 [Cp₂ZrMe₂] have masses in the range 1000–3000 Da. The mass spectra of
The appearance of these spectra is also very sensitive to CV, with the anions able to fragment through loss of one or, at most, two Me₃Al molecules. Some anions, such as that at m/z 1811, are resistant to this process, whereas others, such as that at 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 Me₃Al, although 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(23) revealed a total of ten losses of Me₃Al as the collision energy is systematically increased. Eight of the ten losses occur at relatively low energies (Figure 5), 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 Me₃Al 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 one or, at most, two 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(10c) with perhaps an average of one Me₃Al molecule being bound in this form.

If this is indeed the case for the anions, our original formulae require modification; for example, if the anion at m/z 1853 with formula [(MeAlO)n(Me₃Al)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, for example, [(MeAlO)n(Me₃Al)nAlMe]_{n-6}(MeAlMe)⁻. In other words, the cage-like anions might 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.(16)
be comprised of a mixture of linear and cyclic aluminoxide oligomers. Certainly there is evidence for both of these being present in MAO.\(^5\)

### 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 Me\(_3\)Al 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 \([\text{Cp}_2\text{ZrMe}]_2\) by either of two processes. One possible precursor to this anion is (MeAlO\(_n\))(MeAl)\(_m\) which might react to form the ion pair \([\text{Cp}_2\text{Zr}(\mu-\text{Me})\text{AlMe}]_2[\text{MeAl(OAlMe)}]_n[\text{Me}_2\text{Al}]_m\text{Me}\) through \([\text{MeAl}]^+\) abstraction, or an alternate precursor (MeAlO)\(_n\)(MeAl)\(_m\) could form the ion pair \([\text{Cp}_2\text{ZrMe}]_2[\text{MeAl(OAlMe)}]_n[\text{Me}_2\text{Al}]_m\text{Me}\) through methide abstraction.

These two processes have been studied in detail for the case of (MeAlO)\(_n\)(MeAl)\(_m\) (\(n=1,2\)) and have been shown to be equivalent in the sense that the contact ion pair \([\text{Cp}_2\text{ZrMe}]_2[\mu-\text{Me}(\text{MeAlO})_n\text{MeAl}]\) is the global minimum.\(^6\) However, the cage-like precursor featuring two Me\(_2\)Al molecules is predicted to be significantly more stable than those having only one or none (\(\Delta\Delta G= -9.0\) or \(-15.6\text{ kJ mol}^{-1}\)) so the process of \([\text{MeAl}]^+\) 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 Me\(_3\)Al at equilibrium.\(^9\) 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)\(_n\)(MeAl)\(_m\) (\(m=1–8, n=0–5\)) and the energetics of hydrosylation of Me\(_2\)Al by computational methods.\(^8\) We have studied the full configurational space up to the formation of pentameric structures (\(m=5\)). For \(m=5\), the study of the full configurational space is not practical; that process involved thousands of calculations. For \(m=5–8\) we employed an approximation, whereby only the reactions of the lowest energy isomers at each stage of the Me\(_3\)Al hydrosylation were followed, thus omitting the (very real) possibility that a higher energy species at one step could 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 to be 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)\(_n\)(MeAl)\(_m\). In terms of elementary species, the overall reaction for its formation is:

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

The optimized structure of (MeAlO)\(_n\)(MeAl)\(_m\) that we ended up with (5; Figure 6a) reveals an extended cage structure in accordance with previous findings.\(^9\) The model structure obtained for (MeAlO)\(_n\)(MeAl)\(_m\) is one of the many possible iso-ners 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)\(_n\)_\_cage,\(^9\) for example, often used as a reference, it is favored by 8.6 kJ mol\(^{-1}\) per MeAl unit.

An obvious structural feature is the presence of two Me\(_2\)Al molecules bound to Me\(_2\)Al 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 bridging methyl groups (Me\(_b\)) is Al–Me\(_b\) = 2.134(38) Å vs. Al–Me\(_t\) = 1.955(3) Å for the terminal methyl groups (Me\(_t\)) in these two units.

At the other end of the cage, there are two quasi-tetrahedral Me\(_2\)Al units involved in much weaker bridging interactions with nearby Me groups with Al(3)–Me\(_b\) = 2.2955 and Al(4)–Me\(_b\) = 2.3575 Å, respectively, for the dashed lines depicted in Figure 6b. Unlike the datively bound Me\(_2\)Al molecules, these Me\(_2\)Al 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 Me\(_2\)Al groups...
have "latent" Lewis acidity, which might be relieved through methide abstraction from \( \text{[Cp}_2\text{ZrMe}_2] \).

Since these sites are inequivalent, there are two possible anions that could be formed via methide or chloride (see below) abstraction reactions. Two of the anions that form by reaction at \( \text{Al}(3) \) have the general structure shown in Figure 7 a and b, and in one simplified view can be thought of as adducts between \( \text{Me}_3\text{Al} \) or \( \text{Me}_2\text{AlCl} \) and an anionic aluminoxane cage. These molecules still feature a weak residual \( \text{Al}--\text{Me}_n \) interaction with \( \text{Al}(4)\text{--C} \) distances of 2.405 and 2.429 Å, respectively.

The two isomeric anions formed by methide or chloride abstraction at the other site \( \text{Al}(4), \) Figure 6 b) are analogous but feature much more strongly bridged \( \text{Me} \) groups with \( \text{Al}--\text{Me}_n = 2.177 \) and 2.0977 Å and \( \text{Al}--\text{Me}_n = 2.0915 \) and 2.1775 Å (Figure 8 a and b). 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 \( \text{Me}_3\text{Al} \) site featuring the weakest bridging interaction, \( \text{Al}(4) \), also gives rise to the most stable anion, although the energy difference is largely due to formation of stronger bridges to the remaining unsaturated \( \text{Me}_3\text{Al} \) group.

Ionization of \( \text{[Cp}_2\text{ZrCl}_2] \)

In comparison to the studies described above, activation of \( \text{[Cp}_2\text{ZrCl}_2] \) by MAO is a more complicated process since two processes are involved in catalyst activation, alkylation and ionization. It is suspected that \( \text{Me}_3\text{Al} \) (free or associated with MAO) is responsible for monoalkylation of the catalyst and thus the \( \text{Me}_3\text{Al} \) content of the MAO in addition to the \( \text{Al}/\text{Zr} \) ratio is expected to have an impact on the activation process. Also, the byproduct of monoalkylation, namely \( \text{Me}_2\text{AlCl} \), is known to modify MAO and based on FT-IR studies, it would appear it readily displaces bound \( \text{Me}_3\text{Al} \) in doing so.

At low \( \text{Al}/\text{Zr} \) 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 \( ([\text{Cp}_2\text{ZrMe})_2(\mu-\text{Cl})]^+ \) with \( m/z \) 505 (Figure 9 c) 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 \( \text{[Cp}_2\text{ZrCl}_2] \). On the other hand, a more recent study concerned with activation of (2-Ph-Ind)\(_2\text{ZrCl}_2 \) concludes an analogous ion pair is formed at lower \( \text{Al}/\text{Zr} \) ratios. We thus suspect this is a general phenomenon.
is remarkably the same [Al] 20:1 Al/Zr ratio. Also, in this case, ion speciation is sensitive to solvent polarity. When activation is conducted in pure toluene solution, relative to a 1:1 mixture of that solvent and PhF, dinuclear cations are disfavored in comparison to mononuclear cations at otherwise identical Al/Zr ratios and total concentrations (Figure 9b, inset). Evidently, ionization and alkylation occur at competitive rates, although the rate of the former reaction is understandably more sensitive to solvent polarity.

Having said that, the results are largely counterintuitive if the mechanism for catalyst activation follows that shown in Equations (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 mechanism for catalyst activation follows that shown in Equations (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.

In addition, small quantities of dinuclear cations with m/z 525 and 489 are detected (Figure 9c; see also Scheme 2). The former contains one additional Cl atom based on the isotope pattern and is formulated as (Cp2ZrMe)(μ-Cl)ZrCl(Cp)\(^+\), whereas the latter corresponds to the CH-activation product (Cp2Zr(μ-Cl)(μ-CH3)ZrCl)\(^+\) or an isomer (Cp2Zr(μ-C5H5)(μ-Cl)Zr(μ-Cl)Zr(μ-Cl)Cp)\(^+\) (Scheme 2). There is ample precedent for such C–H activation chemistry in related studies using other Group 4 complexes\(^{26}\) but, to our knowledge, this is the first time this species has been detected in MAO-activated zirconocene dichloride complexes.

If dilute solutions of [(Cp2ZrMe)(μ-Cl)]\(^+\) are allowed to stand at room temperature, the cation with m/z 489 slowly increases in concentration at the expense of cation 2a\(^+\). If more concentrated solutions are prepared, for example, by reaction of MAO with solid [Cp2ZrCl2], not only is [Cp2Zr(μ-Cl)(μ-CH3)ZrCl]\(^+\) prevalent, but a further C–H activation product at m/z 473 is detected, which 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,\(^{27}\) formed by C–H activation of a remaining Cp ring.

At higher Al/Zr ratios, the dinuclear cation 2a\(^+\) is remarkably persistent, in comparison to the situation for [Cp2ZrMe]+ (cf. 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 [Cp2ZrCl]\(^+\) and suggests that ionization of either the catalyst precursor or the monoaIlylated product [Cp2Zr(μ-CH3)Cl], formed in situ, can occur upon reaction with MAO.\(^{28}\)

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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 [Cp2ZrMe]+ (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 20 Da, corresponding to replacement of an AlMe group by an AlCl moiety.

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 [Cp2ZrMe]+ 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 Me3Al readily via CID, are also most prone to chlorination; this is best appreciated by comparing the intensity at m/z 1853 with that at 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 [Cp2ZrCl] 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), 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.

We previously noted the formation of chlorinated anions when using MAO and [Bu₄N][Cl] as an additive. Qualitatively similar effects were noted, although the resulting anion distribution was quite different (i.e., chloride is a less-discriminating base than [Cp₂ZrCl₂]), 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 attributed the formation of chlorinated anions as resulting from reaction of the byproduct of ion exchange [Me₂AlCl; Equation (4)] with MAO via redistribution reactions involving bound Me₂Al.[14] Evidently, this process is more efficient in the case of [Cp₂ZrCl₂].

Finally, we also investigated the use of [Cp₂Zr(Me)Cl] as a precursor, as this complex is known to be the principal product of alkylation of [Cp₂ZrCl₂] by MAO (or Me₃Al). At identical Al/Zr ratios, this complex gives a significantly higher proportion of mononuclear cations (cf. Figures 12 and 9) than does [Cp₂ZrCl₂]. Specifically, when compared under identical conditions of concentration and solvent polarity etc. about half as much MAO is needed to activate [Cp₂Zr(Me)Cl] compared to [Cp₂ZrCl₂] (Figure 13 c and d) where the positive ion spectra are nearly identical.

Figure 11. Ion intensity (mole fraction) as a function of Al/Zr ratio for the anions with m/z 1853, 1873, and 1893. Data for total Cl per mole based on the relative intensities of the peaks at m/z 1873, 1893 and 1913 (not shown), weighted by the number of Cl atoms for each ion. The curves are exponential or logarithmic fits to the observed data and are intended as a guide for the eye only.

Figure 12. Positive-ion mass spectra of MAO and [Cp₂Zr(Me)Cl] in PhF at various Al/Zr ratios: a) 500:1; b) 100:1; c) 50:1; d) 20:1.
this complex ionizes by nearly exclusive formation of \([\text{Cp}_2\text{Zr(Me)}]^{+}\) rather than \([\text{Cp}_2\text{ZrCl}]^{+}\).

We also investigated a 1:1 mixture of \([\text{Cp}_2\text{Zr(Cl)}\text{Me}]\) and \(\text{Me}_2\text{AlCl}\) in comparison to \([\text{Cp}_2\text{ZrCl}_2]\) 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 \([\text{Cp}_2\text{ZrCl}_2]\) and \(\text{Me}_3\text{Al}\) (excess) were pre-mixed prior to activation with MAO.

Unfortunately, the reaction between \(\text{Me}_3\text{Al}\) and \([\text{Cp}_2\text{ZrCl}_2]\) to furnish a mixture of \([\text{Cp}_2\text{ZrMe(Cl)}]\) and \(\text{Me}_2\text{AlCl}\) is an equilibrium reaction, which can be approached from either direction;\(^{29}\) evidently, the \(\text{Me}_2\text{AlCl}\) produced on ionization of (pure) \([\text{Cp}_2\text{Zr(Me)}\text{Cl}]\) is less effective for chlorination of the anions derived from MAO, whereas the combination of \([\text{Cp}_2\text{ZrCl}_2]\) and \(\text{Me}_3\text{Al}\) or \([\text{Cp}_2\text{ZrMe(Cl)}]\) and \(\text{Me}_2\text{AlCl}\) is more effective. A complex between the latter two compounds, \([\text{Cp}_2\text{Zr(Me)(Cl)}\text{AlMe}_2\text{Cl}]\), 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.\(^{21}\) MAO serves several functions during polymerization catalysis, including catalyst alkylation and 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 \(\text{Me}_3\text{Al}\) content of MAO in commercially available solutions is variable, at around 10–20 mol % (of which ca. 75 % is readily available “free” \(\text{Me}_3\text{Al}\)),\(^{10c}\) so a larger excess of MAO is needed compared to simple alkylaluminum 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 between soluble and 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 \([\text{Cp}_2\text{ZrCl}_2]\),\(^{30}\) but not for the other catalyst precursors studied here.

Our studies, and also those by NMR spectroscopy involving activation of \([\text{Cp}_2\text{ZrMe}_2]\), suggest that catalyst activation is largely complete at much lower Al/Zr ratios (typically 100:1), than those used to activate metallocene dichloride complexes. It is known that complexes that are alkylated require much less MAO for high activity in, for example, 1-hexene polymerization.\(^{31}\) In contrast, ion pairing is sensitive to Al/Zr ratio where the limiting dimensions as measured by, for example, diffusion measurements, reveal aggregation at higher absolute Zr concentration.\(^{4c, 32}\) Indeed, based on the invariance of the anion distribution in these reactions to Al/Zr ratio in the case of \([\text{Cp}_2\text{ZrMe}_2]\), 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 \([\text{Cp}_2\text{ZrMe}_2]\).

The current work, involving the activation of \([\text{Cp}_2\text{ZrCl}_2]\), has revealed that the homodinuclear 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–C 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 that 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 \([\text{Cp}_2\text{ZrCl}_2]\) and \([\text{Cp}_2\text{ZrMe(Cl)}]\) as...
chlorination of \([\text{Cp}_2\text{ZrCl}_2]\) do not occur in the simple sequential MS results; in particular, the monoalkylation of \([\text{Cp}_2\text{ZrCl}_2]\) between the first and second process, in agreement with the ESI-1395, respectively. Note the significant difference in energy between the first and second process, which results in chlorination of the latter is competitive with conventional alkylation by Me_3Al [Equation (7)].

\[
\begin{align*}
\Delta G & = -28.7 \text{kJ mol}^{-1} \\
[\text{Cp}_2\text{ZrCl}_2] & + \text{Me}_3\text{Al} \rightarrow [\text{Me}(\text{Al})(\text{C})]\text{Cl} \\
\Delta G & = -5.9 \text{kJ mol}^{-1} \\
[\text{Cp}_2\text{ZrClMe}] & + \text{Me}_3\text{Al} \rightarrow [\text{Me}(\text{Al})(\text{C})]\text{Me} \\
\Delta G & = -16.6 \text{kJ mol}^{-1} \\
2[\text{Cp}_2\text{ZrCl}_2] & + 2\text{Me}_3\text{Al} \rightarrow 2[\text{Cp}_2\text{ZrClMe}] \\
\end{align*}
\]

As to the mechanism for chlorination, in particular, those anions that most readily lose Me_3Al by CID are also the most susceptible to chlorination (e.g., m/z 1853 vs. 1811). This observation initially suggested that it was Me_3AlCl, the byproduct of alkylation, that was the sole agent responsible for these anion modification reactions.

Indeed, if Me_3AlCl is added to solutions of MAO (51:1 Al/Cl ratio) and this mixture is used to activate \([\text{Cp}_2\text{ZrMe}_2]\) (100:1 Al/Zr), the anions present are extensively polychlorinated and even new anions are present that are not observed during activation of \([\text{Cp}_2\text{ZrCl}_2]\), whereas the corresponding positive-ion spectrum does not differ significantly (see the Supporting Information). The extent of polychlorination is much more advanced in the presence of this additive compared with \([\text{Cp}_2\text{ZrCl}_2]\) at the same Al/Cl ratio.

All of these results suggest that alkylation and subsequent ionization of \([\text{Cp}_2\text{ZrCl}_2]\) do not occur in the simple sequential manner depicted in Equations (1) and (2). In particular, they suggest that ionization and conventional alkylation by Me_3Al may occur as competitive processes, as suggested in Scheme 3, whereby the extent of anion chlorination by Me_3AlCl depends upon whether alkylation occurs prior to or after ion-pair formation.

Evidently, part of the reason that such a large excess of MAO is needed for activation of \([\text{Cp}_2\text{ZrCl}_2]\) reflects the complexity of this activation process, coupled with the instability of any dinuclear complexes formed, and changes to ion pairing that would naturally result from the presence of different anions at lower Al/Zr ratios. Although it may be coincidental in this case, the amounts of MAO needed to fully activate \([\text{Cp}_2\text{ZrCl}_2]\) while retaining the native anion distribution seen with \([\text{Cp}_2\text{ZrMe}_2]\) are typical of those used in a laboratory setting.

Conclusion

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 change dramatically as a function of the Al/Zr ratio in the case of \([\text{Cp}_2\text{ZrCl}_2]\), whereas, in the case of a fully alkylated precursor such as \([\text{Cp}_2\text{ZrMe}_2]\), 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 abundant, unless the ions are very similar in both molecular 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 \([\text{Cp}_2\text{ZrCl}_2]\) 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 swirled to dissolve any precipitated content prior to use. Fluorobenzene (Fluorochrome) was refluxed over CaH_2, distilled under N_2 and stored over 4 Å molecular sieves in a glove-box prior to use. \([\text{Cp}_2\text{ZrMe}_2]\) was purchased from Strem Chemicals and was purified by recrystallization from hot hexane containing excess AlMe_3 to remove traces of \([\text{Cp}_2\text{ZrMe}_2]\)O. \([\text{Cp}_2\text{ZrMe}(\text{Cl})]\) was prepared by a method reported elsewhere. \(^1\)H and \(^31\)P NMR spectra of MAO and THF solutions, or MAO and PPh_3 solutions were recorded on a Bruker Avance...
passing it through a manufacturer-installed feed-through. Capillary source, through tubing connected to the source compartment by tubing containing the 1H NMR spectrum of a MAO sample obtained from Sigma Aldrich. M.L. acknowledges support from the Academy of Finland (project no. 251448). The computations were made possible by use of the Finnish Grid Infrastructure resources.

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Keywords: electrospray ionization · mass spectrometry · metallocenes · methylaluminoxane · polymerization

[17] For earlier work employing ESI-MS to study metalloceneium ions or their use in olefin polymerization see: a) F. Rouholahnejad, D. Mathis, P.
This ion was also detected at high Al/Zr ratios in the case of [Cp₂ZrMe₂]- (see Figure 1 c) and in this case must result from reaction of for example, + 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.

For a discussion of this equilibrium and the species formed see ref. (14c) and references therein.


Variations on this mechanism have been proposed by workers at Albermarle in a number of conference abstracts: a) M. Li, S. Diefenbach, Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, March 16 – 20, 2014, CATL-197; b) L. Luo, S. Diefenbach, Abstracts of Papers, 245th ACS National Meeting & Exposition, New Orleans, LA, United States, April 7 – 11, 2013, CATL-65; c) L. Luo, S. Diefenbach, Conference Abstr., Advances in Polyolefins (ACS), Santa Rosa, CA, 2011.

If the mechanism shown in Scheme 3 is correct, it can be estimated that a 100:1–200:1 ratio of Al/Zr is needed to initially ionize [Cp₂ZrCl₂]- using the MAO employed in this study with a total [Me₂Al]- content of between 0.5 and 1.2 mol%.

