

Mass Spectrometry

Mass Spectrometric Characterization of Methylaluminoxane-Activated Metallocene Complexes

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Abstract: Electropray-ionization mass spectrometric studies of poly(methylaluminoxane) (MAO) in the presence of $[\text{Cp}_2\text{ZrMe}_2]$, $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$, and $[\text{Cp}_2\text{ZrCl}_2]$ 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 metallocene 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 $[(\text{MeAlO})_x(\text{Me}_3\text{Al})_{y-z}(\text{Me}_2\text{AlCl})_z\text{Me}]^-$ ($z = 1, 2, 3 \dots$) are observed using metal chloride complexes and under some conditions may predominate over their non-halogen-

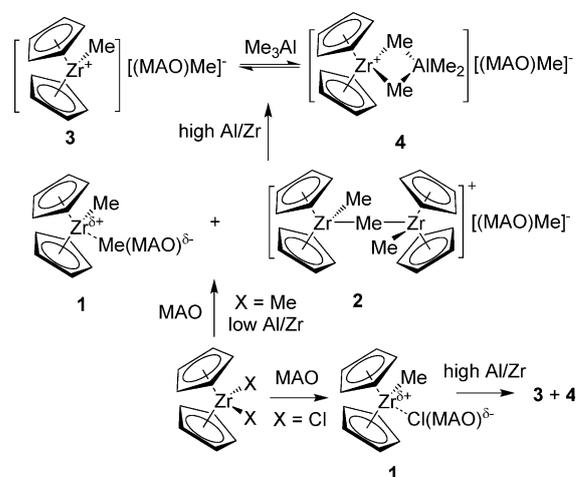
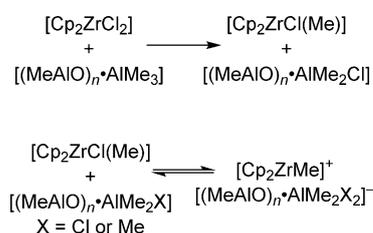
ated precursors $[(\text{MeAlO})_x(\text{Me}_3\text{Al})_y\text{Me}]^-$. Specifically, this halogenation process appears selective for the anions that form in comparison to the neutral components of MAO. Only at very high Al/Zr ratios is the same "native" anion distribution observed when using $[\text{Cp}_2\text{ZrCl}_2]$ when compared with $[\text{Cp}_2\text{ZrMe}_2]$. Together, the results suggest that the need for a large excess of MAO when using metallocene dichloride complexes is a reflection of competitive alkylation vs. ionization, the persistence of unreactive, homodinuclear ion pairs in the case of $[\text{Cp}_2\text{ZrCl}_2]$, 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 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,^[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 Me_3Al adduct **4** pre-



Scheme 1. Ion pairs formed on activation of $[\text{Cp}_2\text{ZrX}_2]$ by MAO.

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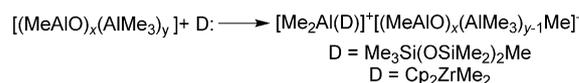
dominates at highest Al/Zr ratios with sterically unhindered metallocene complexes. The relative amount of the various species present is dependent on the zirconocene structure, the use of dimethyl vs. dichloride complexes, the Me₃Al content, and possibly even the source of the MAO used. The basic conclusions of these studies have been corroborated by UV/Vis spectroscopic methods,^[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.^[6] 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,^[2c,7] although more recent studies suggest such cages will be a very minor component of MAO relative to much larger strain-free cages.^[8]

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.^[9] 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,^[10] while metallocene precursors with donor ligands, such as [Cp₂Zr(OMe)₂], also form adducts, such as [Cp₂Zr(μ-OMe)₂AlMe₂][MAO(X)].^[10b,11] Compounds featuring donor-stabilized versions of this cation are known to activate metallocene complexes towards olefin polymerization.^[10a,12] Theoretical studies suggest that electrophilic Me₂Al moieties bonded to MAO are competent for these reactions,^[10c] while it has been known for some time that such structures (i.e., Lewis acidic Me₂Al groups) are present in MAO, as evidenced by ESR spectroscopy in conjunction with the spin label donor TEMPO.^[13]

Although 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 Me₂AlCl as an additive, it is clear from IR spectroscopy^[14] that the neutral components of MAO undergo chlorination reactions—for example, by exchange of bound Me₃Al for Me₂AlCl^[14a]—and implicit from NMR or other spectroscopic studies that contact ion pairs formed at low Al/Zr ratios may feature chlorinated anions (Scheme 1). Chlorinated aluminoxanes can be prepared by the controlled hydrolysis of Me₂AlCl, have been structurally characterized, and are competent cocatalysts for olefin polymerization using, for example, TiCl₄.^[15] In contrast, the ion pairs formed at low Al/Zr ratios using commercial MAO solutions (containing “free” Me₃Al) and metallocene dichlorides are largely inactive for hexene polymerization,^[5a,b,16] and fully chlorinated MAO, formed by modification of MAO using excess Me₂AlCl, was unable to activate [Cp*₂ZrCl₂] for olefin polymerization.^[14c]

Recently, we reported the first studies of MAO by use of electrospray-ionization mass spectrometry (ESI-MS)^[17] in the presence of a variety of donors, including [Cp₂ZrMe₂] 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 [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).



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 ³¹P NMR spectroscopy^[10c] 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 Me₃Al and [Me₂Al]⁺ content using the ¹H NMR spectroscopic techniques reported by Bochmann and co-workers.^[10c] In our hands, the addition of pyridine to these samples (ca 2:1 pyridine/Al) and subsequent analysis by ¹H NMR spectroscopy was not satisfactory; phase separation was observed, leading to very low estimates of [Me₂Al(py)₂]⁺ 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).

Use of excess THF (ca. 4:1 THF/Al) 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 [Me₂Al(THF)₂]⁺ and [Me₃Al(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 [Me₃Al(L)] and [Me₂Al(L)₂]⁺, respectively. It is known that pyridine titration often overestimates Me₃Al content,^[19] so the latter results are considered more reliable and they show that the pyridine method, at least for MAO obtained from Sigma-Al-

drich, underestimates $[\text{Me}_2\text{Al}]^+$ 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 $[\text{Me}_3\text{Al}(\text{THF})]$ and $[\text{Me}_2\text{Al}(\text{THF})_2]^+$. Evidently, the Me_3Al content of MAO purchased from the same lot increased slightly with time (from 11 to ca. 13 mol%), whereas the $[\text{Me}_2\text{Al}]^+$ 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 $[\text{Cp}_2\text{ZrMe}_2]$

These results have been reported elsewhere,^[18] but are reiterated here in greater detail (Figure 1). At Al/Zr ratios of 50:1 or

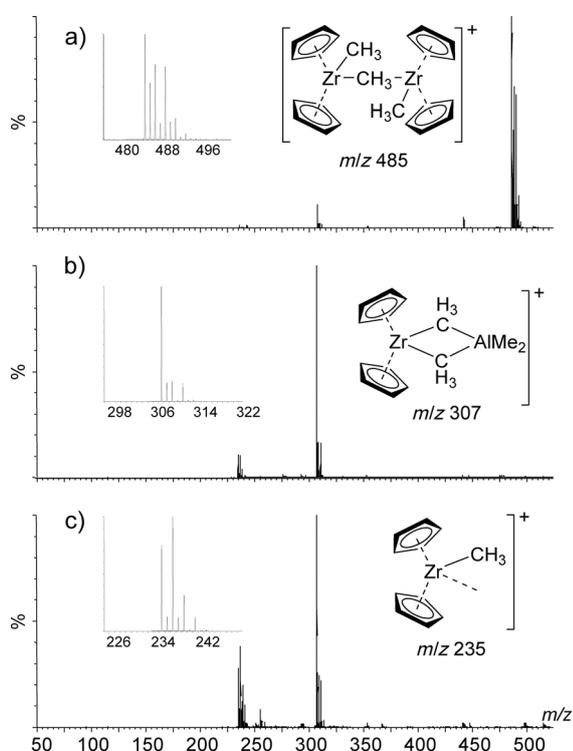


Figure 1. Positive-ion mass spectra of MAO + $[\text{Cp}_2\text{ZrMe}_2]$ in PhF ($[\text{Al}] = 0.05 \text{ M}$) at various Al/Zr ratios: a) 25:1; b) 100:1; c) 500:1. Insets: Iso-topo patterns and structures for major ions of interest.

lower, the dominant cation is $[(\text{Cp}_2\text{ZrMe}_2)(\mu\text{-Me})]^+$ (2^+) (Figure 1a). At higher Al/Zr ratios, the heterodinuclear cation $[\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$ (4^+) predominates (Figure 1b–c) in agreement with earlier spectroscopic studies.^[3–5] Variable amounts of the parent metallocenium ion $[\text{Cp}_2\text{ZrMe}]^+$ with m/z 235 (3^+) 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., $M + \text{H}_2\text{O} - \text{CH}_4$), 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 \approx 100:1) leads to essentially complete conversion of 4^+ to 3^+ via loss of AlMe_3 (Figure 2).

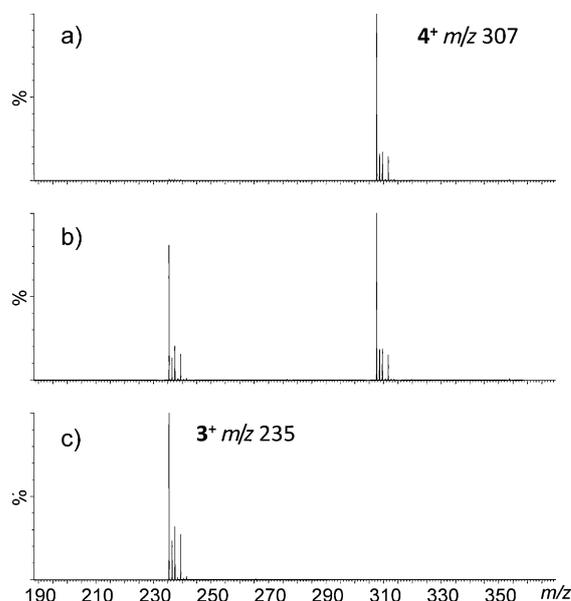


Figure 2. Positive-ion ESI-MS of MAO + $[\text{Cp}_2\text{ZrMe}_2]$ in PhF (100:1 Al/Zr) at various cone voltages: a) 8 V; b) 16 V; c) 32 V.

Surprisingly, at constant CV, the relative amounts of 3^+ and 4^+ appeared insensitive to the Me_3Al content of the MAO used. To further clarify this issue, an additional amount of Me_3Al (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” Me_3Al 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 $[\text{Cp}_2\text{ZrMe}_2]$ have masses in the range 1000–3000 Da. The mass spectra of

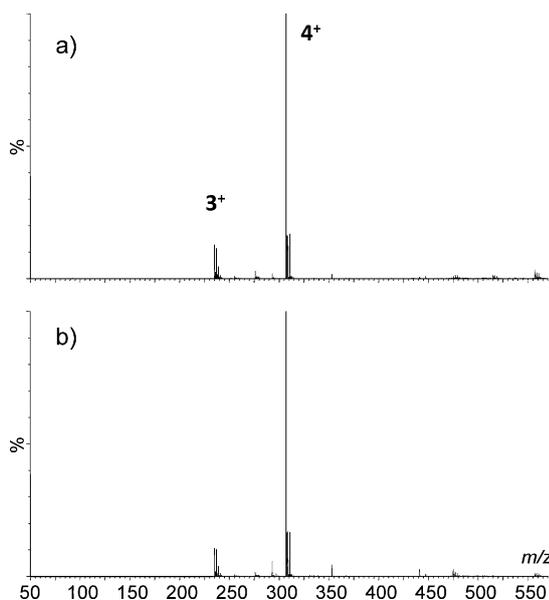


Figure 3. Positive-ion mass spectra of $[\text{Cp}_2\text{ZrMe}_2]$ in PhF in the presence of a) MAO (100:1 Al/Zr) + 19 mol% added Me_3Al and b) MAO (100:1 Al/Zr) as supplied (containing 19 mol% total Me_3Al as determined by ^{31}P NMR spectroscopy).

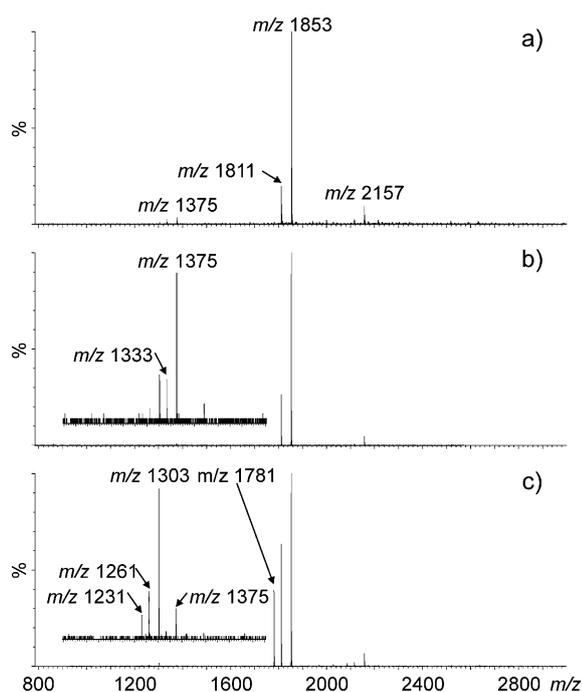


Figure 4. Negative-ion ESI-MS of MAO and $[\text{Cp}_2\text{ZrMe}_2]$ in PhF: a) Al/Zr = 300:1; b) Al/Zr = 100:1; c) the same sample as (b) recorded at a CV of 32 V vs. 16 V, showing prominent $[M-72 \text{ Da}]$ (i.e., $[M-\text{Me}_3\text{Al}]$) peaks at m/z 1781, 1303, 1261, and even two Me_3Al losses at m/z 1231 (Inset to Figure 4c).

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.^[18]

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 Me_3Al 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 Me_3Al , 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 Me_3Al as the collision energy is systematically increased. Eight of the ten losses occur at relatively low energies (Figure 5), suggesting at least two different

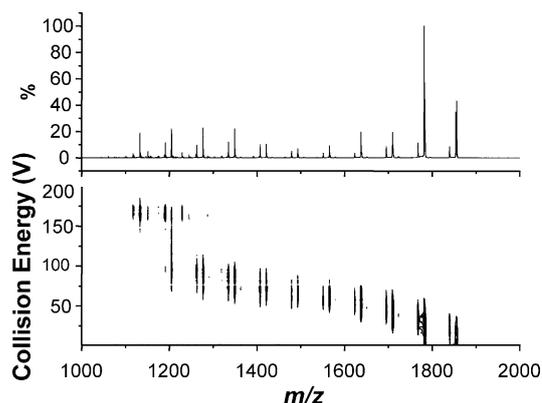


Figure 5. ED-ESI-MS/MS spectrum of the anion at m/z 1853 with the conventional MS/MS spectrum shown at top. Two series of fragment ions due to loss of Me_3Al appear, separated by 14 Da, because the parent ions at m/z 1853 (M^+) and 1855 ($M+2$) were both mass selected in this experiment. The latter ions, which contain one AIOH group (and one fewer AlMe group), also fragment by loss of CH_4 .

processes that result in fragmentation. In examining the conventional MS/MS spectrum, it is seen that loss of the first Me_3Al 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 Me_3Al , with the remaining fragmentations resulting from much more strongly bound Me_3Al molecules, or resulting from rearrangement of these anions. It is important to emphasize that the true amount of bound Me_3Al is of importance in correctly formulating these anions and thus their ultimate structure. Other experimental and theoretical work suggests that the amount of bound Me_3Al per neutral molecule of MAO is also variable,^[10c] with perhaps an average of one Me_3Al 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 $[(\text{MeAlO})_{23}(\text{Me}_3\text{Al})_7\text{Me}]^-$ only contains one molecule of bound Me_3Al , then the remaining 6 molecules dictated by MS/MS studies must result from rearrangement and an alternate formulation is, for example, $[(\text{MeAlO})_5[\text{Me}(\text{MeAlO})_3-\text{AlMe}_2]_6(\text{Me}_3\text{Al})\text{Me}]^-$. 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.^[2]

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(Me₃Al)₇, which might react to form the ion pair [Cp₂Zr(μ-Me)₂AlMe₂][{Me₂Al(OAlMe)₄Me₂(Me₃Al)₂-Me}] through [Me₂Al]⁺ abstraction, or an alternate precursor (MeAlO)₁₆(Me₃Al)₆ could form the ion pair [Cp₂ZrMe₂][{Me₂Al(OAlMe)₄Me₂(Me₃Al)₂Me}] through methide abstraction.

These two processes have been studied in detail for the case of (MeAlO)₈(Me₃Al)_{*n*} (*n* = 1,2) and have been shown to be equivalent in the sense that the contact ion pair [Cp₂ZrMe₂][μ-Me(MeAlO)₈(Me₃Al)] is the global minimum.^[9] However, the cage-like precursor featuring two Me₃Al molecules is predicted to be significantly more stable than those having only one or none ($\Delta\Delta G = -9.0$ 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 Me₃Al 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)_{*m*}(Me₃Al)_{*n*} (*m* = 1–8, *n* = 0–5) and the energetics of hydrolysis of Me₃Al by computational methods.^[8d,9] 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 Me₃Al hydrolysis 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)₁₆(Me₃Al)₆. In terms of elementary species, the overall reaction for its formation is:



The optimized structure of (MeAlO)₁₆(Me₃Al)₆ that we ended up with (**5**; Figure 6a) reveals an extended cage structure in accordance with previous findings.^[8b,c] The model structure obtained for (MeAlO)₁₆(Me₃Al)₆ is one of the many possible iso-

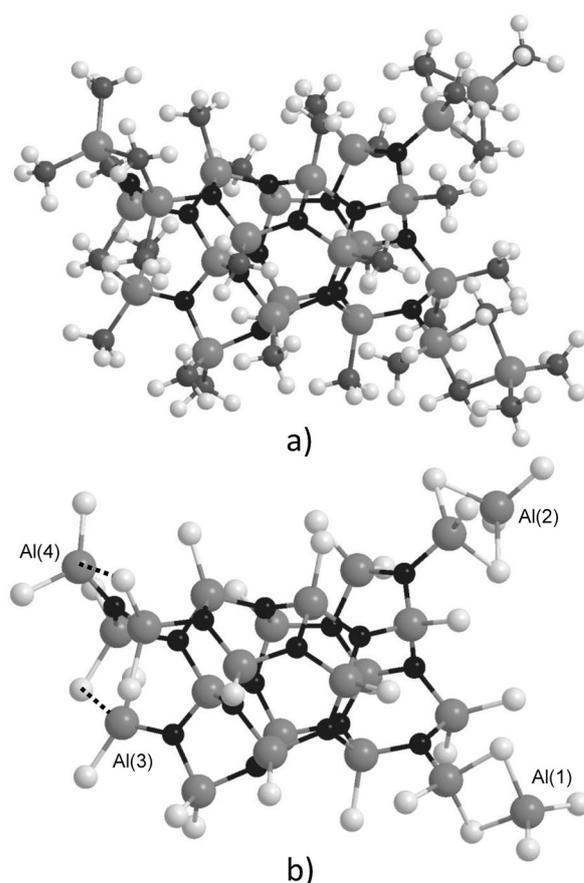


Figure 6. Optimized structure of one isomer of the molecule (MeAlO)₁₆(Me₃Al)₆ (**5**), a possible precursor for ionization of [Cp₂ZrMe₂]: a) Structure with all atoms depicted (Al light grey, O black, C dark grey, H white); b) structure with H atoms omitted, datively bound Me₃Al units labelled Al(1) and Al(2), and strained Me₂Al units labelled Al(3) and Al(4) with weak bridging interactions denoted by dashed lines (Al light grey, O black, C white).

mers 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,^[7] 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 Me₃Al molecules bound to Me₂Al end groups, with the former labelled 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_{br}) is Al–Me_{br} = 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 Me₂Al units involved in much weaker bridging interactions with nearby Me groups with Al(3)–Me_{br} = 2.2955 and Al(4)–Me_{br} = 2.3575 Å, respectively, for the dashed lines depicted in Figure 6b. Unlike the datively bound Me₃Al 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 acidity,^[6] 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 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 Me_3Al or Me_2AlCl and an anionic aluminoxane cage. These molecules still feature a weak residual $\text{Al}-\text{Me}_{\text{br}}$ interaction with Al(4)–C distances of 2.405 and 2.429 Å, respectively.

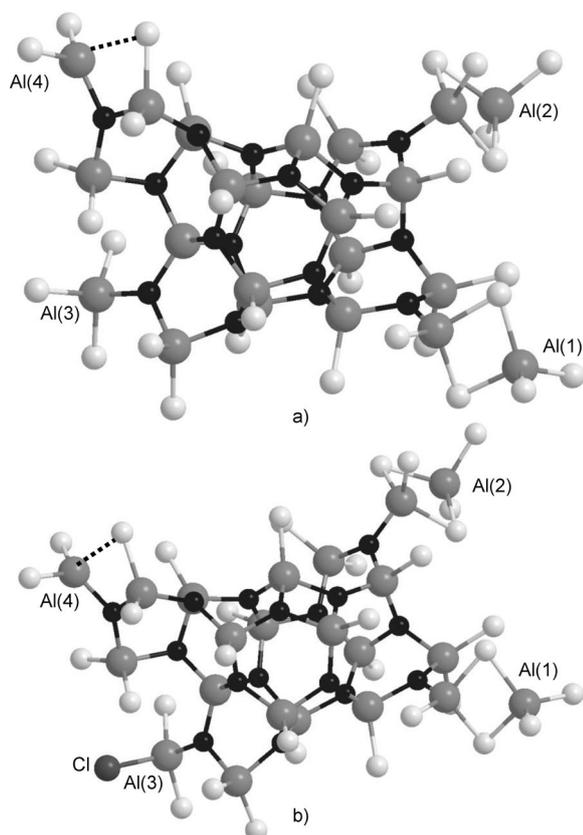


Figure 7. a) Optimized structure of the anion formed from **5** by the process of methide abstraction involving Al(3). The one remaining weak bridging interaction is denoted by a dashed line; b) optimized structure of the anion formed from **5** by the process of chloride abstraction involving Al(3). (Al light grey, Cl dark grey, O black, C white).

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 $\text{Al}-\text{Me}_{\text{br}}=2.177$ and 2.0977 Å and $\text{Al}-\text{Me}_{\text{br}}=2.0915$ 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 Me_2Al site featuring the weakest bridging interaction, 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 Me_2Al group.

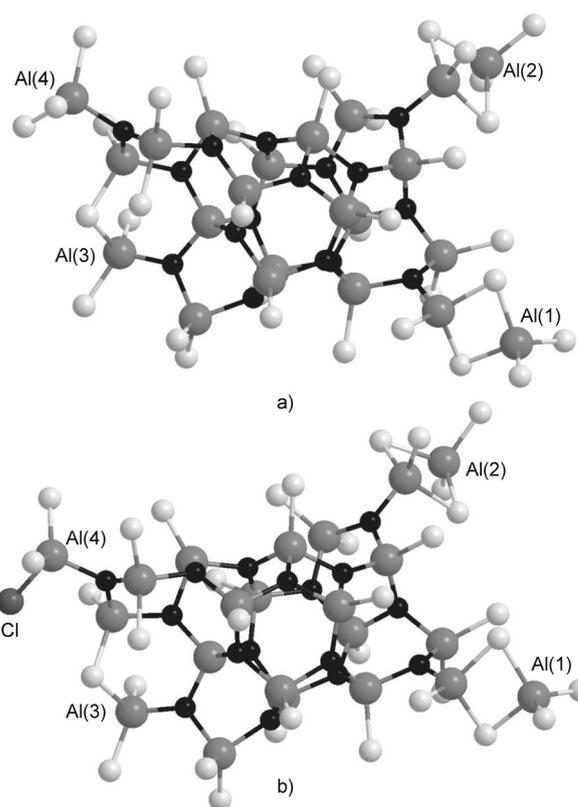


Figure 8. a) Optimized structure of the anion formed from **5** by the process of methide abstraction involving Al(4); b) optimized structure of the anion formed from **5** by the process of chloride abstraction involving Al(4). (Al light grey, Cl dark grey, O black, C white).

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 Me_3Al (free or associated with MAO) is responsible for monoalkylation of the catalyst and thus the Me_3Al content of the MAO in addition to the Al/Zr ratio is expected to have an impact on the activation process. Also, the byproduct of monoalkylation, namely Me_2AlCl , is known to modify MAO and based on FT-IR studies,^[14] it would appear it readily displaces bound Me_3Al in doing so.

At low Al/Zr ratios of 50:1, ESI-MS spectra revealed a somewhat unexpected outcome in comparison to prior work.^[4a] 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 (**2 a⁺**; 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,^[24] 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 $(2\text{-Ph-Ind})_2\text{ZrCl}_2$ concludes an analogous ion pair is formed at lower Al/Zr ratios.^[25] We thus suspect this is a general phenomenon.

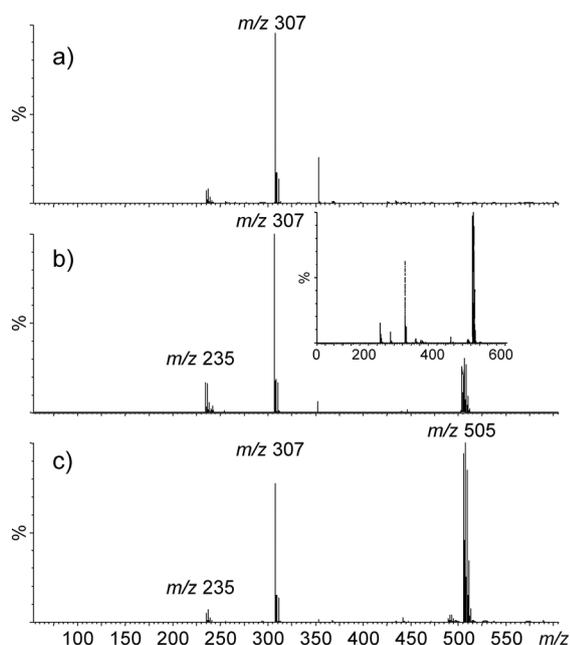
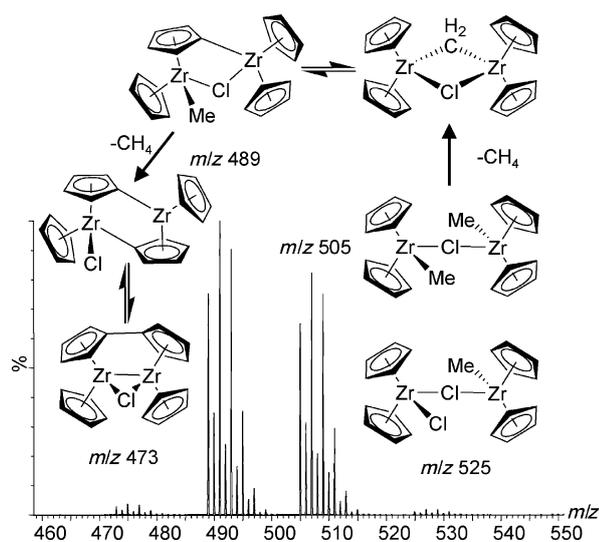


Figure 9. Positive-ion ESI-MS of MAO + $[\text{Cp}_2\text{ZrCl}_2]$ in PhF at a) 500:1, b) 100:1, and c) 50:1 Al/Zr ratios. Inset to Figure 9b shows spectrum of a mixture of MAO + $[\text{Cp}_2\text{ZrCl}_2]$ prepared in a 1:1 v/v mixture of toluene and PhF at the same $[\text{Al}] = 0.75 \text{ M}$ and Al/Zr ratio.



Scheme 2. Dinuclear cations formed from $[\text{Cp}_2\text{ZrCl}_2]$ and MAO in concentrated toluene solution (solid $[\text{Cp}_2\text{ZrCl}_2]$ + 10 wt % toluene solution of MAO) at a 20:1 Al/Zr ratio.

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 $[(\text{Cp}_2\text{ZrMe})(\mu\text{-Cl})\text{Zr}(\text{Cl})\text{Cp}_2]^+$, whereas the latter corresponds to the CH-activation product $[\text{Cp}_2\text{Zr}(\mu\text{-Cl})(\mu\text{-CH}_2)\text{ZrCp}_2]^+$ or an isomer $[\text{Cp}_2\text{Zr}(\sigma\text{-C}_5\text{H}_4)(\mu\text{-Cl})\text{Zr}(\text{Me})\text{Cp}]^+$ (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 $[(\text{Cp}_2\text{ZrMe})_2(\mu\text{-Cl})]^+$ 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 $[\text{Cp}_2\text{ZrCl}_2]$, not only is $[\text{Cp}_2\text{Zr}(\mu\text{-Cl})(\mu\text{-CH}_2)\text{ZrCp}_2]^+$ 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 $[\text{Cp}_2\text{ZrMe}_2]$ (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 $[\text{Cp}_2\text{ZrCl}]^+$ and suggests that ionization of either the catalyst precursor or the monoalkylated product $[\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}]$, formed in situ, can occur upon reaction with MAO.^[28]

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 spectra (Figure 10c) are barely recognizable compared to those observed upon activation of $[\text{Cp}_2\text{ZrMe}_2]$ (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 $[\text{Cp}_2\text{ZrMe}_2]$ 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_3Al 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 $[\text{Cp}_2\text{ZrCl}_2]$ added, with respect to total MAO. In the specific case of the anion at m/z

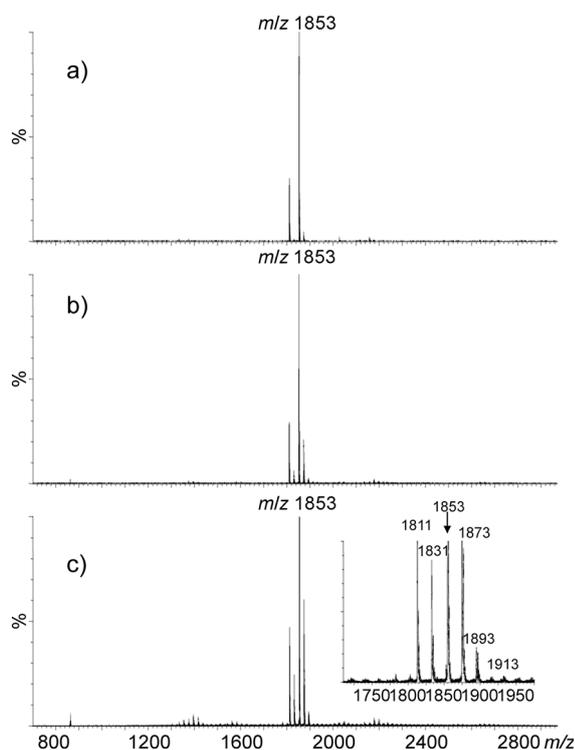


Figure 10. Negative-ion mass spectra of MAO and $[\text{Cp}_2\text{ZrCl}_2]$ at a) 500:1, b) 100:1, and c) 50:1 Al/Zr ratios. Inset to Figure 10c shows expansion of the mass spectrum showing anions arising from chlorination of the species at m/z 1853 and 1811.

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 con-

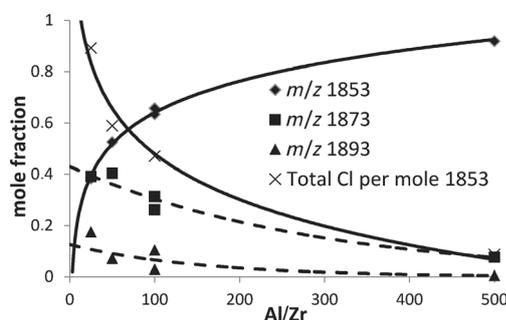
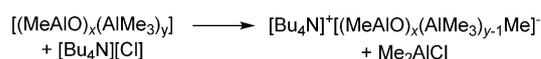


Figure 11. Ion intensity (mole fraction) as a function of Al/Zr ratio for the anions with m/z 1853, 1873, and 1893. Data for total Cl per mole based on the relative intensities of the peaks at m/z 1873, 1893 and 1913 (not shown), weighted by the number of Cl atoms for each ion. The curves are exponential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

clusion 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 $[\text{Bu}_4\text{N}][\text{Cl}]$ as an additive.^[18] Qualitatively similar effects were noted, although the resulting anion distribution was quite different (i.e., chloride is a less-discriminating base than $[\text{Cp}_2\text{ZrCl}_2]$), 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 attributed the formation of chlorinated anions as resulting from reaction of the byproduct of ion exchange $[\text{Me}_2\text{AlCl}]$; Equation (4)] with MAO via redistribution reactions involving bound Me_3Al .^[14] Evidently, this process is more efficient in the case of $[\text{Cp}_2\text{ZrCl}_2]$.



Finally, we also investigated the use of $[\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}]$ as a precursor, as this complex is known to be the principal product of alkylation of $[\text{Cp}_2\text{ZrCl}_2]$ by MAO (or Me_3Al). At identical Al/Zr ratios, this complex gives a significantly higher proportion of mononuclear cations (cf. Figures 12 and 9) than does

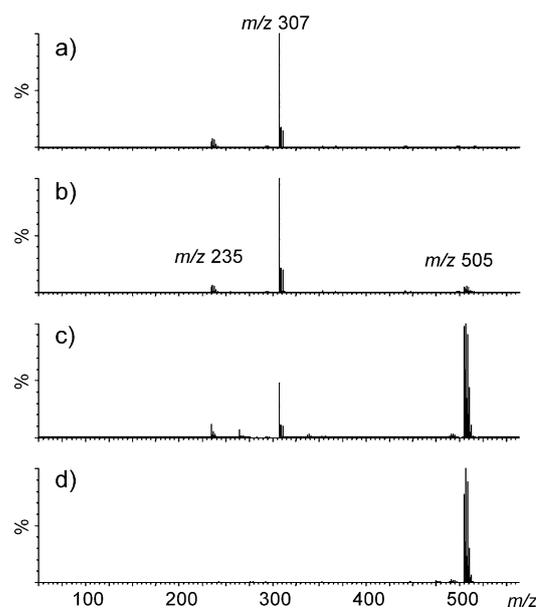


Figure 12. Positive-ion mass spectra of MAO and $[\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}]$ in PhF at various Al/Zr ratios: a) 500:1; b) 100:1; c) 50:1; d) 20:1.

$[\text{Cp}_2\text{ZrCl}_2]$. Specifically, when compared under identical conditions of concentration and solvent polarity etc. about half as much MAO is needed to activate $[\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}]$ compared to $[\text{Cp}_2\text{ZrCl}_2]$ (Figure 13c and d) where the positive ion spectra are nearly identical.

Furthermore, at identical Al/Cl ratios this complex is much less effective in forming chlorinated anions than $[\text{Cp}_2\text{ZrCl}_2]$ (cf. Figure 13a and b), despite the fact that a similar amount of Me_2AlCl should be formed in both reactions as a byproduct. Also, neither the cation with m/z 525 nor 255 is present in significant amounts when using $[\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}]$, suggesting that

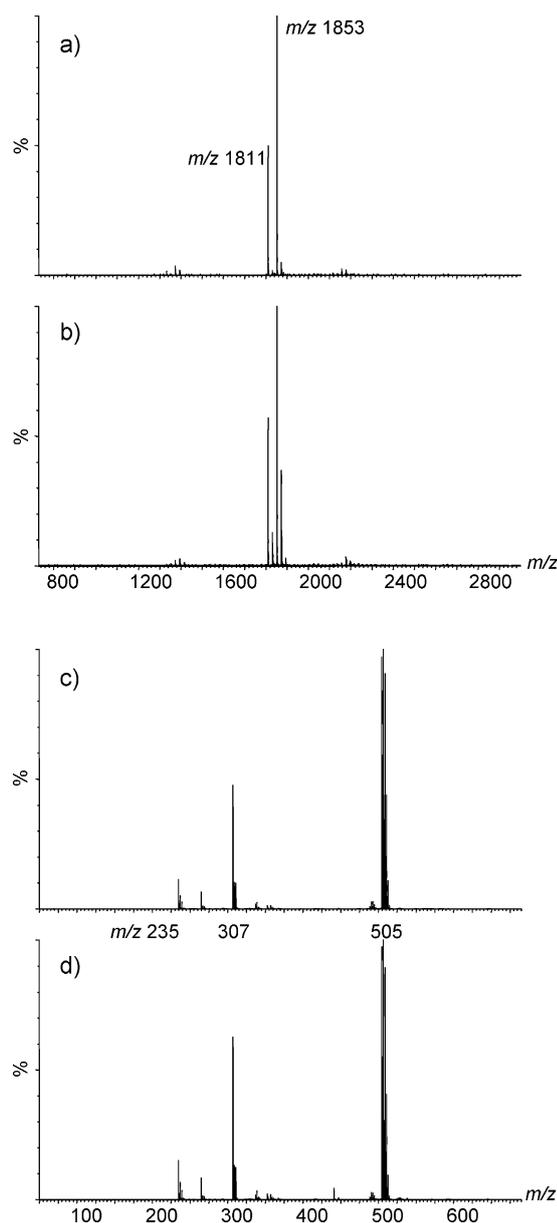


Figure 13. a) and c) Negative- and positive-ion mass spectra of mixtures of MAO and $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$ at a 50:1 Al/Zr ratio prepared in a 1:1 mixture of toluene and PhF. b) and d) Negative- and positive-ion mass spectra of mixtures of MAO and $[\text{Cp}_2\text{ZrCl}_2]$ at a 100:1 ratio prepared in a 1:1 mixture of toluene and PhF.

this complex ionizes by nearly exclusive formation of $[\text{Cp}_2\text{ZrMe}]^+$ rather than $[\text{Cp}_2\text{ZrCl}]^+$.

We also investigated a 1:1 mixture of $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$ and Me_2AlCl 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 Me_3Al (excess) were pre-mixed prior to activation with MAO.

Unfortunately, the reaction between Me_3Al and $[\text{Cp}_2\text{ZrCl}_2]$ to furnish a mixture of $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$ and Me_2AlCl is an equilibrium reaction, which can be approached from either direc-

tion;^[29] evidently, the Me_2AlCl produced on ionization of (pure) $[\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}]$ is less effective for chlorination of the anions derived from MAO, whereas the combination of $[\text{Cp}_2\text{ZrCl}_2]$ and Me_3Al or $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$ and Me_2AlCl is more effective. A complex between the latter two compounds, $[\text{Cp}_2\text{Zr}(\text{Me})(\mu\text{-Cl})\text{AlMe}_2\text{Cl}]$, has been detected by IR spectroscopy.^[29]

Discussion

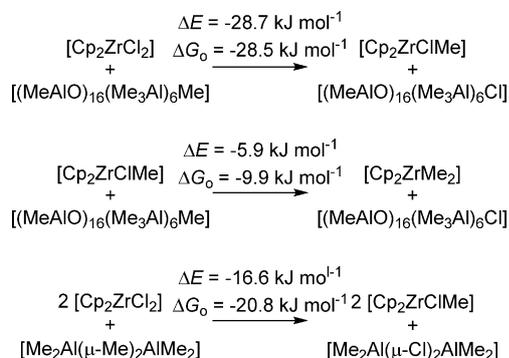
The need for a large excess of MAO for catalyst activation has been attributed to a number of factors.^[2] MAO serves several functions during polymerization catalysis, including catalyst alkylation and ionization and as a scavenger of poisons present in the solvent or monomers used. Under practical conditions, the last of these roles is actually fairly important. The Me_3Al content of MAO in commercially available solutions is variable, at around 10–20 mol% (of which ca. 75% is readily available “free” $\text{Me}_3\text{Al}^{[10\text{c}]}$), 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–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 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 $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$ as

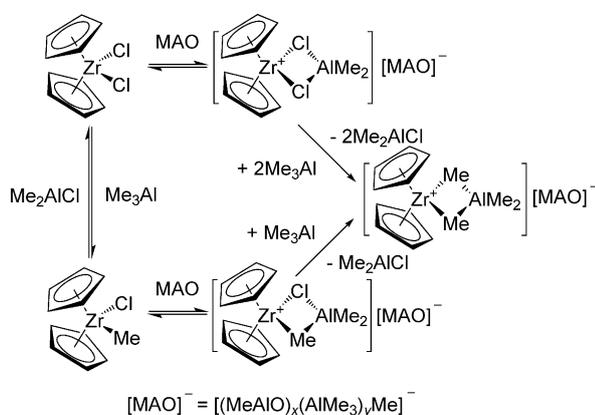
chlorinating agents [Equations (5) and (6)] using the most stable anions (Figure 8) identified in the case of m/z 1375 and 1395, respectively. Note the significant difference in energy between the first and second process, in agreement with the ESI-MS results; in particular, the monoalkylation of $[\text{Cp}_2\text{ZrCl}_2]$ by an anion (which results in chlorination of the latter) is competitive with conventional alkylation by Me_3Al [Equation (7)].



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_2AlCl , the byproduct of alkylation, that was the sole agent responsible for these anion modification reactions.

Indeed, if Me_2AlCl 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,^[33] whereby the extent of anion chlorination by



Scheme 3. Alkylation vs. ionization of $[\text{Cp}_2\text{ZrCl}_2]$ by MAO.

Me_2AlCl 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,^[34] 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.^[35] 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 (Fluorochem) 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 $[(\text{Cp}_2\text{ZrMe}_2)_2\text{O}]$. $[\text{Cp}_2\text{ZrMe}(\text{Cl})]$ was prepared by a method reported elsewhere.^[36] ^1H and ^{31}P NMR spectra of MAO and THF solutions, or MAO and PPh_3 solutions were recorded on a Bruker Avance

500 MHz instrument using 5–10 vol% [D₆]benzene as a lock solvent using procedures reported elsewhere.^[10c]

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 metallocene 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) to give the desired Al/Zr ratio (10:1–1000:1). After 15–30 min at room temperature, an aliquot was removed and diluted with dry PhF 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 Micromass QTOF *micro* spectrometer, with a Z-spray electrospray ionization source, through tubing connected to the source compartment by passing it through a manufacturer-installed feed-through.^[37] Capillary voltage was set at 2900 V, source and desolvation gas temperatures were at 70–90 °C and 140–175 °C, respectively. Desolvation gas flow rate was typically 200–400 Lh⁻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 became coated with an electrically insulating deposit of aluminosilicate 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. Baking out of the source compartment under a flow of N₂ desolvation gas for several hours is required before the instrument can be used again for these experiments.

Theoretical calculations of neutral and anionic MAO molecules were based on techniques described elsewhere.^[8,9] 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 $T=298.15$ K and $p=101\,325$ Pa. No scaling factors were applied.

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Keywords: electrospray ionization • mass spectrometry • metallocenes • methylaluminumoxane • polymerization

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