Activation of Substituted Metallocene Catalysts Using Methylaluminoxane

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Introduction

Group 4 metallocene- or other transition metal-catalyzed olefin polymerization probably constitutes one of the most widely studied modern processes of industrial significance.[1] Following its initial discovery, research activity focused on the use of methylaluminoxane (MAO) or related activators as these combine alkylation, scavenging, and activation in one activator.[2] Subsequent development of alternate methods of activation involving Lewis acidic perfluoroarylboranes in combination with di-alkylated metallocenes,[3] or ternary systems featuring metallocene dichlorides, [Ph₂Cp₂][B(C₆F₅)₄][4] or [R₂NH][B(C₆F₅)₄][5] activators, and aluminum alkyls, including MAO, as scavenging and alkylating agents. These and other studies shed great insight into the structure and behavior of the catalytically active metallocene ion species.[6] Now, a variety of alternate activators are available, featuring yet more weakly coordinating anions,[7] and most recently also combining catalyst alkylation, ionization and scavenging as with MAO.[8]

At the same time, extensive spectroscopic studies have been used to study the activation process in the case of MAO,[9,10,11,12] where the efficacy of the catalyst generated in situ is dependent on both the catalyst precursor, as well as the Al/Zr ratio used for catalyst activation.[9,12] In the case of unhindered dimethylated precursors (Scheme 1), one possible activation process involves ionization by methide [Me⁻] abstraction (highlighted in red) by Lewis acidic components of MAO to form an adduct 1, which reacts with excess Cp₂ZrMe₂ to form the outer-sphere, dinuclear ion-pair 2 at low Al/Zr ratios.

At higher Al/Zr ratios, these species are transformed into a mixture of two ion-pairs, an outer-sphere ion-pair featuring the homodinuclear cation 3 in equilibrium with a “loose” contact ion-pair featuring the mononuclear cation 4. This equilibrium, and that between 2 and contact ion-pairs like 1, is sensitive to the structure of the metallocene. Cation 3 might also form directly from MAO by a different ionization mechanism, first reported in the patent literature,[14] but subsequently studied by NMR spectroscopy,[15] and DFT methods.[16] This involves abstraction of a [Me₂Al]⁻ moiety (highlighted in blue) from a suitable site on MAO, and these sites are thought to be most important in MAO that contains free Me₂Al.[15]

[BuCp₂ZrMe₂AlMe₂][MAO(Me)] 3 and deactivated ((BuCp₂Zr)₂[μ-H]₃CH₃)[μ-C][MAO(Me)] 9 complexes were detected in leaching experiments using a SiO₂-MAO-supported BuCp₂ZrCl₂ catalyst and excess MAO. DFT studies of the structure and UV-Vis spectra calculated for the dinuclear cations 9 detected by ESI-MS suggest that these species may account for long-wavelength absorption seen in experimental spectra of complexes like BuCp₂ZrCl₂ upon activation with MAO.

Scheme 1. Ionization of Cp₂ZrMe₂. Methide [Me⁻] abstraction highlighted in red. [Me₂Al]⁻ abstraction highlighted in blue.

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In the case of metallocene dichlorides, mono-alkylation occurs involving either free Me$_2$Al or structural Me$_3$Al$^{[19]}$ in the case of MAO physically or chemically$^{[20]}$ depleted of free Me$_2$Al. The evidence for this was based on pioneering UV-Vis studies of EBIZrCl$_2$ catalyst activation where a hypsochromic shift, consistent with mono-alkylation is seen at low Al:Zr ratios, followed by a bathochromic shift, consistent with ionization at higher Al:Zr ratios.$^{[20]}

Ionization is thought to involve reaction of Cp$_2$Zr(Me)Cl with Lewis acidic components of MAO forming initially poorly active, contact ion-pairs with chlorinated, MAO-based anions (Scheme 2), while at higher Al:Zr ratios these poorly characterized species are transformed into the ion-pairs 3 (and 4) shown in Scheme 1. By analogy, dinuclear Zr$_2$ ion-pairs featuring a µ-Cl bridge (5) form at lower Al:Zr ratios, and these have been detected in favorable cases.$^{[20]}

An alternate mechanism of activation has been proposed more recently, largely on the basis of model studies using metallocone dichlorides, excess Me$_2$Al and [Ph$_3$C][B(C$_6$F$_5$)$_2$]$_2$ as an activator.$^{[21]}$ In these model systems, the metallocone dichloride is directly ionized to form ion-pair 6, which is then alkylated by excess Me$_2$Al to form ion-pair 3, presumably involving the intermediary of [Cp$_2$ZrCl(Me)(Me)AlMe]$_3$ (7), though this cation has not been detected. Ion-pairs 6 have been characterized in both the solid state$^{[22]}$ and solution.$^{[22]}

The by-product of this sequence, as well as the first, involving conventional alkylation and then ionization, is dimeric Me$_2$AlCl and this additive is known to displace structural Me$_2$Al from MAO and impede metallocone dichloride activation when present in significant amounts.$^{[23]}$ On the other hand, as reported in the patent literature, related additives such as (Me$_2$AlF)$_n$ or (Me$_2$AlOCF$_3$)$_2$ are known to increase the [Me$_2$Al]$^+$ activator content of MAO,$^{[14b]}$ while (Me$_2$AlF)$_n$ or related compounds can separately activate alkylated metallocone catalysts.$^{[26]}

ESI-MS has also been used to study the activation process involving MAO.$^{[25]}$ The outer sphere ion-pairs with cations 2, 3, 5 and 7 have been detected using this technique in fluorobenzene (PhF) solvent, following activation in toluene media. Neither we nor others have detected ion-pairs 6 in these studies despite the sensitivity of this technique.

These studies also shed insight into MAO-based anion composition, though unfortunately the earliest studies involved the use of commercial MAO that was both aged$^{[26]}$ and oxidized.$^{[27]}$ More recent DFT and ESI-MS studies using neutral donor (i.e. Lewis base) additives show that the major anion present in commercial$^{[26]}$ or synthetic,$^{[28]}$ hydrolytic MAO has the composition [(MeAlO)$_n$(Me$_2$Al)$_m$Me]$^-$ (hereinafter $^{[16,6]}$) and likely possesses a 2-dimensional sheet structure,$^{[29]}$ featuring a chelated, anionic Me$_2$Al–Me–AlMe$_3$ moiety. Further, these studies reveal that MAO and the anions formed from it are susceptible to chlorination by either the metallocone dichloride precursor, or the Me$_2$AlCl by-product,$^{[24,25]}$ and to modification by AlR$_3$,$^{[30]}$ where polymerization studies involving the latter indicate both catalyst activity and polymer MWD are affected.$^{[31]}

The studies discussed above are based on catalyst activation in solution. Yet, it is appreciated that supported catalysts are widely used commercially, and in the case of metallocone catalysts this is usually accomplished by using silica, impregnated with MAO and a metallocone dichloride complex.$^{[32]}$ With supported catalysts diffuse reflectance UV-Vis (DR UV-Vis) spectroscopy is a sensitive method to relate supported catalyst speciation$^{[33]}$ to activation in solution, especially when model complexes and the activation process have been studied using this technique.$^{[34]}

Moreover, it is also well known that supported metallocone catalysts of this type are susceptible to leaching in the presence of additional MAO, especially when that contains free Me$_2$Al.$^{[22,23]}$ Studies of this type suggest that the active species that leach from the support are similar to the corresponding soluble catalyst but to our knowledge definitive proof for this concept has not been presented.

Recently ion-pairs analogous to 3 and 6 were invoked as major species present on a SiO$_2$–MAO supported (1-“Bu-3-Me-n”-C$_3$H$_7$)$_2$ZrCl$_2$ catalyst.$^{[36]}$ The assignment of 6 (and 3) was based on deconvolution of the DR UV-Vis spectra as a function of the Al:Zr ratio using a library of possible metallocone structures and their calculated spectra. Other possible species such as ion-pairs 2 and 5, or their decomposition products (vide infra) were not included in this study.

In this paper we study metalloocene ion-pair speciation during MAO activation of BuCp$_2$ZrCl$_2$ and EBIZrCl$_2$, precursors by ESI-MS in solution. Activation of these or related precursors have been widely studied by other spectroscopic techniques both in solution and also supported on SiO$_2$–MAO, and there are some useful trends to document compared with the Cp$_2$ZrCl$_2$ system studied earlier. We then relate these results to the ion-pairs which leach out from a SiO$_2$–MAO supported BuCp$_2$ZrCl$_2$ catalyst showing that both active and deactivated species are susceptible to this process. Finally, we also study the

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**Scheme 2.** Activation of Cp$_2$ZrCl$_2$. [Me$_2$Al]$^+$ abstraction processes in blue, [Cl]$^-$ abstraction in green.
cations summarized in Schemes 1 and 2 and others detected by ESI-MS using TD DFT calculations and simulate their UV-Vis spectra.

**Results and Discussion**

**Structure of dinuclear ions 2, 5 and 8**

To our knowledge, only complexes 2 featuring a μ-CH₃ group have been characterized by X-ray crystallography, though a complex analogous to 5, but featuring a μ-F atom has been structurally characterized for a substituted, ansa-Me₆CCp(Flu)Zr complex.[34] In both cases, the Zr–X–Zr moiety features a near linear arrangement in the solid state. It is known from solution NMR work that the μ-CH₃ group is approximately sp³ hybridized based on the magnitude of 1JCH[35,36]. Recently, DFT calculations on a wide variety of complexes 2 confirm these experimental details.[37]

On the other hand, as reported elsewhere for adducts of [(η⁵-Cp)₂Zr][MeB(C₆F₅)₃] with either Cp₂ZrCl₂ or (η⁵-Cp)ZrCl the Zr–Cl–Zr linkage is bent to varying degrees at Cl.[38]

In this work we examined the structure of these complexes at the M06-2X/TZVP level of theory and determined two stable geometries for complexes 2, gauche and syn-periplanar, as shown in Scheme 3. We also examined the μ-F analog of complex 5 and determined that a linear anti geometry was adopted in both gas and condensed phase (see Supporting Information). However, both complexes 5 and 8 adopt geometries which are bent at the bridging Cl to varying degrees depending on substitution of the Cp rings.

This preference for a bent geometry is retained even at the highest levels of theory based on single-point CCSD(T) calculations at the M06-2X/TZVP optimized geometry (Supporting Information, Table S-1). Considering that several months of processor time was involved in these calculations, the calculations are at the practical limit of what can be achieved using modern, parallel processors.

Since the barriers to interconversion of these conformers are low (< 10 kJ mol⁻¹ for 5, ca. 2 kJ mol⁻¹ for 2) the adoption of a linear vs. a bent geometry may have a steric component that is as important as any possible π-character to the Zr–X bonds. We do note that the frontier molecular orbital (FMO) analogy between bent vs. linear AH₂ molecules and these structures, as proposed by Erker and co-workers, is strictly applicable when both metalloocene fragments are coordinately and electronically unsaturated.

**Metallocene catalyst activation**

As mentioned in the introduction, activation of Cp₂ZrX₂ (X=Me, Cl) is complicated by formation of homo-dinuclear Zr₂ complexes at low Al:Zr ratios. In the case of Cp₂ZrCl₂ these are more persistent in solution when compared with Cp₂ZrMe₂ at higher Al:Zr ratios. Moreover, complex 5 is unstable with respect to C–H activation forming both complex 9 and then 10a and/or 10b (indistinguishable by ESI-MS) via successive processes of this type (Scheme 4). During this period (ca. 15–30 minutes at room temperature in toluene with [Al] ~ 0.75 M) the initially clear or very pale yellow solutions develop long wavelength adsorption that tails off into the visible (yellow to orange).

As shown in Figure 1, the activation chemistry of BuCp₂ZrCl₂ is similar to that of Cp₂ZrCl₂ in the sense that a dinuclear ion with m/z 729 containing one Cl atom (and another at m/z 749 containing two, Figure 1c) dominates at low Al:Zr ratios and which persists in solution at higher Al:Zr ratios (Figure 1b). At high Al:Zr ratios, an ion with m/z 419 dominates though lesser amounts of two ions with m/z 347 and 331 are present (Figure 1a and 1b). Note that the intensity of those two ions, relative to m/z 419 is sensitive to the Al:Zr ratio used for catalyst activation (Figure 1b vs. 1a). Their intensity, with respect to each other and also to m/z 419, is also sensitive to cone voltage though is otherwise invariant with time (Supporting Information, Figure S-1).

Evidently, the ion-pair [BuCp₂ZrMe][MAO(Me)] is present in solution at higher Al:Zr ratios while the C–H activation product shown with m/z 331 might be formed from this ion-pair. This process is known for PrCp₂ZrMe₂ using either B(C₆F₅)₃ or [Ph₃C][B(C₆F₅)₄] activators and an isomer analogous to that shown is produced.[40]

DFT calculations on [BuCp₂ZrMe]⁺ indicate that the most stable structure has an agostic interaction with the β-CH₃ moiety of one Bu group (Supporting Information). The m/z 331 ion could be directly formed from this structure or an isomer.
Formation of the ion with m/z 331 and CH$_4$ from [BuCp$_2$ZrMe]$^+$ is exothermic by 7–23 kJ mol$^{-1}$, depending on which isomer is formed. The most stable product is the $\delta$-isomer.

We suspect this ion is formed on collision induced fragmentation of [BuCp$_2$ZrMe]$^+$ in gas phase as the amount relative to that ion is sensitive to cone voltage. Moreover, the amount of this ion does not increase with time at room temperature (at constant cone voltage) as would be expected if it were being formed in solution from [BuCp$_2$ZrMe]${[(\text{MAO})\text{Me}]}$. As with the Cp$_2$ZrCl$_2$ system, the dinuclear ion [([BuCp$_2$ZrMe]$\mu$-Cl)]$^+$ with m/z 729 is prone to C-H activation forming a species analogous to complex 9 with m/z 713, containing one Cl atom. This process was monitored by withdrawing aliquots as a function of time at a 25 : 1 Al : Zr ratio and has an initial half-life of ca. 80–90 minutes at room temperature (Supporting Information Figure S-3). Qualitatively this is somewhat slower than observed for the parent Cp$_2$ZrCl$_2$ system.

We did not observe this reaction for ion-pair 2 under the same conditions, nor even on prolonged standing at room temperature. To our knowledge this reaction has never been observed in solution at room temperature involving [L$\mu$-ZrMe]${[(\text{Me})]}$ complexes partnered with a weakly coordinating anion.$^{34,35,36,37}$ However, this $\alpha$-C–H activation reaction has been observed for cationic fulvalene$^{3}$ complexes of zirconium analogous to 2, and is thought to be a possible mechanism for metallocene catalyst deactivation.$^{42}$ Moreover, fulvalene complexes analogous to 9 have been prepared and their insertion chemistry studied.$^{43}$ They are not reactive towards olefin insertion polymerization.

It is likely the higher reactivity of 5 compared with 2 towards C–H activation may be due to the more favorable $\text{syn}$ or $\text{gauche}$ geometry for this process, as with fulvalene complexes, which of necessity must adopt a bent geometry at $\mu$-X.

Thus, we expect formation of complexes 9 in the case of dichloride complexes corresponds to a deactivation reaction unique to these precursors and which will be important whenever activation is incomplete at lower Al : Zr ratios. The MAO-based anions are chlorinated in the same manner and to similar extents as observed previously (Figure 2).$^{25}$ The chlorine content, relative to total anion intensity for [16,6]$^-$ and its chlorinated congeners, was determined by integration of the individual ion intensities, weighted by the number of chlorine atoms. The values are 0.24 ± 0.01, 0.59 ± 0.02 and 1.34 ± 0.02 for Al : Cl ratios of 250 : 1, 50 : 1 and 12.5 : 1, respectively.
Since 16,6 as 22 Al atoms, a statistical labeling of this anion with the Me₄AlCl by-product would produce chlorinated ions in the amounts of 0.088, 0.44 and 1.76 for these Al : Cl ratios. Evidently, the substitution of the 16,6 anion is occurring to a greater extent than predicted on a statistical basis at higher Al : Zr ratios, especially considering that the amount of structural Me₃Al incorporated into this anion is a fraction (ca. 27 %) of the total amount of Al. This indicates that anion chlorination is more facile than chlorination of the corresponding neutral components of MAO, and earlier experiments where MAO was treated with Me₄AlCl prior to vs. after activation of Cp₂ZrMe₂ support this conclusion.[25a] Note that higher m/z anions (e.g. 23,7) are more prominent at an Al : Zr ratio of 500 : 1 vs. 100 : 1 (Figure 2a vs. 2b). We saw this same trend on activation of Cp₂ZrMe₂.[25d] It is important to note that this behavior is not observed with neutral donors such as OMTS at similar Al : OMTS ratios.[26] Evidently, metalloence complexes are much more discriminating towards the Lewis acidic components of MAO, latent vs. otherwise.

It is also interesting to note that the reactivity of different anions towards the Me₄AlCl is not the same; for example the next most intense anion after 23,7 has m/z 1815 and based on its isotope pattern it is mono-chlorinated (Supporting Information, Figure S-2), suggesting the parent anion 22,7 is more reactive towards chlorination than 23,7 (or 16,6).

We also examined activation of EBizrCl₂, which is commonly used to study propene polymerization. Using a 30 wt % formulation of MAO activation of this complex involved somewhat different conditions in that it is sparingly soluble in toluene and so a slurry in toluene was treated with MAO (50 or 200 equiv.) and dissolution occurred rapidly at room temperature. The concentrated solution was then diluted with PhF prior to analysis.

As shown in Figure 3, even at a lower ratio of Al : Zr of 50 : 1 the only major ion detected [EBizrMe₂AlMe₂]⁺ has m/z 433. Vertical expansion of this spectrum shows two other weak ions with m/z 361 [EBizrMe⁺] and 757 [(EBizrMe)₂μ-Cl]⁺. At higher cone voltages the former ion was much more intense (Figure S-4) while the latter was unaffected and contained 1 Cl and 2 Zr atoms based on its isotope pattern (Figure S-5).

Formation of homo-dinuclear complexes is much less favorable for this ansa-metallocene (cf. Figure 3 with Figure 1b). Note that the amount of [EBizrMe⁺] relative to [EBizrMe₂AlMe₂]⁺ is significantly lower than for either Cp or BuCp complexes at similar concentrations and cone voltages (Supporting Information, Figure S-4). This finding is in qualita-
Leaching experiments using a silica-MAO supported BuCp2ZrCl2 catalyst

Supported catalysts prepared from BuCp2ZrCl2 and SiO2-MAO have been evaluated in ethylene polymerization as reported in detail elsewhere. This and related studies confirm that the supported catalysts are in the presence of additional MAO, especially if that material contains free Me3Al.

Following the literature procedure, a SiO2-MAO co-catalyst was prepared from PQ silica (MS 3040, 415 m2/g), calcined at 600 °C, and excess MAO (10 wt% solution) to give a material that was ≤17.5 wt% Al after washing and drying.

The supported co-catalyst was treated with BuCp2ZrCl2 in toluene at room temperature (Al/Zr = 100:1), thoroughly washed with toluene, and dried in vacuo to provide a supported catalyst as a pale yellow solid which analyzed as 12.25 wt% Al and 0.15 wt% Zr (surface Al/Zr ~ 250:1).

After a week of storage in a glove-box, the dried material was contacted with excess 10 wt% MAO in toluene (Al/Zr ~ 30:1), thoroughly washed with toluene, and stored in a PTFE filter. After 20 min, the resulting silica column was then eluted with dry toluene, and the eluate diluted to [Al] ~ 0.05 M with dry PhF prior to analysis by ESI-MS.

As shown in Figure 4, the resulting leachate is dominated by the cations [BuCp2ZrMe3AlMe2]+ with m/z 419 and [(BuCp2Zr)][μ-Cl][μ-CH3]+ with m/z 713. The former is expected to leach from the support as [BuCp2ZrMe3AlMe3][MAO(X)] and is precursor to the active catalyst, while the latter ion is not active. Since this ion is formed from [(BuCp2ZrMe3)][μ-Cl]+ (5 with m/z 729) in solution (vide supra), and yet this precursor is not detected in the leachate, the observed result suggest that [(BuCp2ZrMe3)][μ-Cl]+[MAO(X)] has undergone unimolecular C-H activation on the support or during preparation of the supported catalyst to provide [(BuCp2Zr)[μ-CH3][μ-Cl]][MAO(X)]. We do note that the initial fractions in these experiments were enriched in [BuCp2ZrMe3AlMe3]+ suggesting that this species or a precursor is more susceptible to leaching by excess MAO.

The corresponding negative ion spectrum of the leachate was similar to that observed upon activation of BuCp2ZrCl2 by a large excess of MAO (Supporting Information, Figure S-7 vs. Figure 2a). Evidently, even a large excess of MAO is unable to reconvert [(BuCp2Zr)[μ-CH3][μ-Cl]][MAO(Me)] in agreement with the hypothesis that its formation corresponds to an irreversible deactivation reaction.

It should be stated that while this experiment shows what species leach from a SiO2-MAO supported catalyst, it does not provide direct information as to catalyst speciation on the support. Consider the recent results of Velthoen et al. where the presence of ions analogous 3 and 6 was inferred from the DR UV-Vis spectrum. It is obvious that treatment of a mixture like this with a large excess of MAO would convert 6 to 3 and likewise 5 to 3 if any of that complex was also present (Scheme 5). Thus ESI-MS must be used in concert with other techniques such as DR UV-Vis to study supported catalysts further. In particular, the use of ESI-MS to monitor catalyst activation prior to supporting the MAO-catalyst mixture should be instructive.

TD DFT calculations of excitation energies

As mentioned in the introduction, soluble and supported catalysts have been widely characterized by UV-Vis spectroscopy though none of the homo-dinuclear Zr cations detected in this and previous ESI-MS studies have been characterized using this technique to our knowledge. One expects they may be important when activating unhindered metalloocene dichloride complexes at low Al/Zr ratios as shown here, and these
conditions correspond to those usually employed for supporting metalloocene complexes.

To that end we determined vertical excitation energies for the complexes shown in Scheme 4 and these are summarized in Table 1, for both the parent zirconocene complex, as well as the Bu-substituted systems studied here. Complete details for all neutral and charged species reported here, as well as elsewhere, are included as Supporting Information along with simulated UV-Vis spectra.

The dinuclear Cp, Zr complexes 2, 5, and 8 all show intense LMCT transitions in the region 290–320 nm (Table 1) and thus are probably not easily distinguished on that basis. There are weaker longer wavelength transitions at ca. 346, 357 and 363 nm for 2, 5 and 8, respectively shifted to longer wavelength with increasing chlorine content that tail into the blue end of the visible spectrum (Figure 5). The latter transitions involve extensive orbital mixing and are sensitive not only to the bridging and terminal groups but also to geometry, and to a lesser extent conformation. The situation is best discussed with reference to the natural transition orbitals involved.30

In the case of complex 2, which exists in syn or gauche linear conformers (gauche→syn ΔG = 2.2 kJ mol⁻¹ with a barrier of ca. 2 kJ mol⁻¹ between the two) with idealized C₂ or C₃ symmetry, this transition involves excitation of an electron from a terminal Zr–CH₂ bonding orbital on one Zr center to a more delocalized, orbital that however, involves mainly the same Zr atom. Since we did not enforce symmetry in the DFT or TD DFT calculations, this excitation occurs as two, near degenerate transitions at longest wavelengths for complexes 2 (Figure 5, blue curve and dashed lines).

In the case of the less symmetrical complexes 5 and 8 with a bent Zr–μ-Cl–Zr geometry, these adopt anti- and gauche-like conformers (anti→gauche ΔG = −5.5 kJ mol⁻¹ and −2.1 kJ mol⁻¹ for 5, and 8, respectively) this degeneracy is lifted and 3–4 transitions are seen at longest wavelengths which are however, related to those seen for 2 in that they involve excitation of terminal Zr–X bonding electrons, again mainly localized to one metal to empty orbitals of the same type. Further details are provided as Supporting Information.

Evidently, none of these complexes ought to be strongly colored and this is in keeping with the very pale yellow color of these solutions when first prepared.

On the other hand the C–H activation product 9 which forms from 5 (and also forms in the case of the BuCp analogue) does have long wavelength adsorption in the visible region with a HOMO-LUMO transition at 22345 cm⁻¹ (448 nm) with f = 0.0754. As shown in Figure 6, this excitation involves the HOMO which is localized to the Zr–CH₂–Zr bridge, and a LUMO which is delocalized over the entire complex but can be partly viewed

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**Table 1.** Wavelengths, and extinction coefficients for UV-Vis transitions for homo-dinuclear Cp and BuCp zirconocene complexes detected by ESI-MS.

| Cation | L₂ | X | Y | Z | λmax (nm) | εmax (×10⁶ M⁻¹ cm⁻¹) |
|-------|----|---|---|---|-----------|----------------------|
| 2     | Cp₂ | Me | Me | Me | 293 (2)   | 8.92, 3.59            |
| 5     | Cp₂ | Me | Cl | Cl | 308 (2)   | 5.85, 5.53            |
| 8     | Cp₂ | Me | Cl | Cl | 313 (2)   | 6.39, 4.75            |
| 2     | BuCp₂ | Me | Me | Me | 303 (3)   | 7.16, 5.67, 3.68      |
| 5     | BuCp₂ | Me | Cl | Cl | 326 (2), 352 | 14.9, 6.25, 3.33 |
| 8     | BuCp₂ | Me | Cl | Cl | 319, 336  | 5.30, 11.9            |
| 9     | Cp₁ | μ-CH₂ |     | Cl | 448      | 17.5                 |
| 9     | BuCp₁ | μ-CH₂ | Cl | Cl | 446      | 23.1                 |
| 10a   | Cp₁ | – | – | Cl | 464      | 11.6                 |
| 10b   | Cp₁ | – | – | Cl | 391      | 33.1                 |

[a] A complete list of complexes studied, their structures and calculated spectral data are included as Supporting Information. [b] For structures consult Scheme 4. [c] For the most intense LMCT transitions occurring in the region 285–750 nm. Where a value is shown with a number in parentheses, the latter refers to the number of nearly degenerate transitions that occur at the indicated wavelength.

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**Figure 5.** Simulated UV-Vis spectra of syn·[(Cp₂ZrX)(μ-ZrY=Cp₂)]⁺ 2 (blue curve: X=Y=Z=Me), gauche 5 (green curve: X=Y=Me, Z=Cl), and gauche 8 (red curve: X=Me, Y=Z=Cl) and depiction of the natural transition orbital involved in the longest wavelength transition for complex 2. Dashed lines are at the vertical excitation wavelengths and are proportional to oscillator strength.
as the in-phase combination of empty in plane dz^2 orbitals on each Zr.

There is a modest charge-transfer component to this transition (%Zr 16.8 to 38.4) but since the HOMO has no significant contribution from the Cp π orbitals, while they are only slightly involved in the LUMO, this transition is somewhat insensitive to the nature of those ligands (cf. trace for m/z 713, the Bu analogue).

The other complexes 10a and/or 10b detected in the case of Cp₂ZrCl₂ also have strong transitions with λ_{max} = 464 and 391 nm, respectively. Complex 10b, which contains two Zr(III) centers, has a low energy singlet S₀ state though the S₀→T₁ gap is very low in energy at 1065 cm⁻¹ compared with neutral Zr(III) complexes of this type. In fact, geometry optimization of the T₁ state at the MN15/def2-TZVP level indicates it will be lower than S₀ by 4.3 kJ mol⁻¹ and thus this complex may be paramagnetic.

The S₀ state shows very low energy adsorptions in the near IR region of the electromagnetic spectrum associated with the Zr-Zr interaction (Natural Bond Order = 0.747 with a Zr-Zr separation of 3.25 Å) with two low energy excitations at 4850 (HOMO-LUMO) and 10250 cm⁻¹ (HOMO-1 to LUMO). Theory suggests that structure 10b in the singlet state is favored over 10a by 6.2 kJ mol⁻¹ in gas phase.

Cations 10a and/or 10b were only detected in more concentrated solutions using a slurry of solid Cp₂ZrCl₂ and MAO with [Al]=1.5 M, and we did not detect them in activation reactions involving the BuCp analogue. DFT calculations suggest complexes 10a don’t form as readily from complexes 9 once the Cp ring is substituted (Supporting Information Table S-2). Our calculations indicate that these two isomers could be readily distinguished using UV-Vis or possibly ESR spectroscopy. Both structural motifs have been characterized on reduction of group 4 metalloocene complexes.

Structure and TD DFT calculations for [Cp₂ZrMe][MAO(Me)]

We have conducted TD DFT calculations on [Cp₂ZrMe]⁺ and other analogous cations detected in gas-phase by ESI-MS and the details are reported as Supporting Information. However, this data is not relevant to catalyst speciation in solution where this cation is paired with a counter-anion.

In the case of complexes 2 and 3 (and presumably 5–8) these are outer-sphere ion pairs in solution[6a] and we expect that the UV-Vis spectra are not as sensitive to the nature of the anion.[16] However, in the case of [Cp₂ZrMe]⁺ that will not be the case, and it is likely the ion-pair features a direct interaction with the counter-anion in the case of MAO.[16]

We recently reported a new sheet structure for the most stable activator present in hydrolytic MAO,[29] as well as the structure of the most stable anion formed from it.[28–29] It therefore seemed important to investigate the structure of the most stable species formed from e.g. Cp₂ZrMe₂ and this activator, and determine its UV-Vis spectrum.

The structure of this Lewis base-acid adduct is depicted in Figure 7 and it is analogous to those formed between this metalloocene and other models for MAO.[16] The terminal and bridging Zr–CH₂ distances are significantly different at 2.271 and 2.359 Å. There are some higher energy isomers which feature weaker interaction between Zr and the Al–Me group (e.g. Zr–CH₂ = 2.251 and 2.459 Å with ΔG = 11.9 kJ mol⁻¹) but their longest wavelength UV-Vis spectra are not significantly affected by this feature (Supporting Information).

Though the whole UV-Vis spectrum is shown for the most stable structure, the most intense excitations would not be detectable in toluene solution (cut off 285 nm). In fact, as shown in Figure 7, it is likely one could not distinguish between this species and the outer-sphere, ion-pairs 3 or 5 by UV-Vis spectra.

![Figure 6. Simulated UV-Vis spectra of [(Cp₂Zr)(μ-CH₂)(μ-Cl)]⁻ (9) (gold trace) vs. [(BuCp₂Zr)(μ-CH₂)(μ-Cl)]⁺ (orange trace) and depiction of the frontier orbitals involved in the long wavelength transition at 448 nm.](image-url)

![Figure 7. Structure and simulated UV-Vis spectrum (purple) of Cp₂ZrMe₂(MAOPr₂) (16). H-atoms omitted for clarity. The simulated spectra of [Cp₂ZrMe₂AlMe₂]⁺ (8) and cis-[Cp₂ZrMe₂(μ-Cl)]⁺ (8) are shown in blue and green for comparison. The region obscured by toluene solvent is shaded grey, while the offset, dashed curve represents the combined UV-Vis spectrum of a mixture of these species approximating that shown in Figure 1b for the BuCp analogue.](image-url)
spectroscopy alone as the lowest energy transitions are incompletely resolved, as well as partly obscured by the solvent. These same findings apply to the BuCp analogues, based on the calculated spectra of outer-sphere ions 2–8, though the LMCT transitions are shifted systematically to lower energy (see Supporting Information).

Structure and TD DFT calculations for EBIZr complexes

The UV-Vis spectra of EBIZrCl, which exists as a mixture of forward (f) and backward (b) conformers, and its MAO-activation have been studied in detail elsewhere. The activation process is complicated in the sense that both inactive and active species feature similar absorption maxima, while the experimental spectra are sensitive to the Al:Zr ratio over a wide range. Further, the activation chemistry of EBIZrMe differs significantly from the dichloride precursor while the UV-Vis spectra are dependent on MAO- vs. PhNHMe activation in this case.

It is well known that activation of related dimethyl complexes using ammonium or triyl borates salts is complicated by the formation of homo-dinuclear complexes analogous of complex 2. Definitive studies by Bochmann and Brintzinger and co-workers suggest that complexes 2 serve as reservoirs of the active catalyst, analogous to the situation for complexes 3, in the sense that both species can be inhibited by a large excess of the dimethyl complex or MeAl, respectively. Our ESI-MS studies indicate that complexes 2 and even 5 do not form in significant amounts in the case of MAO-activation of the EBIZrCl complex in agreement with this work. However, we decided to simulate their UV-Vis spectra for sake of completion and to interpret the results for the EBIZr complexes.

As summarized in Table 2, the lowest energy LMCT transitions are found or tail into the visible region of the spectrum for the catalyst precursors and their activation products. We confirm the hypsochromic shift on mono-alkylation, as well as the bathochromic shift upon ionization, though the extent of the latter is dependent on structure of the ions formed (Table 2 and Figure 8). In comparing our calculated values vs. those reported in the literature for the neutral precursor (427 nm), its mono- and di-methylation product (396 and 367 nm) and the ion-pair corresponding to complex 3 (470 nm) it seems that the MN15/def2-TZVP approach overestimates excitation energies, by 15–25 nm (0.10 to 0.15 eV) in the case of chlorinated and/or charged complexes.

In the case of homo-dinuclear complexes analogous to 2 and 5, an added complexity to simulation of UV-Vis in that these can exist as [R,R]- and [R,S]-diastereomers in addition to anti-syn conformers. The latter can interconvert through rotations about the Zr–Zr bond whereas the diastereomers cannot. Studies on analogous [(MeSi(Ind),ZrMe)(μ-Me)]+ complexes indicate that these diastereomers are in slow exchange on the NMR time scale, and will thus contribute to the observed UV-Vis spectrum.

We do note that homo-dinuclear complexes 5 absorb at wavelengths intermediate between that of the neutral precursors vs. ion-pair 3 and this may explain some of the complexity observed upon activation of this complex as a function of the Al:Zr ratio. In essence both active and inactive species are reported to absorb at ca. 440 nm and they obviously cannot be the same vs. a species with longer wavelength absorption at 470 nm usually attributed to ion-pair 3.

Finally, we investigated contact ion-pairs formed from EBIZrMe and 16,6 and as for the Cp system, the longest wavelength LCMT transition is shifted to higher energy compared with any outer-sphere ions (Figure 8). The position is quite sensitive to EBI conformation in this case but one would be hard pressed to detect this species by UV-Vis spectroscopy without an authentic sample. In fact, the position of these adsorptions is nearly coincident with that of various neutral precursors.

Table 2. Calculated wavelengths, and extinction coefficients for LCMT transitions for EBIZr complexes.[a]

| Complex | b:f | λ_{max} (nm) | ε_{max} (10^4 M^{-1} cm^{-1}) |
|------------------|-----|--------------|-------------------------------|
| EBIZrCl           | 85:15 | 404          | 8.84                          |
| EBIZrCl(Me)       | 74:26 | 384          | 10.2                          |
| EBIZrMe           | 82:18 | 371          | 11.8                          |
| EBIZrMe(Me)       | 53:47 | 390, 363     | 5.60, 4.91                    |
| [EBIZr(Me)(μ-Me)]  | 10:90 | 402          | 6.62                          |
| EBIZr(Me)(μ-Me)AlMe₂ (3) | 84:16 | 444          | 7.80                          |
| EBIZr(μ-Me)(μ-Cr)AlMe₂ (7) | 74:26 | 488          | 8.52                          |
| EBIZr(μ-Cr)(μ-Me)AlMe₂ (3) | 52:48 | 554          | 8.98                          |
| [R,R]-EBIZr(Me)    | 50:50 | 364, 402, 444 | 5.07, 5.60, 7.94              |
| [R,R]-EBIZr(Me)(μ-Me) (2) | 33:37 | 422, 435, 444 | 7.94, 7.13                    |

[a] A complete list of complexes studied, their structures and calculated spectral data are included as Supporting Information. [b] Ratio of backward to forward conformers calculated by DFT in gas phase. [c] For the longest wavelength LMCT transitions for the major conformer present. [d] Lewis base acid adduct between Cp,ZrMe₂ and 16,6 (see Supporting Information). [e] Contact ion-pair with a weak Zr-μ-Me-Al interaction (Figure 8). [f] Anti isomer is present at ca. 4 mol% which does not affect the spectrum.

Figure 8. Simulated UV-Vis spectra of neutral precursors and cationic species generated upon activation of noc-EBIZrCl by MAO. Neutral precursors EBIZrCl (green) and EBIZr(MeCl) (blue) in solid lines, contact ion-pairs EBIZr(μ-Me)AlMe₂-16,6 are dotted lines (forward vs. backward conformers in green vs. blue) and outer-sphere cations [R,R]-[(EBIZr(Me)+Cp(Me)] (orange) and [R,R]-[(EBIZr(Me)+AlMe₂)]² (red) are in dashed lines. The structure of the most stable contact ion-pair is shown with H-atoms omitted for clarity.
To our knowledge, no one has detected an ion-pair corresponding to 6 upon activation of EBIZrCl₂ with MAO[46] though the predicted LMCT transition at $\lambda_{\text{max}} = 554$ nm would render this complex purple, in agreement with work on [EBIZrCl₂AlMe₃][B(C₆F₅)₄] complexes.[21]

Conclusions

The ESI-MS results and TD DFT calculations make clear that one should expect the development of colored solutions during activation of RCP₃ZrCl₂ catalysts at low Al:Zr ratios, at least for complexes where formation of homo-dinuclear complexes is not impeded by steric or other effects. Also, inactive complexes 5 (and 8) would be rather difficult to distinguish from “active” catalyst 3 (or even neutral precursors) solely on the basis of their UV-Vis spectra as illustrated in Figure 7. In contrast, deactivated species such as 9 (and 10 if present) would be easily distinguished from either type of catalyst precursor.

Our leaching experiment serves to illustrate that both 3 (or possible precursors such as 6) and 9 (with variable amounts of its precursor 5) ought to be present on a supported catalyst, though the use of excess MAO as a leaching agent would presumably convert both 5 and 6 to complex 3.

Our ESI-MS and DFT calculations support the basic conclusions made about activation of EBIZrCl₂ using MAO in the sense that homo-dinuclear complexes are not significant species compared with the other complexes studied.

Considering this different behavior, as well as the different possibilities for catalyst activation summarized in this paper it seems useful to reinvestigate catalyst activation using our new sheet models for MAO. This will be a basis for future research.

Experimental Section

ESI-MS Experiments. In a typical procedure, a solution (1.5 mL) was prepared from MAO (0.75 mL of 10 wt % MAO in toluene [Al] = 1.5 M) and BuCp₂ZrCl₂ (30.2 mg in 5.0 mL of toluene [Zr] = 0.015 M, 0.75 mL) to give an Al:Zr ratio of ~100:1. After mixing and stirring at room temperature for 5–10 min, an aliquot of this solution was diluted with PhF so as to provide a final solution ca. 0.05 M in Al.

This solution was analyzed using a QTOF Micro spectrometer via pumping it at ca. 40 μL/min through PTFE tubing (1/16” o.d., 0.005” i.d.) to the ESI-MS probe and source using a syringe pump. Capillary voltage was set at 2900 V with source and desolvation gas temperature at 85 °C and 185 °C, respectively with the desolvation gas flow at 400 L/h. In the case of EBIZrCl₂, a weighed amount of catalyst (e.g. 38.5 mg, 0.092 mmol) was suspended in 1.0 mL of toluene, and treated with 1.0 mL of MAO (30 wt% in toluene, [Al] = 4.5 M) with stirring. The slurry rapidly dissolved accompanied by a colour change (bright yellow to orange-red). After dissolution was complete, a 0.2 mL aliquot was diluted to 10 mL with PhF ([Al] = 0.045 M) and analysed as discussed above.

Leaching experiment. A stirred suspension of 0.968 g of calcined PQ silica in 10 mL of toluene was cooled to 0 °C in a double-sided Schlenk tube equipped with a glass frit. Then 15 mL of MAO (10 wt% in toluene) was added via syringe at this temperature. Methane evolution was noted on warming the stirred suspension to room temperature. After gas evolution had slowed, the suspension was heated to 55 °C for 2 hr and then cooled to room temperature. It was filtered under partial vacuum, washing the SiO₂–MAO with a total of 20 mL of toluene. The entire apparatus was evacuated to dryness at room temperature to provide 3.3 g of crude material. This was transferred to a tared, Schlenk tube and further dried at 55 °C for 2 hr in vacuo to constant weight affording 1.60 g of a white solid (≤ 17.5 wt% Al).

A solution of BuCp₂ZrCl₂ (19.5 mg, 0.048 mmol) in toluene (2.0 mL) was added to a slurry of the SiO₂–MAO (0.807 g) in 3.5 mL of toluene at room temperature. The pale yellow suspension was stirred for 2 hr at room temperature, and then filtered, washing with 3 × 2 mL of toluene until the filtrate was colorless. The supported catalyst was dried in vacuo to provide 0.739 g of a pale yellow solid that analyzed as 11.25 wt% Al and 0.15 wt% Zr.

In a typical leaching experiment 100 mg of the supported catalyst (ca. 0.37 μmol Zr) and 0.5 mL of toluene was placed in a 2.0 mL syringe equipped with a syringe filter. The resulting silica column was then treated with 410 μL of MAO (10 wt% solution in toluene, 0.615 mmol Al, Al:Zr ~ 1670:1) at room temperature and kept for 30 min at room temperature. The column was then eluted under N₂ pressure with 3 × 1 mL of toluene, and the eluate collected in one fraction.

One mL of the eluate was diluted with 3.3 mL of PhF to give a solution that was ca. 0.04 M in [Al] and this was analyzed by ESI-MS as described above. The cleanest positive ion spectrum obtained is shown in Figure 6 while it was noted in earlier experiments[48] that the first fractions were enriched in [BuCp₂ZrMe₂AlMe₃] (MAO[X]), while later fractions contained more of the homo-dinuclear complex with m/z 713. Negative ion ESI-MS spectra of the eluate showed very little anion chlorination in keeping with the high Al:Zr ratio used for the leaching experiment. See Supporting Information Figure S-7. Control experiments revealed no detectable catalyst leaching if excess MAO was not present in these experiments.

DFT calculations. All geometry optimizations and electronic energy calculations employed the M06-2X density functional,[51] in conjunction with a TZVP basis set[52] as implemented within Gaussian 16.[53] Time dependent DFT calculations employed the MN15 density functional[54] in combination with a def2-TZVP basis set.[55] Simulated UV-Vis spectra employed the GaussView program with gaussian functions centred at the excitation energies, using a FWHM value of 0.4 eV for spectra shown in Figures 5 to 8.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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