Activation of Metallocenes for Olefin Polymerization as Monitored by IR Spectroscopy

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Abstract
The binary mixtures of Cp₂ZrMe₂, Cp₂ZrCl₂, DMAC, TMA, and MAO have been studied by in situ IR spectroscopy in order to clarify the activation mechanism of metallocenes with MAO. In the mixture of MAO and Cp₂ZrMe₂, a new unidentified stable complex is observed with an IR band at 822 cm⁻¹. It is rapidly formed at low Al/Zr ratio and may be a precursor to the active catalyst. A new mechanism is proposed for the activation of metallocenes with MAO, that may explain the need for a large MAO excess. The new feature of the mechanism is formation of a MAO cage dimer that hides the protruding charged methide from the electrophilic cation.

Introduction
The oligomeric compound methylaluminoxane (MAO) is known as a highly efficient activator for metallocene catalysts for olefin polymerization [1,2]. Despite considerable effort to resolve its structure and determine how MAO takes part in the activation of the catalyst, these questions are still largely unanswered. The metallocene part of the catalyst system is far better understood, mainly due to studies of well defined boron activators [1]. Several intermediates in the boron-based systems have been identified by NMR spectroscopy or X-ray diffraction. By comparison of NMR shifts, corresponding cationic species have also been identified in the metallocene/MAO system [3,4]. The dynamic behavior and the complexity of the MAO solutions result in broad featureless NMR signals that reveal only little about the structure of MAO. Infrared (IR) spectroscopy is a method that offers complementary information. IR and solution state NMR spectroscopy, due to their different characteristic time scales, respond differently to fast chemical exchange among multiple components. In IR spectroscopy, individual components are in principle observed, while just an average signal appears in the NMR spectrum. Recently, new results on the structure of MAO have been obtained by in situ IR spectroscopy [5,6]. In particular, bridging methyl groups were identified as an essential part of the MAO structure and found to be crucial for the metallocene activation. The bridging methyl groups were not recognized in NMR studies.

In the activation of metallocenes by MAO, it has been shown that the cationic species [(Cp₂ZrMe)₂(µ-Me)]⁺, [Cp₂Zr(µ-Me)₂AlMe₂]⁺, and [Cp₂ZrMe]⁺ are formed. TMA constitutes a significant part of commercial MAO solutions, but its role in the activation is not clear. It is able to monomethylate the metallocene and it reacts to form the [Cp₂Zr(µ-Me)₂AlMe₂]⁺ cation. Dimethylaluminum chloride (DMAC) is a by-product in the methylation
reaction, but in the presence of MAO it rapidly gives off its chlorine to MAO and is converted back to TMA [6]. It is therefore likely that TMA is important to the activation mechanism, also through formation of transient compounds.

In the present IR study, we have investigated binary mixtures of Cp₂ZrMe₂, Cp₂ZrCl₂, TMA, DMAC, and MAO, as well as mixtures of C₆H₅₃[BF₄]₄ and boron based activators. All reactions were studied in situ using a custom-built liquid flow cell to meet the challenge to material inertness and sample handling posed by these reactive systems [10]. The IR spectra of known and anticipated metallocene species were also investigated by density functional theory (DFT). We focus on the band corresponding to the out-of-plane vibration of the hydrogen atoms on the Cp ring, around 800 cm⁻¹. The position of this band is sensitive to changes in the bonding environment around the zirconium atom, and correlations are found between observed band position and calculated structural parameters. Of particular interest are the metallocene/MAO systems, where stable intermediates are observed already at unexpected low Al/Zr ratios. Possible structural candidates for these intermediates are discussed, as well as mechanisms to account for the need of excess MAO.

**Experimental**

**General:**

All operations were carried out under dry nitrogen or argon atmosphere (99.999%) by standard Schlenk technique. Solids were handled in a glovebox. Solutions were transferred and metered with lubricant-free disposable syringes or gas tight micro syringes. The IR spectra were recorded on a BrukerIFS66v spectrometer, using a custom-built liquid flow cell [7]. Silicon and germanium windows were used, since MAO reacts with halide salts. The spectra were recorded with a nominal resolution of 2 cm⁻¹ and zero-filled to 0.5 cm⁻¹. To obtain spectra of the solute, the solvent bands spectrum was digitally removed using a spectrum of the neat pure solvent. Due to strong bands of toluene around 740 and 690 cm⁻¹, some regions of the spectra, around 740 and 690 cm⁻¹, are obscured.

The formation of a heavy oil phase in concentrated MAO/metallocene systems induces disturbances in the spectra. The disturbance concerns the overall intensity, while the IR fingerprint is not changed. A similar phase separation is observed in the [C₆H₅₃][BF₄]₄/Cp₂ZrMe₂ system and is responsible for the dual set of ¹H NMR peaks observed [8]. The heavy phase appears to contain basically the same species as the lighter liquid, but in higher concentration, since there were no notable changes in the fingerprint with time, just in the overall intensity. For the purpose of observing the relative changes in IR bands, the spectra of the MAO/metallocene system were scaled to equal intensity at 790 cm⁻¹. Studies of more dilute solutions were attempted, but were not successful.

**Materials:**

Trimethylaluminum (TMA) and dimethylaluminum chloride (DMAC) were purchased from Aldrich Co. and used without further purification. The absence of air contamination of MAO, TMA, and DMAC was verified by absence of methoxy IR bands around 990 cm⁻¹. Toluene, benzene, and tetrahydrofuran (THF) were refluxed over
sodium/benzophenone and distilled under nitrogen before use. Pentane was dried with molecular sieves (3Å). MAO (Albemarle Corp., 10 wt% in toluene) was dried under reduced pressure at room temperature. Cp₂ZrMe₂ (Strem Chemicals Inc.), Cp₂ZrCl₂ (Boulder Scientific Co.), tris(pentafluorophenyl)boron (Strem Chemicals Inc.), and trityl tetra(pentafluorophenyl)boron (Albemarle Corp.) were used as received.

**Preparations:**

TMA-depleted MAO was prepared by removing TMA and solvent from commercially available MAO solution, at room temperature and reduced pressure (to about 0.07 mbar). The solid MAO was redissolved in toluene and the procedure was repeated to reduce the amount of TMA. The solid was dried at less than 0.1 mbar for at least 2h. Cp₂ZrMeCl was prepared from equimolar amounts of Cp₂ZrCl₂ and Cp₂ZrMe₂. The reaction took place over 2-3 weeks in benzene at room temperature. Cp₂ZrMe(μ-Me)B(C₆F₅)₃ was prepared by mixing equimolar amounts of solid Cp₂ZrMe₂ and B(C₆F₅)₃. Benzene was added at –65°C and the mixture was slowly heated and stirred for 2h. Dry pentane was added and the precipitate was filtered and washed three times with pentane.

(Cp₂ZrMe)₂O was prepared by reacting Cp₂ZrMe₂ with water in THF. Besides (Cp₂ZrMe)₂O the product contained (Cp₂ZrO)₃, as verified by 'H NMR. [(Cp₂ZrMe)₂(μ-Me)]⁺ was prepared by mixing solutions of trityl tetra(pentafluorophenyl)boron and Cp₂ZrMe₂ directly in the in situ IR apparatus at room temperature. [Cp₂Zr(μ-Me)₂AlMe₂]⁺ was prepared by adding excess TMA to the previous mixture and by adding a solution of Cp₂ZrMe₂ to a freshly prepared solution of trityl tetra(pentafluorophenyl)boron and TMA.

**Computational details:**

All calculations are based on DFT. We have used ADF 2.3 provided by Scientific Computing and Modeling [9] and Gaussian 03 provided by Gaussian Inc. [9A]. Different levels of computation have been used to verify observed trends and correlations between experiment and theory.

In ADF, the density functionals used were those of Vosko, Wilk, and Nusair (VWN) [10] for the local density part. Gradient corrections, based on the functionals proposed by Becke [11] for exchange and Perdew and Wang [12] for correlation (i.e., "BPW91"), were included self-consistently. We used a double-ζ Slater-type orbital basis set extended with a polarization function (DZP) for all atoms except Zr, for which a triple-ζ basis set (TZP) was used. The 1s to 3d orbitals on Zr, the 1s to 2p orbitals on Al and Cl, and the 1s orbital on B, C, F, and O were treated within the frozen-core approximation.

In Gaussian, the following combinations of density functionals and basis sets were used: BPW91/3-21G** (G₁), B3LYP/3-21G** (G₂), and B3LYP/6-31+G(d,p) (G₃). In the latter case, the effective core potential basis set LANL2DZ was used for Zr.
Results

Overview

The various aluminum-based mixtures are depicted in Fig. 1. Dashed lines indicate binary mixtures where no new products were detected by IR spectroscopy after mixing. Comparative studies were performed with the two well-characterized boron cocatalysts B(C$_6$F$_5$)$_3$ and C(C$_6$H$_5$)$_3$B(C$_6$F$_5$)$_4$, using both IR and NMR spectroscopy.

![Diagram](image)

**Fig. 1** Overview of the aluminum-based systems studied. Dashed lines connect components whose mixture yielded no detectable new species.

Table 1 Experimental and calculated band positions of the out-of-plane deformations of the aromatic C–H bonds of Cp for selected zirconocenes and complexes in aromatic solution (cm$^{-1}$). A) Simple zirconocenes, B) complexes verified by $^1$H NMR. ADF: BPW91/DZP,TZP, G$_1$: BPW91/3-21G**, G$_2$: B3LYP/3-21G**, G$_3$: B3LYP/6-31+G(d,p), LANL2DZ. See computational details.

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<th>G$_3$</th>
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**B**

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<th>G$_3$</th>
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<td>818</td>
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<td>839</td>
<td>834</td>
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Table 2 Calculated band positions of the Cp out-of-plane deformation based on the calculated Mulliken charge on the Cp ring (q) and the distance between Zr and the center of the Cp ring (d). See caption of Table 1 and main text for details.

<table>
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<tr>
<th>Compound</th>
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<th>G$_3$</th>
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**B**

<table>
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<tr>
<th>Compound</th>
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<th>G$_2$</th>
<th>G$_3$</th>
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<td>821.9</td>
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<tr>
<td>[Cp$_2$Zr(μ-Me)$_2$AlMe$_3$]$^+$</td>
<td>831.2</td>
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</table>
The η5-cyclopentadienyl ligands of metallocenes have a relatively simple IR spectrum with a few strong bands [13]. The strongest band, due to the out-of-plane deformations of the aromatic C–H bonds, is also the most sensitive to changes in the coordination of Zr. It is therefore suitable for monitoring reactions. The position of this band for simple zirconocenes and NMR-verified zirconocene complexes in solution is shown in the rightmost column of Table 1. These complexes are discussed in detail in the following sections.

Theoretical IR spectra were calculated within the harmonic approximation. A single conformation with respect to the relative rotation of the cyclopentadienyl rings was used in the calculations. In general, this yields several close bands. The relative intensity of these bands varies somewhat with the chosen level of computation. Therefore, Lorentzians with widths between 5 (G2) and 20 (ADF) cm
-1 were applied to form a single broad band, as observed in the experiments. The general appearance of the calculated spectra of Cp2ZrMe2, Cp2ZrMeCl, and Cp2ZrCl2 is in good agreement with experiment. A comparison (G2) is shown for Cp2ZrMe2 in Fig. 2A between 400 and 1500 cm
-1. In Fig. 2B, calculated (G2) and experimental Cp out-of-plane deformation bands at about 800 cm
-1 are shown for all three zirconocenes. As argued below, four additional zirconocene complexes have been verified with NMR spectroscopy. In Fig. 3, calculated (ADF) and experimental band positions of the Cp out-of-plane deformations are compared for all seven verified complexes. The trend line is given by \( v(\text{exp}) = 1.005 v(\text{ADF}) + 17 \). Corresponding trend lines for the correlation between experiment and band positions calculated with Gaussian are \( v(\text{exp}) = 0.829 v(G_1) + 158 \), \( v(\text{exp}) = 0.799 v(G_2) + 163 \), and \( v(\text{exp}) = 1.083 v(G_3) - 72 \).

In the present work considerable effort has been directed towards gaining insight into how the position of the band due to the Cp out-of-plane deformation is influenced by changes in the steric and electronic environment around the zirconium atom. A multivariate analysis based on the seven compounds listed in Table 1 showed that the band position correlates well with the calculated Mulliken charge on the Cp ring (in agreement with [13]) as well as the distance between Zr and the center of the Cp ring. Other parameters, such as the charge on Zr and the Cp-Cp opening angle, showed poor correlation. Roughly speaking, these results suggest a shift to higher frequencies when the Cp ring becomes more strongly bound to Zr, i.e., when the remaining ligands become less attached to Zr. The best linear fit to the observed band positions is given by the equations \( v \) (cm
-1) = 1501 + 91 q - 279 d (ADF), \( v \) (cm
-1) = 1561 + 65 q - 326 d (G1), \( v \) (cm
-1) = 1853 + 27 q - 459 d (G2), and \( v \) (cm
-1) = 1629 + 27 q - 362 d (G3), with q = Q(Cp) in units of the electron charge (-e) and d = d(Zr-Cp) in Å. Predicted band positions based on this model are included in Table 2. The observed trends, which are independent of the choice of density functional and basis set, may be summarized as follows: 1) Neutral compounds have smaller-lower frequency v than cations. Starting from a neutral compound, formation of a cation results in a smaller |Q(Cp)| (i.e., less negative). Also, the Zr-Cp distance becomes shorter since terminal ligands are converted into bridging ligands or removed. 2) Compounds with terminal ligands have smaller-lower v than compounds with bridging ligands. Terminal ligands are more strongly bound to Zr than bridging ones, resulting in a longer Zr-Cp distance in the former case. 3) Compounds with methyl ligands have smaller-lower v than compounds with chlorine ligands. Methyl is less electronegative than Cl, resulting in a larger |Q(Cp)| in the former case. 4) Compounds with oxygen ligands tend to have small-low values of v. The two-coordinate oxygen is a good electron donor, resulting in high values of |Q(Cp)|. Even in a 2- or 3-coordinated
bridging position between Zr and aluminum, oxygen forms a bond of “normal” strength to Zr, resulting in a fairly long Zr-Cp distance.

Fig. 22 Comparison of calculated (G₃) and measured IR spectra. Lorentzians with width 7 cm⁻¹ are used in the calculated spectrum. A: Cp₂ZrMe₂ in the range 400 to 1500 cm⁻¹. B: Cp₂ZrMe₂ (solid), Cp₂ZrMeCl (dashed), Cp₂ZrCl₂ (dotted) in the range 780 to 840 cm⁻¹. The band at about 750 cm⁻¹ in the experimental spectrum is probably the Zr-O stretch in (Cp₂MeZr)O, which is caused by traces of oxygen impurities.

Fig. 33 Comparison of measured and calculated (ADF) frequencies for the out-of-plane C–H deformations of Cp. For the methyl bridged complex with the boron cocatalyst, CF₃ model ligands on B were used: R=CF₃ (calculation), C₆F₅ (experiment). Corresponding curves based on band positions calculated with Gaussian show a similar correlation, with an exception of level G₁. Deviations from the fitted line are characterized by r² values of 0.98 (ADF), 0.82 (G₁), 0.95 (G₂), and 0.99 (G₃).
Reactions with Aluminum Alkyls

In the mixture of Cp₂ZrCl₂ and Cp₂ZrMe₂, a slow exchange takes place and Cp₂ZrMeCl is formed in good yield [14]. The reaction proceeds over several weeks, and is far too slow to be studied in situ. While the original bands diminish, a new strong band appears at 809 cm⁻¹, characteristic of the product.

In agreement with earlier reports, Cp₂ZrMeCl was obtained in moderate yield in the reaction of TMA with Cp₂ZrCl₂ [4,15]. No IR band attributable to Cp₂ZrMe₂ was observed. The ability of TMA to fully methylate the zirconocene was further investigated in a separate experiment by adding TMA to Cp₂ZrMeCl. No Cp₂ZrMe₂ was observed, instead the IR spectrum showed the presence of a new species with the out-of-plane Cp deformation band at 815 cm⁻¹. The source of this absorption is not clear but is likely due to a simple reversible adduct of the two reactants. We expect chlorine rather than methyl to form the bridge between zirconium and aluminum, since a methyl bridge implies an unfavorable two-electron three-center bonding structure. The only new zirconocene species observed in the proton NMR spectrum of the mixture of Cp₂ZrCl₂ and a large excess of TMA was Cp₂ZrMeCl, but the methyl resonance of this solution was unusually wide, 25 Hz, indicating the presence of a dynamic process.

No new compounds were observed in the mixture of Cp₂ZrMe₂ and TMA. As expected, the double methyl bridge of the TMA dimer is preferred to the single bridge in Cp₂ZrMe(μ-Me)AlMe₃. Addition of DMAC to Cp₂ZrMe₂ rapidly gave Cp₂ZrMeCl and TMA as the first products. Further additions gave Cp₂ZrCl₂ in high yield, identified by its IR band at 814 cm⁻¹, and a new product observed as a well-defined shoulder at 820 cm⁻¹. The changes of the spectra in this region are shown in Fig. 4. After the initial exchange reaction, the system contains several compounds that may form adducts: Cp₂ZrMe₂, Cp₂ZrMeCl, Cp₂ZrCl₂, DMAC, and TMA. A band in this position, i.e., near 820 cm⁻¹, was not observed in any of the binary mixtures with TMA. The addition of the same amount of DMAC to Cp₂ZrCl₂ was insufficient to reproduce the band, but the shoulder was observed when the amount of DMAC was raised one order of magnitude until Al/Zr = 48. The most likely cause of the shoulder at 820 cm⁻¹ is formation of a chlorine-bridged adduct Cp₂ZrMe(μ-Cl)AlMe₂Cl. We were not able to confirm this complex by NMR. However, calculations (ADF) support the interpretation since with a band position is predicted at 818 cm⁻¹, whether it is based on the calculated spectrum or the empirical relation involving the Cp charge and the Zr-Cp distance.
In summary, TMA is not able to dimethylate the zirconocene, but forms Cp$_2$ZrMeCl. In systems containing chlorine, new products are formed, presumably chlorine bridged bi-metallic adducts. The equilibrium constants are small as none of the complexes were observed as the major component of their mixtures. Consistent with this are the small calculated reaction energies for the formation of such adducts.

**Reactions with Boron Activators**

The literature contains extensive studies of the activation of metallocenes with boron-based activators [2]. In the present work, activation using the two well-characterized activators B(C$_6$F$_5$)$_3$ and [C(C$_6$H$_5$)$_3$]$^+\cdot[B(C$_6$F$_5$)$_4$]$^-\cdot$ has been investigated with in situ IR spectroscopy. These cocatalysts are known to produce the cations [(Cp$_2$ZrMe)$_2$(μ-Me)]$^+$ and [Cp$_2$ZrMe]$^+$. The latter will presumably form tight ion pairs with the countermions MeB(C$_6$F$_5$)$_3$ and B(C$_6$F$_5$)$_4^-$, respectively. The purpose of the present study was to obtain experimental frequencies of reaction products with Cp$_2$ZrMe$_2$ for comparison. Solutions of the reagents were prepared and mixed directly in the in situ IR apparatus at room temperature. Samples were also prepared for NMR by the same procedures as for the IR experiments, and the main products and their order of appearance were confirmed by $^1$H NMR.

When B(C$_6$F$_5$)$_3$ was added to Cp$_2$ZrMe$_2$, the first new band in the 800 cm$^{-1}$ region was observed at 818 cm$^{-1}$ (B/Zr = 0.3). Further addition of B(C$_6$F$_5$)$_3$ gave a new strong band at 825 cm$^{-1}$. Bands due to free B(C$_6$F$_5$)$_3$ were not observed until the B/Zr ratio exceeded unity. At this point the reaction seemed complete as no further change was observed in the spectrum of the zirconocene. When the reactants were added in opposite order, the band at 818 cm$^{-1}$ did not appear. In this system, the cation [(Cp$_2$ZrMe)$_2$(μ-Me)]$^+$ is known to be formed at low B/Zr ratios while [Cp$_2$ZrMe]$^+$ (or rather: Cp$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$) is formed at higher B/Zr ratios [4,16]. We therefore attribute the band at 818 cm$^{-1}$ to [(Cp$_2$ZrMe)$_2$(μ-Me)]$^+$ and the band at 825 cm$^{-1}$ to [Cp$_2$ZrMe]$^+$. The latter was also prepared outside the IR cell at low temperature as described in the literature [17]. The resulting IR spectrum essentially contained the same bands, including a weak and variable band around 813 to 818 cm$^{-1}$. It is not clear whether this weak band is due to the binuclear cation or another product.
The reactions of Cp₂ZrMe₂ with [C(C₆H₅)₃]⁺[B(C₆F₅)₄]⁻ were monitored in a similar experiment. A single band at 818 cm⁻¹ was clearly observed immediately after mixing, but moved slowly to 824 cm⁻¹ within few hours. In this system, the binuclear cation [(Cp₂ZrMe)(μ-CH₃)]⁺ appears to be kinetically preferred and is formed even with excess cocatalyst before it is slowly converted into [Cp₂ZrMe]⁺ (or rather: weakly coordinating Cp₇ZrMe..(C₆F₅)₃B ion pairs) [8]. The band at 818 cm⁻¹ is accordingly attributed to the binuclear cation and the band at 824 cm⁻¹ to [Cp₂ZrMe]⁺. Addition of TMA to this mixture immediately gave a new band at 832 cm⁻¹. The same band was obtained when Cp₂ZrMe₂ was added to a mixture of TMA and boron activator. We attribute this band to [Cp₂Zr(μ-CH₃)₂AlMe₃]⁺. In Fig. 4, the 800 cm⁻¹ region of the IR spectra of three reaction mixtures in these systems is shown.

The IR data obtained in the boron-based systems shows that important intermediates are identified by IR spectroscopy as well as by NMR spectroscopy. Also, the DFT calculations support the assignment of the experimentally observed IR bands (see Table 1 and Fig. 3). Using the linearly fitted lines between calculated and observed band positions, the dimeric cation [(Cp₂ZrMe)(μ-CH₃)]⁺ is predicted within the range 815 -820 cm⁻¹ at all four computational levels. The methyl bridged complex Cp₂ZrMe(μ-CH₃)B(C₆F₅)₃ is correspondingly predicted within the range 824-829 cm⁻¹. Somewhat surprisingly, perhaps, the "naked" cation [Cp₂ZrMe]⁺ is predicted to have its band position within the range 825-830 cm⁻¹, in good agreement with experiment. Based on its high small Cp charge and low Zr-Cp distance, one might have expected a higher band position at higher frequency. Finally, the band position of the cation [Cp₂Zr(μ-CH₃)₂AlMe₃]⁺ is predicted in the range 827-833 cm⁻¹.

**Fig. 5** IR spectra of the reaction mixtures

Cp₂ZrMe₂/[C(C₆H₅)₃]⁺[B(C₆F₅)₄]⁻ (band position at 818 and 824 cm⁻¹ after 2 and 155 min, respectively), Cp₂ZrMe₂/[C(C₆H₅)₃]⁺[B(C₆F₅)₄]⁻/TMA, and Cp₂ZrMe₂/B(C₆F₅)₃.
Reactions with MAO

In this section, we report the results of *in situ* IR studies of reactions of Cp₂ZrMe₂ and Cp₂ZrCl₂ with MAO at relatively low Al/Zr ratios. In both systems, a new band was immediately observed, at 820 and 822 cm⁻¹ with Cp₂ZrCl₂ and Cp₂ZrMe₂, respectively, indicating that at least one new stable product is formed. Using Cp₂ZrCl₂, there was a substantial decrease in the band at 1257 cm⁻¹ attributed to bridging methyl groups in MAO. As shown in Fig. 6, the changes are similar to those produced by addition of DMAC to MAO, where MAO is chlorinated by DMAC. The left frame shows a comparison between MAO and the same MAO after reaction with DMAC, while the right frame shows MAO before and after addition of Cp₂ZrCl₂. We have previously shown that in MAO only the bridging methyls are exchangeable with the chlorine of DMAC [6]. Even in the presence of TMA, the chlorinated MAO was unable to activate Cp*₂ZrCl₂. Clearly, the bridges are essential to the methylation of the catalyst. In the mixture of MAO and Cp₂ZrCl₂, it was not possible to determine whether the chlorine remains as Al–Cl–Zr links or go into Al–Cl–Al environments with methyl as the bridging unit between MAO and the zirconocene. The difference of only 2 cm⁻¹ in the observed band positions in mixtures of MAO with Cp₂ZrMe₂ and Cp₂ZrCl₂, respectively, is too small to be significant. DFT calculations suggest that Al-Cl-Al and Zr-Me-Al is preferred by about 5 kcal/mol.

The subsequent studies were performed with Cp₂ZrMe₂ to exclude any ambiguity concerning chlorine or methyl groups. In Fig. 7, spectral changes upon addition of Cp₂ZrMe₂ to MAO are shown. A series of IR spectra was recorded at progressively higher concentrations of zirconocene. Unfortunately, in concentrated samples a phase separation takes place. The random distribution of the two phases in the IR cell influences the observed concentration of the solutes. A quantitative analysis is in this case not possible, but a careful scaling of the spectra allows trends to be observed based on the shape of the band envelope. The scaling procedure is described in greater detail in the Experimental section.
Fig. 7 | IR spectra of mixtures of Cp<sub>2</sub>ZrMe<sub>2</sub> and MAO in toluene at progressively higher concentrations of zirconocene. c<sub>Al(start)</sub>=0.5M. The spectrum for the pure Cp<sub>2</sub>ZrMe<sub>2</sub> is shown by the dashed line. The solvent component of the spectra has been removed. The spectra have been slightly scaled to compensate for the random variations in intensity due to phase separation (see Experimental section).

Distinct changes indicative of a reaction are observed in two regions of the IR spectrum when Cp<sub>2</sub>ZrMe<sub>2</sub> and MAO are mixed. The bands in the region 1150–1300 cm<sup>-1</sup>, shown in Fig. 7 (right frame) are symmetric deformations of methyls on MAO. The Cp out-of-plane deformation bands around 800 cm<sup>-1</sup> (left frame) are in this case superimposed on the strong, broad Al-O stretching/methyl rock band centered at 808 cm<sup>-1</sup>. At high Al/Zr ratios, the only new band in this region is observed at 822 cm<sup>-1</sup>. The absence of a sharp band at 803 cm<sup>-1</sup> indicates that all or most of the zirconocene is reacted. The band at 803 cm<sup>-1</sup> was not observed until further addition of zirconocene addition brought the Al/Zr ratio below 30. The bands attributed to the symmetric methyl deformations of MAO at 1200–1270 cm<sup>-1</sup> changed in shape with the addition of Cp<sub>2</sub>ZrMe<sub>2</sub> until an Al/Zr ratio of 15–20 was reached. Further additions had little effect on these bands, while free Cp<sub>2</sub>ZrMe<sub>2</sub> was clearly observed (803 cm<sup>-1</sup>). Changes were observed also in the region of C–H stretching, but the interpretation is complicated due to band overlap. Except for the fluctuations due to the phase separation, the spectrum was stable for several hours. From the described behavior, there appears to be two distinct regions of Al/Zr ratios: one where no free Cp<sub>2</sub>ZrMe<sub>2</sub> is observed while the MAO is changing, and the other where Cp<sub>2</sub>ZrMe<sub>2</sub> is observed, but no changes are seen in the MAO bands. In other words, MAO appears to consume all the added Cp<sub>2</sub>ZrMe<sub>2</sub> until a level of saturation, at Al/Zr about 15–20, where it becomes “unreactive”.

Addition of excess TMA to a mixture of MAO and Cp<sub>2</sub>ZrMe<sub>2</sub> did not initiate other substantial changes in the IR spectrum than the appearance of TMA bands. Surprisingly, no band due to [Cp<sub>2</sub>Zr(μ-<sup>Me</sup>-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> was observed at 832 cm<sup>-1</sup>. Hence, the species responsible for the band at 822 cm<sup>-1</sup> appears to be a tightly bound adduct, not an ion pair. Otherwise, one would expect it to be easily transformed into [Cp<sub>2</sub>Zr(μ-<sup>Me</sup>-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>.

Monomer insertion

To study the changes in the IR spectrum on monomer insertion, 1-hexene was added to solutions of activated catalyst. When 1-hexene was added to the Cp<sub>2</sub>ZrMe<sub>2</sub>/MAO system, the IR band at 822 cm<sup>-1</sup> disappeared, and a broad band appeared around 815 cm<sup>-1</sup>. This was followed by a decrease in the bands attributed to the olefinic group of 1-hexene. The appearance of a new band at 886 cm<sup>-1</sup> is diagnostic for vinyldene end groups of poly-1-hexene, i.e., it verifies catalytic activity. When MAO was added to a solution of 1-hexene and Cp<sub>2</sub>ZrMe<sub>2</sub>, the band at 822 cm<sup>-1</sup> did not appear at all and catalytic activity was observed. Monomer was also added to a solution of
The band at 825 cm\(^{-1}\) attributed to this complex immediately disappeared followed by 1-hexene consumption.

**Discussion**

A substantial problem in the use of metallocene based catalysts is the large MAO excess needed to obtain high polymerization activity. Although some MAO is simply consumed in the reaction with impurities, a solid understanding of the need for such a great excess is not at hand. One possible explanation is that the activation is carried out by a minority species holding extraordinary properties such as very high Lewis acidity or charge capacity. This would suggest a large potential for improvement if such a rare MAO species could be identified and its formation optimized. On the other hand, if the large amount of MAO is needed to force an equilibrium reaction in the desired direction, the answer to the problem is different.

The observation of a new IR band at 822 cm\(^{-1}\) in the MAO/Cp\(_2\)ZrMe\(_2\) system, the accompanying changes in the bands around 1200 cm\(^{-1}\), and the absence of the Cp\(_2\)ZrMe\(_2\) fingerprint at 803 cm\(^{-1}\) all indicate that an extensive reaction is taking place, even at very low Al/Zr ratios. When the Al/Zr ratio is brought below 15-20 by adding more Cp\(_2\)ZrMe\(_2\), the changes in the MAO bands cease and the Cp\(_2\)ZrMe\(_2\) bands appear, suggesting a MAO unit of 15-20 aluminum atoms that is able to react with a single zirconocene molecule. It is interesting that this number corresponds to the average size of MAO molecules as determined by cryoscopy. Several groups have reached the conclusion that the average composition of the MAO molecules is close to (Me\(_6\)Al\(_4\)O\(_3\))\(_n\). Assuming 3-coordinate oxygen, methyl and oxygen together provide 15n bonds to aluminum, while the 4n aluminum atoms require 16n bonds to become 4-coordinate. Thus, there will be n acidic 3-coordinate aluminum atoms, n methyl bridges, or a combination thereof. A molecule with 15-20 Al atoms therefore contains about 4-5 acidic sites which seems sufficient to facilitate adduct formation.

Two modes of bonding between the metallocene and MAO have been discussed in the literature[ 4]. In the mixture of Cp\(_2\)ZrMe\(_2\) and B(C\(_6\)F\(_5\))\(_3\), a methyl bridged compound is formed. Although the Lewis acidity of MAO may be less than for the boron activator, similar methyl bridged adducts are likely. A weak NMR signal was observed and attributed to the methyl bridge by Babushkin et al.[ 4]. Another possible mode of binding is through an oxygen, and a Zr-O bond has already been verified for a tert-butyl aluminoxane with strained structure and no alkyl bridges [5]. The tert-butyl aluminoxane cage reacts in a similar manner with TMA[ 4]. Strained bonds ("latent Lewis acidic sites") are thereby opened. Since a significant amount of TMA is always present in commercial MAO solutions, we argue that these “latent Lewis acidic” sites are already occupied by TMA and no longer available for the metallocene. The incorporation of TMA results in reactive methyl bridges, consistent with previous IR studies of MAO [ 5].

It has not been possible to identify the species responsible for the observed band at 822 cm\(^{-1}\). Although the cation [(Cp\(_2\)ZrMe\(_2\)(μ-Me))]\(^+\) gives a band roughly in the right position, NMR results show that it is not generated in high yield at this low Al/Zr ratio[ 4]. The predicted band positions of the oxygen-bridged models Cp\(_2\)ZrMe(O)AlMe\(_2\) and Cp\(_2\)ZrMe(O)Al\(_2\)Me\(_5\) are 797 and 812 cm\(^{-1}\), respectively. The calculations of the methyl bridged adducts of Cp\(_2\)ZrMe\(_2\) and small MAO cage models with bridging methyls predict band positions around 810 cm\(^{-1}\) for the Cp out-of-plane deformation. Since both predictions show similar deviations from the observed band at 822 cm\(^{-1}\), we are
not able to differentiate the two options. However, formation of a Zr-O bond requires that an Al-O bond is broken (assuming only three-coordinate oxygen). Since MAO contains methyl bridges, it is more likely that a methyl bridge is opened to form the new connection. Also, NMR evidence of a methyl bridged adduct was found by Babushkin [1]. The following discussion is therefore based on the methyl-bridged adduct.

The results suggesting that Cp₂ZrMe₂ rapidly and quantitatively reacts with MAO, have implication to the discussion of the activation process. If Cp₂ZrMe₂ reacts that easily with MAO, why is such a large excess of MAO needed? Consider a simple two-step activation process starting with Eq. 1 followed by Eq. 2, and that the product of Eq. 2 is active or is activated by the monomer.

\[
\text{Cp}_2\text{ZrMe}_2 + \text{MAO} = \text{Cp}_2\text{ZrMe(μ-Me)MAO} \quad (1)
\]

\[
\text{Cp}_2\text{ZrMe(μ-Me)MAO} = [\text{Cp}_2\text{ZrMe}]^+ \ldots [\text{Me–MAO}]^- \quad (2)
\]

The large excess of MAO needed may indicate that the position of Eq. 1 is far to the reactant side whereas no extra MAO seems to be necessary for the proceeding of Eq. 2. NMR results seem to support this picture since free Cp₂ZrMe₂ is claimed to be present even with a large excess of MAO [3]. However, the present IR results indicate that most of the Cp₂ZrMe₂ is quickly consumed by MAO. Hence, the position of Eq. 1 seems rather to be on the product side [18]. We will assume that the IR results are valid, i.e., MAO willingly reacts with the zirconocene, and production of a "free" cation is the limiting step. How can excess MAO help in this case? Possibly, a minority species with extraordinary acidity may be needed to sufficiently weaken the Zr–Me bond to produce a cation. In this case the product of Eq. 1 may acts as a temporary storage until the proper MAO species comes by. In our view, a more likely explanation is that [Me–MAO]– is assisted by additional MAO cages in for hiding the negative charge away from the electrophilic cation by formation of larger anions, e.g. a [MAO–Me–MAO]– dimeric cage. The second equilibrium then becomes:

\[
\text{Cp}_2\text{ZrMe(μ-Me)MAO} + \text{MAO} = [\text{Cp}_2\text{ZrMe}]^+ \ldots [\text{MAO–Me–MAO}]^- \quad (3)
\]

Calculations, using a Me₁₂Al₈O₆ cage model with methyl bridges, show that the energy expense on forming a separated ion pair is lowered with as much as 20 kcal/mol with Eq. 3 instead of Eq. 2. This contribution to ion pair separation is of the same order as the effect of monomer coordination. The charge of the accepted methyl anion is more effectively spread out by formation of the dimeric cage. The activation sequence is depicted in Fig. 9. The MAO cages are viewed directly along their C₂ axis, with the central four-membered ring hiding an equivalent ring mirrored by the paper plane.

For simplicity, we have not considered TMA and formation of [Cp₂Zr(μ-Me)₂AlMe₂]⁺ and [{Cp₂ZrMe₂(μ-Me)}⁻ in this model. The failure to observe [Cp₂Zr(μ-Me)₂AlMe₂]⁺ when MAO and TMA was added may be a consequence of the low Al/Zr ratio, or possibly that this band is masked by changes in the underlying shoulder at 840 cm⁻¹ in the MAO spectrum. The present model is easily expanded to include these bimetallic cations.
Fig. 9. Ball and stick model of the suggested mechanism for zirconocene activation. A relatively small MAO cage model, $\text{Me}_{10}(\mu$-$\text{Me})_2\text{Al}_8\text{O}_6$, is used and viewed along its $C_2$ axis. (Hydrogens are not shown.)

**Conclusion**

In the binary mixtures of $\text{Cp}_2\text{ZrMe}_2$, $\text{Cp}_2\text{ZrCl}_2$, DMAC, and TMA, new products were observed, except for TMA/$\text{Cp}_2\text{ZrMe}_2$ (and TMA/DMAC). The new products were $\text{Cp}_2\text{ZrMeCl}$ and unidentified hetero-bimetallic complexes.

In the mixture of MAO and $\text{Cp}_2\text{ZrMe}_2$, a new unidentified stable complex is observed with an IR band at 822 cm$^{-1}$. It is rapidly formed at low Al/Zr ratio and may be a precursor to the active catalyst. A new mechanism is proposed for the activation of metallocenes with MAO, that may explain the need for a large MAO excess. The new feature of the mechanism is formation of a MAO cage dimer that hides the protruding charged methide from the electrophilic cation.

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16. The conflicting interpretations of the IR and NMR results will need further work to be resolved. A tentative explanation is the difference between these techniques in their response to fast equilibria.