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 can be 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 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 metallocenes 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 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 Bruker IFS66v 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 were removed using a spectrum of the neat solvent. Due to strong bands of toluene, 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 \([\text{C}(\text{C}_6\text{H}_5)_3][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Cp}_2\text{ZrMe}_2\) system and is responsible for the dual set of \(^1\text{H} \) NMR peaks observed [8]. The heavy phase appears to contain basically the same species as the lighter liquid, but in higher concentration, since there is no notable change in the fingerprint. 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 ¹H 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.  [nmr data!!]

**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].

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**, B3LYP/3-21G**, and B3LYP/6-31+G(d,p). In the latter case, the basis set LANL2DZ was used for Zr.

(Her mangler litt mer diskusjon om hvorfor ulike metoder er benyttet...)

**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 $\text{B(C}_6\text{F}_5)_3$ and $\text{C(C}_6\text{H}_5)_3\text{B(C}_6\text{F}_5)_4$, using both IR and NMR spectroscopy.

![Diagram of aluminum-based systems](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. $G_1$: Gaussian, BPW91/3-21G**, $G_2$: Gaussian, B3LYP/3-21G**, $G_3$: Gaussian, B3LYP/6-31+G(d,p) (LANL2DZ for Zr).

<table>
<thead>
<tr>
<th>Compound</th>
<th>ADF</th>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>Exp</th>
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<td>Cp$_2$ZrMe$_2$</td>
<td>781</td>
<td>779</td>
<td>804</td>
<td>807</td>
<td>803</td>
</tr>
<tr>
<td>Cp$_2$ZrMeCl</td>
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<td>783</td>
<td>807</td>
<td>814</td>
<td>809</td>
</tr>
<tr>
<td>Cp$_2$ZrCl$_2$</td>
<td>793</td>
<td>783</td>
<td>809</td>
<td>820</td>
<td>814</td>
</tr>
<tr>
<td>(Cp$_2$ZrMe)$_2$(μ-O)</td>
<td>777</td>
<td>780</td>
<td>797</td>
<td>814</td>
<td></td>
</tr>
<tr>
<td>[(Cp$_2$ZrMe)$_2$(μ-Me)]$^+$</td>
<td>794</td>
<td>799</td>
<td></td>
<td>820818</td>
<td></td>
</tr>
<tr>
<td>Cp$_2$ZrMe(μ-Me)BR$_3$</td>
<td>806</td>
<td>810</td>
<td>825</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cp$_2$Zr(μ-Me)$_2$AlMe$_2$]+</td>
<td>810</td>
<td>807</td>
<td>839</td>
<td>834</td>
<td>832</td>
</tr>
</tbody>
</table>

**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>
<thead>
<tr>
<th>Compound</th>
<th>ADF</th>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp$_2$ZrMe$_2$</td>
<td>803.7</td>
<td>804.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$_2$ZrMeCl</td>
<td>810.7</td>
<td>811.4</td>
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<tr>
<td>Cp$_2$ZrCl$_2$</td>
<td>816.8</td>
<td>817.8</td>
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<tr>
<td>(Cp$_2$ZrMe)$_2$(μ-O)</td>
<td>795.2</td>
<td>794.4</td>
<td></td>
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<tr>
<td>[(Cp$_2$ZrMe)$_2$(μ-Me)]$^+$</td>
<td>818.9</td>
<td>819.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$_2$ZrMe(μ-Me)BR$_3$</td>
<td>823.2</td>
<td>821.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cp$_2$Zr(μ-Me)$_2$AlMe$_2$]+</td>
<td>831.6</td>
<td>830.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The η$_5$-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. A somewhat exaggerated broadening (Lorentzians with width up to 20 cm$^{-1}$) was applied to form a single broad band, as observed in the experiments. The general appearance of the calculated spectra of Cp$_2$ZrMe$_2$, Cp$_2$ZrMeCl, and Cp$_2$ZrCl$_2$ is in good agreement with experiment. A comparison is shown for Cp$_2$ZrMe$_2$ in Fig. 2A in the range from 400 to 1500 cm$^{-1}$. In Fig. 2B, a comparison is shown for the Cp out-of-plane deformation band at about 800 cm$^{-1}$ 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 $\nu(\text{exp}) = 1.01 \nu(\text{ADF}) + 16$. Corresponding trend lines for the correlation between experiment and band positions calculated with Gaussian are $\nu(\text{exp}) = 0.84 \nu(G_1) + 147$, $\nu(\text{exp}) = 0.80 \nu(G_2) + 160$, and $\nu(\text{exp}) = 1.08 \nu(G_3) - 72$.

In the present work considerable effort has been directed towards gaining more 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 $\nu$ (cm$^{-1}$) = 1536 + 89 $q$ - 295 $d$ (ADF), $\nu$ (cm$^{-1}$) = 1536 + 89 $q$ - 295 $d$ (G$_1$), $\nu$ (cm$^{-1}$) = 1536 + 89 $q$ - 295 $d$ (G$_2$), and $\nu$ (cm$^{-1}$) = 1536 + 89 $q$ - 295 $d$ (G$_3$), 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 frequency $\nu$ 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 $\nu$ 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 $\nu$ 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 have small values of $\nu$. 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 other atom(s), aluminum, oxygen forms a bond of "normal" strength to Zr, resulting in a fairly long Zr-Cp distance.
Fig. 232 Comparison of calculated and measured IR spectra. A: $\text{Cp}_2\text{ZrMe}_2$ in the range 400 to 1500 cm$^{-1}$. Lorentzians with width 5 cm$^{-1}$ are used in the calculated spectrum. B: $\text{Cp}_2\text{ZrMe}_2$ (solid), $\text{Cp}_2\text{ZrMeCl}$ (dashed), $\text{Cp}_2\text{ZrCl}_2$ (dotted) in the range 750 to 850 cm$^{-1}$. Lorentzians with width 20 cm$^{-1}$ are used in the calculated spectra.

Fig. 343 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, smaller CF$_3$ model ligands on B were used: $R=\text{CF}_3$ (calculation), $\text{C}_6\text{F}_5$ (experiment). (I skrivende stund tror jeg rett og slett en figur med “de 7” og en lineær fit til alle disse er det jeg helst vil ha her.... Muligens alle 4: ADF, G1, G2, G3 for å se effekt av programvalg, funksjonal, basissett...)

Reactions with Aluminum Alkyls

In the mixture of $\text{Cp}_2\text{ZrCl}_2$ and $\text{Cp}_2\text{ZrMe}_2$, a slow exchange takes place and $\text{Cp}_2\text{ZrMeCl}$ 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 new product.
In agreement with earlier reports, Cp$_2$ZrMeCl is obtained in moderate yield in the reaction of TMA with Cp$_2$ZrCl$_2$ [4,15]. No IR band attributable to Cp$_2$ZrMe$_2$ was observed. The ability of TMA to fully methylate the zirconocene was further investigated in a separate experiment by adding TMA to Cp$_2$ZrMeCl. No Cp$_2$ZrMe$_2$ 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. Since a methyl bridge implies an unfavorable two-electron three-center bonding structure, we expect chlorine rather than methyl to form the bridge between zirconium and aluminum. The only new zirconocene species observed in the proton NMR spectrum of the mixture of Cp$_2$ZrCl$_2$ in and a large excess of TMA was Cp$_2$ZrMeCl, 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 Cp$_2$ZrMe$_2$ and TMA. As expected, the double methyl bridge of the TMA dimer is preferred to the single bridge in Cp$_2$ZrMe(μ-Me)AlMe$_3$. Addition of DMAC to Cp$_2$ZrMe$_2$ rapidly gave Cp$_2$ZrMeCl and TMA as the first products. Further additions of DMAC gave Cp$_2$ZrCl$_2$ 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 reaction, the system contains several compounds that may form adducts: Cp$_2$ZrMe$_2$, Cp$_2$ZrMeCl, Cp$_2$ZrCl$_2$, DMAC, and TMA. A band in this position was not observed in any of the binary mixtures with TMA. The addition of the same amount of DMAC to Cp$_2$ZrCl$_2$ 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 is formation of a chlorine-bridged adduct Cp$_2$ZrMe(μ-Cl)AlMe$_3$Cl. We were not able to confirm this complex by NMR. The calculated spectrum predicts a band position at 821 cm$^{-1}$, though the calculated energy turned out endothermic.

In summary, TMA is not able to dimethylate the zirconocene, but forms instead Cp$_2$ZrMeCl. In systems containing chlorine, new products are formed, presumably chlorine bridged hetero-bi-metallic adducts. The equilibrium constants are small as none of the complexes was observed as the major component of their mixtures.
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 $\text{B(C}_6\text{F}_5\text{)}_3$ and $[\text{C(C}_6\text{H}_5\text{)}_3]^+[\text{B(C}_6\text{F}_5\text{)}_4]^-$ have been investigated using in situ IR spectroscopy. These cocatalysts are known to produce "tight" and "weak" ion pairs, involving the cations $[(\text{Cp}_2\text{ZrMe})_2(\mu-\text{Me})]^+$ and $\text{Cp}_2\text{ZrMe}^+$ and the counter-ions MeB($\text{C}_6\text{F}_5\text{)}_3$ and B($\text{C}_6\text{F}_5\text{)}_4$, respectively. The purpose was to obtain experimental frequencies of reaction products with $\text{Cp}_2\text{ZrMe}_2$ 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 was confirmed by $^1\text{H}$ NMR.

When $\text{B(C}_6\text{F}_5\text{)}_3$ was added to $\text{Cp}_2\text{ZrMe}_2$, the first new band in the 800 cm$^{-1}$ region was observed at 818 cm$^{-1}$ ($\text{B/Zr} = 0.3$). Further addition of $\text{B(C}_6\text{F}_5\text{)}_3$ gave a new strong band at 824 cm$^{-1}$. Bands due to free $\text{B(C}_6\text{F}_5\text{)}_3$ 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 did not appear. In this system, the cation $[(\text{Cp}_2\text{ZrMe})_2(\mu-\text{Me})]^+$ is known to be formed at low B/Zr ratios while $[\text{Cp}_2\text{ZrMe}]^+$ (actually, Cp$_2$ZrMe(μ- Me)B($\text{C}_6\text{F}_5\text{)}_3$) is formed at higher B/Zr ratios [4,16]. We therefore attribute the band at 818 cm$^{-1}$ to $[(\text{Cp}_2\text{ZrMe})_2(\mu-\text{Me})]^+$ and the band at 825 cm$^{-1}$ to $[\text{Cp}_2\text{ZrMe}]^+$. 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 $\text{Cp}_2\text{ZrMe}_2$ with $[\text{C(C}_6\text{H}_5\text{)}_3]^+[\text{B(C}_6\text{F}_5\text{)}_4]^-$ were monitored in a similar experiment. A single band at 820-818 cm$^{-1}$ was clearly observed immediately after mixing, but moved slowly to 824 cm$^{-1}$ within few hours. In this system, the binuclear cation $[(\text{Cp}_2\text{ZrMe})_2(\mu-\text{Me})]^+$ appears to be kinetically preferred and is formed even with excess cocatalyst before it is slowly converted into $[\text{Cp}_2\text{ZrMe}]^+$ (actually, weakly coordinating $\text{Cp}_2\text{ZrMe}...(\text{C}_6\text{F}_5\text{)}_4\text{B}$ ion pairs) [8]. The band at 820-818 cm$^{-1}$ is accordingly attributed to the binuclear cation and the band at 825 cm$^{-1}$ to $[\text{Cp}_2\text{ZrMe}]^+$. Addition of TMA to this mixture immediately gave a new band at 832 cm$^{-1}$. The same band was obtained when $\text{Cp}_2\text{ZrMe}_2$ was added to a mixture of TMA and boron activator. We attribute this band to $[\text{Cp}_2\text{Zr(μ-Me)}_2\text{AlMe}_2]^+$. In Fig. 4 is shown the 800 cm$^{-1}$ region of the IR spectra of three reaction mixtures in these systems.

The IR data obtained in the boron-based systems shows that important intermediates are identified by IR spectroscopy as well as by NMR spectroscopy.
Fig. 56. IR spectra of the reaction mixtures \( \text{Cp}_2\text{ZrMe}_2/[\text{C}(\text{C}_6\text{H}_5)_3]^+\text{[B(C}_6\text{F}_5)_4^-} \) (after 2 and 155 min), \( \text{Cp}_2\text{ZrMe}_2/[\text{C}(\text{C}_6\text{H}_5)_3]^+\text{[B(C}_6\text{F}_5)_4^-]/\text{TMA} \) (also shown \( \text{C}(\text{C}_6\text{H}_5)_3]^+\text{[B(C}_6\text{F}_5)_4^-]/\text{TMA} \)), and \( \text{Cp}_2\text{ZrMe}_2/\text{B(C}_6\text{F}_5)_3 \).

Discussion of predictions based on DFT

Predictions based directly on the harmonic IR spectra calculated with DFT:

- The chlorine bridged adduct of \( \text{Cp}_2\text{ZrMeCl} \) and TMA is predicted to have a band position at 821 cm\(^{-1}\).
- The chlorine bridged adduct of \( \text{Cp}_2\text{ZrMeCl} \) and DMAC is predicted to have a band position at 821 cm\(^{-1}\).
- The calculations predict band positions at 816 and 827 cm\(^{-1}\) for the binuclear cation and the methyl-bridged \( \text{Cp}_2\text{ZrMe(μ-Me)}\text{B(CF}_3)_3 \), respectively.
- The calculations predict a band position at 831 cm\(^{-1}\) for \( \text{[Cp}_2\text{Zr(μ-Me)}_2\text{AlMe}_2]^+ \).

Predictions of the linear models based on Q(Cp) and d(Zr-Cp):

- ...
- ...
- ...

(Forsøker med et eget lite kapittel om prediksjoner basert på DFT, før de "vanskelige" MAO-resultatene kommer... Hmm, ikke sikker på om disse prediksjonene fortjener et eget kapittel likevel.... Muligens kunne en lage en egen tabell med "spekulative" strukturer og f.eks. Cp2ZrMe+...
I skrivende stund har jeg gjort noen endringen nedenfor her, men noe gjenstår fremdeles...)
Reactions with MAO

In this section, we report the results of in situ IR studies of reactions of Cp$_2$ZrMe$_2$ and Cp$_2$ZrCl$_2$ with MAO at relatively low Al/Zr ratios. In both systems, a new band was immediately observed, at 820 and 822 cm$^{-1}$ with Cp$_2$ZrCl$_2$ and Cp$_2$ZrMe$_2$, respectively, indicating that at least one new stable product is formed. Using Cp$_2$ZrCl$_2$, 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 Cp$_2$ZrCl$_2$. Clearly, the bridges are essential to the methylation of the catalyst. We have previously shown that in MAO only the bridging methyls are exchangeable with the chlorine of DMAC [67]. The terminal methyls do not take part in the methylation. In the mixture of MAO and Cp$_2$ZrCl$_2$, 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 Cp$_2$ZrMe$_2$ and Cp$_2$ZrCl$_2$, respectively, is too small to be significant. However, the DFT calculations suggest that the latter Al–Cl–Al is preferred by about 5 kcal/mol.

**Fig. 6** Left figure shows the IR spectra of normal and chlorinated MAO (MAO+ reacts DMAC). Right figure shows the effect on the spectrum of MAO by addition of Cp$_2$ZrCl$_2$ (Al/Zr=....).

The subsequent studies were performed with Cp$_2$ZrMe$_2$ to exclude any ambiguity concerning chlorine or methyl groups. In Fig. 7Fig. 8, spectral changes upon addition of Cp$_2$ZrMe$_2$ to MAO are shown. A series of IR spectra is 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. This makes a careful scaling of the spectra necessary. The scaling allows a comparison based on the shape of the band envelope, rather than the absolute intensity. The scaling procedure is described in greater detail in the Experimental section.
**Fig. 78** IR spectra of mixtures of Cp₂ZrMe₂ and MAO in toluene at progressively higher concentrations of zirconocene. c_{Al(start)}=0.5M. The spectra for the pure Cp₂ZrMe₂ 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 Cp₂ZrMe₂ and MAO are mixed. The bands in the region 1150-1300 cm⁻¹, shown in Fig. 7, are attributed to out-of-plane deformations of Cp (left frame) and symmetric deformations of methyls on MAO (right frame), respectively. The CP out-of-plane deformation band is around 800 cm⁻¹ (left frame) are in this case superimposed on the strong, broad Al-O stretching/methyl rock band centered at 808 cm⁻¹. At high Al/Zr ratios, the only new band observed is at 822 cm⁻¹. The absence of a sharp band at 803 cm⁻¹ indicates that all or most of the zirconocene is reacted. The band at 803 cm⁻¹ was not observed before further zirconocene addition brought the Al/Zr ratio below 30. The bands attributed to the symmetric methyl deformations of MAO at 1200–1270 cm⁻¹ changed in shape with the addition of Cp₂ZrMe₂ until an Al/Zr ratio of 15–20 was reached. Further additions had little effect on these bands, while free Cp₂ZrMe₂ was clearly observed (803 cm⁻¹). 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 Cp₂ZrMe₂ is observed while the MAO is changing, and the other where Cp₂ZrMe₂ is observed, but no changes is seen in the MAO bands. In other words, MAO appears to consume all the added Cp₂ZrMe₂ 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 Cp₂ZrMe₂ did not initiate other substantial changes in the IR spectrum than the appearance of TMA bands. Surprisingly, no band due to [Cp₂Zr(μ-Me)₂AlMe₂⁺] was observed at 832 cm⁻¹. Hence, the species responsible for the band at 822 cm⁻¹ appears to be a tightly bound adduct, not an ion pair. Otherwise, one would expect it to be easily transformed into [Cp₂Zr(μ-Me)₂AlMe₂⁺].

**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 Cp₂ZrMe₂/MAO system, the IR band at 822 cm⁻¹ disappeared, and a broad band appeared around 815 cm⁻¹. 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⁻¹ is diagnostic for vinylidene end groups of poly-1-hexene, i.e., it verifies catalytic activity. When MAO was added to a solution of 1-hexene and Cp₂ZrMe₂, the band at 822 cm⁻¹ did not appear at all and catalytic activity was observed. Monomer was also added to a solution of [Cp₂ZrMe]⁺[MeB(C₆F₅)₃]⁻. The band at 825 cm⁻¹ attributed to this complex immediately disappeared and catalytic activity was observed 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/C\(_2\)ZrMe\(_2\) system, the accompanying changes in the bands around 1200 cm\(^{-1}\), and the absence of the C\(_2\)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 C\(_2\)ZrMe\(_2\), the changes in the MAO bands cease and the C\(_2\)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. In the mixture of C\(_2\)ZrMe\(_2\) and B(C\(_6\)F\(_5\))\(_3\), a methyl bridged compound is easily formed. Although the Lewis acidity of MAO may be less than for the boron activator, similar stable methyl bridged adducts are likely. A weak NMR signal was observed and attributed to the methyl bridge by Babushkin et al. Why just one and not all 4-5 acidic aluminum of an average MAO molecule is able to connect to a metallocene is peculiar, if true. Another possible mode of binding with MAO is through an oxygen. Earlier discussions on the mechanism of activation have also involved oxo-bridges in an intermediate step. A, and a Zr-O bond has already been verified for a tert-butyl aluminoxide with strained structure and no alkyl bridges. The tert-butyl aluminoxide cage reacts in a similar manner to with TMA. Strained bonds (“latent Lewis acidic sites”) are thereby opened. Since a significant amount of TMA is always present in commercial MAO solutions, we will argue that these “latent Lewis acidic” sites are already occupied by TMA and no longer available for the metallocene, unless a replacement reaction takes place. The incorporation of TMA introduces reactive methyl bridges, consistent with previous IR studies of MAO.

Identification of It has not been possible to identify the species responsible for the observed band at 822 cm\(^{-1}\). Although the cation [(C\(_2\)ZrMe\(_2\))(μ-Me)]\(^+\) gives a band in the right position, NMR results show that it is not likely that it is not generated in high yield at this low Al/Zr ratio. More likely candidates are methyl- or oxo-bridged adducts. The predicted band positions of the oxygen-bridged models, such as C\(_2\)ZrMe\(_2\)(OMe)\(_2\) and C\(_2\)ZrMe\(_2\)(OAlMe\(_2\))\(_2\), are in the range 797- and 812 cm\(^{-1}\), respectively. The calculations of the methyl bridged adducts of C\(_2\)ZrMe\(_2\) and small MAO cage models with bridging methyls predict band positions around 810 cm\(^{-1}\) for the Cp out-of-plane deformation.

The deviation from the observed band at 822 cm\(^{-1}\) is larger than the expected error in these calculations, suggesting that the metallocene is not linked to MAO through oxygen.
The results suggesting that \( \text{Cp}_2\text{ZrMe}_2 \) rapidly and quantitatively reacts with MAO, have implication to the discussion of the activation process. If \( \text{Cp}_2\text{ZrMe}_2 \) 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.

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

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

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 \( \text{Cp}_2\text{ZrMe}_2 \) is claimed to be present even with a large excess of MAO [3]. However, the present IR results indicate that most of the \( \text{Cp}_2\text{ZrMe}_2 \) 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 act as a temporary storage until the proper MAO species comes by. In our view, a more likely explanation is that \([\text{Me}–\text{MAO}]^-\) is assisted by additional MAO cages in hiding the negative charge from the electrophilic cation by formation of larger anions, e.g. a \([\text{MAO}–\text{Me}–\text{MAO}]^-\) dimeric cage. The second equilibrium then becomes:

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

Calculations, using a \( \text{Me}_{12}\text{Al}_8\text{O}_6 \) 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 is slightly more than the effect of monomer coordination to the formed cation. The calculation also indicates that the added methyl bears a significant part of its charge of the single-cage MAO anion. This charge is effectively (hidden or) spread out by the second MAO cage. Eq. 3 may need a large excess of MAO to be driven towards the product side, since the additional MAO must compete with the cation for the negatively charged point. The activation sequence is depicted in Fig. 8.

The MAO cages are viewed directly along their \( C_2 \) 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 \([\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+\) and \([\text{Cp}_2\text{ZrMe}]_2(\mu\text{-Me})]^+\) in this model. The failure to observe \([\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+\) 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. 8.** Ball and stick model of the suggested mechanism for zirconocene activation. A relatively small MAO cage model, Me₆(µ-Me)₂Al₆O₆, is used and viewed along its C₂ axis. (Hydrogens are not shown.)

**Conclusion (ikke endret...)**

In the binary mixtures of Cp₂ZrMe₂, Cp₂ZrCl₂, DMAC, and TMA, new products were observed, except for TMA/Cp₂ZrMe₂ (and TMA/DMAC). The new products were Cp₂ZrMeCl and unidentified hetero-bimetallic complexes.

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.

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**References**

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.