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Activation of Metallocenes for Olefin Polymerization As Monitored by IR Spectroscopy

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Binary mixtures of Cp_2ZrMe_2, Cp_2ZrCl_2, dimethylaluminum chloride, trimethylaluminum, and methylaluminoxane (MAO), as well as Cp_2ZrMe_2 with boron-based activators, have been studied by in situ IR spectroscopy (Cp = cyclopentadienyl, Me = methyl). The position of a strong band near 800 cm^{-1}, corresponding to the out-of-plane vibration of the Cp hydrogen atoms, is sensitive to the bonding environment around Zr and can be used to monitor reactions and the formation of new products in these mixtures. Harmonic frequencies determined by density functional theory correlate well with experimental values and have been used to assist in the interpretation of the data. The frequency of the Cp out-of-plane vibration, ranging from 797 to 832 cm^{-1} in our experiments, is found to increase with increasing electron density on the Cp ring and decreasing Zr–Cp distance. In the mixture of MAO and Cp_2ZrMe_2, a stable complex is rapidly formed at low Al/Zr ratios. A mechanism that may explain the need for a large MAO excess is proposed for the activation of metallocenes with MAO. The proposed mechanism involves the formation of dimers or oligomers of MAO cages that tend to dissipate the charge of the anion. This destabilization of the Cp_2ZrMe_2–MAO complex facilitates the formation of the catalytically active cation.

Introduction

The oligomeric compound methylaluminoxane (MAO) is known as a highly efficient activator for metallocene catalysts of 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, because of studies with well-defined boron activators.[1] Several intermediates in boron-activated systems have been identified by NMR spectroscopy or X-ray diffraction. By comparison of NMR shifts, several cationic Zr species have also been identified in the metallocene/MAO system.[3,4] Further evidence has been obtained by UV−vis spectroscopy, which is insensitive to the large amount of MAO present under normal polymerization conditions.[5] IR and NMR spectroscopy respond differently to fast chemical exchange among multiple components because of their different characteristic time scales. In IR spectroscopy, the individual components are observed, while in the NMR spectrum, an average signal appears. Recently, new results on the structure of MAO have been obtained by in situ IR spectroscopy.[6,7] In particular, bridging methyl groups were identified as an essential part of the MAO structure and found to be crucial to the metallocene activation. The bridging methyl groups were not recognized in NMR studies.

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In the activation of metallocenes by MAO, the first step is the reversible formation of an adduct.[3] This is followed by the formation of the cationic species $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+$, $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$, and $[Cp_2ZrMe]^+$ (Cp = cyclopentadienyl, Me = methyl).[3,4] The unprotected cation $[Cp_2ZrMe]^+$ is probably rare, and it has been proposed that the MAO anion coordinates through an unsymmetrical methyl bridge.[3] Trimethylaluminum (TMA) constitutes a significant part of commercial MAO solutions, but its full role in the activation is not clear.[2,8] TMA is able to monomethylate the metallocene, and then it reacts to form the $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ cation.[4,5]

In the present IR study, we investigated binary mixtures of Cp_2ZrMe_2, Cp_2ZrCl_2, TMA, DMAC (dimethylaluminum chloride), and MAO, as well as mixtures of Cp_2ZrMe_2 and boron-based activators. All reactions were studied in situ using a custom-built liquid flow cell constructed to meet the challenges of material inertness and sample handling posed by these reactive systems. The IR spectra of known and anticipated metallocene species were also investigated by density functional theory (DFT), focusing on the band corresponding to the out-of-plane vibration of the hydrogen atoms on the Cp ring, at around 800 cm^{-1}. The position of this band is sensitive to changes in the bonding environment around the zirconium atom, and the correlation between observed band position and calculated structural parameters was investigated.

The metallocene/MAO systems, in which stable intermediates are observed at unexpectedly low Al/Zr ratios, are particularly interesting.[9,10] Possible structural candidates for these intermediates are discussed, as well as a mechanism to explain the need for a large MAO excess for the reaction.

Experimental Section

General. All operations were carried out under a dry nitrogen or argon atmosphere (99.999%) using standard Schlenk techniques. Solids were handled in a glovebox. Solutions were transferred and metered with lubricant-free disposable syringes or gastight microsyringes. The IR spectra were recorded on a Bruker IFS66v spectrometer using a custom-built liquid flow cell.[11] The cell and the attached glass equipment make a closed loop consisting of a glass mixing tank (20 mL), a micropump to circulate the liquid, and the IR cell. The circulation ensures rapid mixing and constant sampling of the studied solution. Uniform mixing is achieved within 1−2 min after reactant addition. The entire sample passes through the loop during this time. A flow split leads about 10% of the flow between the windows. Silicon and germanium windows were used because MAO reacts with halide salts.[12] The spectra were recorded with a nominal resolution of 2 cm^{-1} and zero-filled to 0.5 cm^{-1}. To obtain the spectra of the solute, the solvent spectrum was digitally removed using a spectrum of the pure solvent. The regions around 740 and 690 cm^{-1} are obscured because of the strong bands for toluene.

The phase separation observed in the concentrated MAO/metallocene systems induces fluctuations in the intensity of the IR spectra.[13] A similar phase separation is observed in the $C(C_6H_5)_3B(C_6F_5)_4/Cp_2ZrMe_2$ system and is responsible for the observed double set of ^1H NMR peaks.[14] The spectra were recorded over 2 min (300 scans) with a constant circulation of the sample solution to ensure that the spectra were representative for both phases. Still, this was not adequate to average all fluctuations. The spectra of the MAO/metallocene system were therefore scaled to equal intensity at 790 cm^{-1} for the purpose of observing relative changes in the IR bands. Studies of more dilute solutions were attempted to avoid phase separation, but a reliable analysis was, in this case, prevented by a low signal-to-noise ratio.

Materials. Trimethylaluminum (TMA) and dimethylaluminum chloride (DMAC) were purchased from Aldrich and used without further purification. The absence of air contamination products in MAO, TMA, and DMAC was verified by the 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 (3 Å). The MAO solution (Albemarle, 10 wt % in toluene) was solidified at room temperature under reduced pressure. Cp_2ZrMe_2 (Strem Chemicals), Cp_2ZrCl_2 (Boulder Scientific), tris(pentafluorophenyl)boron (Strem Chemicals), and trityl tetra(pentafluorophenyl)boron (Albemarle) were used as received.

Preparations. TMA-depleted MAO was prepared by removing the TMA and solvent from a commercial MAO solution by reduced pressure (to about 0.07 mbar) at room temperature. The solid MAO was redissolved in toluene, and the procedure was repeated to further reduce the amount of TMA. The solid was evacuated at less than 0.1 mbar for at least 2 h. $Cp_2ZrMeCl$ was prepared from equimolar amounts of Cp_2ZrCl_2 and Cp_2ZrMe_2.[15] The reaction took place over 2−3 weeks in benzene at room temperature. ^1H NMR (d^8 toluene): δ 0.45, Me; 5.78, Cp. IR: 809 cm^{-1}. $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ was prepared by mixing equimolar amounts of solid Cp_2ZrMe_2 and $B(C_6F_5)_3$.[16] Benzene was added at −65 °C, and the mixture was slowly heated and stirred for 2 h. Dry pentane was added, and the precipitate was filtered and washed three times with pentane. ^1H NMR (d^8 toluene): δ 0.26, 0.11, Me; 5.45, Cp. IR: 825 cm^{-1}. $(Cp_2ZrMe)_2(\mu\text{-}O)$ was prepared via the reaction of Cp_2ZrMe_2 with water in THF. Cp_2ZrMe_2 (0.13 g) was dissolved in 5 mL of tetrahydrofuran (THF), and the mixture was cooled to −35 °C. Water (4.6 mg) dissolved in THF was added slowly, and the solution was slowly heated to room temperature. The solvent was removed by evaporation, and the solid residue was dissolved in toluene. ^1H NMR (d^6 benzene): δ 0.23, Me; 5.74, Cp. IR: 797 (Cp oop), 740 cm^{-1} (Zr−O stretch). The NMR peaks are in agreement with literature data.[17] In addition to $(Cp_2ZrMe)_2(\mu\text{-}O)$, the product contained $(Cp_2ZrO)_3$. ^1H NMR: δ 6.21, Cp.[18] [(Cp_2-

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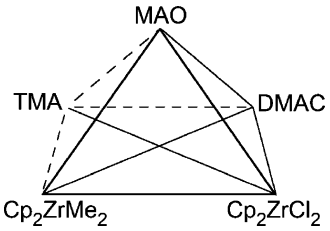

Figure 1. Overview of the aluminum-based systems studied. Dashed lines connect components whose mixture yielded no detectable new species. Solid lines indicate the formation of a new compound.

$ZrMe)_2(\mu\text{-Me})]^+$ was prepared by mixing solutions of $C(C_6H_5)_3B(C_6F_5)_4$ and Cp_2ZrMe_2 directly in the in situ IR apparatus at room temperature. ^{1}H NMR (d^6 benzene): δ −0.09, −1.22, Me; 5.61, Cp. IR: 818 cm^{-1}. $[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+$ was prepared by adding excess TMA to the previous mixture and by adding TMA and a solution of Cp_2ZrMe_2 to a solution of $C(C_6H_5)_3B(C_6F_5)_4$. ^{1}H NMR (d^6 benzene): δ −0.40, −0.73, Me; 5.44, Cp. IR: 832 cm^{-1}.

Computational Details. All calculations are based on DFT. The programs used were ADF 2.3 (Scientific Computing and Modeling)[19] and Gaussian 03 (Gaussian Inc.).[20] Different levels of computation were used to verify observed trends and correlation between the experiment and theory.

In ADF, the density functionals used were those of Vosko, Wilk, and Nusair (VWN)[21] for the local density part. Gradient corrections, based on the functionals proposed by Becke[22] for exchange and Perdew and Wang[23] 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−3d orbitals on Zr, the 1s−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** (G_1), B3LYP/3-21G** (G_2), and B3LYP/6-31+G(d,p) (G_3). 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 Figure 1. Dashed lines indicate binary mixtures where no new products were detected by IR spectroscopy. Comparative studies were performed with the two well-characterized boron cocatalysts $B(C_6F_5)_3$ and $C(C_6H_5)_3B(C_6F_5)_4$ using both IR and NMR spectroscopy.

Table 1. Experimental and Calculated Band Positions (cm^{-1}) of the Out-of-Plane Deformations of the C−H Bonds of the Cp Ring for Selected Zirconocenes and Complexes in Aromatic Solution

	compound	ADF[b]	G_1[c]	G_2[d]	G_3[e]	exp
A[a]	Cp_2ZrMe_2	781	779	804	807	803
	$Cp_2ZrMeCl$	790	783	807	814	809
	Cp_2ZrCl_2	793	783	809	820	814
B[a]	$(Cp_2ZrMe)_2(\mu\text{-O})$	777	780	797	803	797
	$[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$	794	799	822	821	818
	$Cp_2ZrMe(\mu\text{-Me})BR_3$	806	810	828	824	825
	$[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+$	810	807	839	834	832

[a] A: simple zirconocenes. B: complexes verified by ^{1}H NMR. [b] BPW91/DZP, TZP. [c] BPW91/3-21G**. [d] B3LYP/3-21G**. [e] B3LYP/6-31+G(d,p), LANL2DZ. See Experimental Section for details.

The η_5-cyclopentadienyl ligands of metallocenes have a relatively simple IR spectrum with a few strong bands.[24] The strongest band, caused by the out-of-plane deformations of the C−H bonds, is also the band most sensitive to changes in the coordination of Zr and therefore suitable for monitoring reactions. The positions of this band for simple zirconocenes (A) and four zirconocene complexes (B) are given in Table 1.

Theoretical IR spectra were calculated within the harmonic approximation. A single conformation with respect to the relative rotation of the Cp 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 (G_2)[25] and 20 cm^{-1} (ADF)[25] were applied to form a single band, as observed in the experiments. The general appearance of the calculated spectra of Cp_2ZrMe_2, $Cp_2ZrMeCl$, and Cp_2ZrCl_2 is in good agreement with experiment. A comparison (G_3)[25] is shown for Cp_2ZrMe_2 in Figure 2B. In Figure 2A, calculated (G_3) and experimental Cp out-of-plane deformation bands at around 800 cm^{-1} are shown for all three zirconocenes. Four additional zirconocene complexes have been verified with NMR spectroscopy. In Figure 3, calculated (ADF) and experimental band positions of the Cp out-of-plane deformations are compared for all seven verified complexes. The best linear fit is given by $\nu(\text{exp}) = 1.005\nu(\text{ADF}) + 17$. Corresponding lines obtained with Gaussian calculations are $\nu(\text{exp}) = 0.829\nu(G_1) + 158$, $\nu(\text{exp}) = 0.799\nu(G_2) + 163$, and $\nu(\text{exp}) = 1.145\nu(G_3) - 122$.

In the present work, considerable effort has been directed toward gaining insight into how the position of the band resulting from the Cp out-of-plane deformation is influenced by changes in the steric and electronic environment of the zirconium atom. A multivariate analysis on the basis of 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 ref 24) 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. The results suggest a shift

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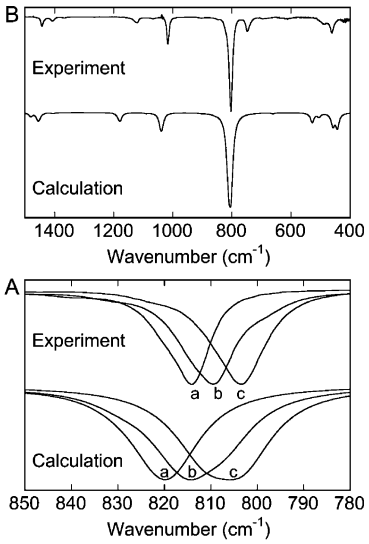

Figure 2. Comparison of calculated (G_3)[25] and measured IR spectra. Lorentzians with a width of 7 cm^{-1} are used in the calculated spectra. A: (a) Cp_2ZrCl_2, (b) $Cp_2ZrMeCl$, and (c) Cp_2ZrMe_2 in the 780−850 cm^{-1} range. B: Cp_2ZrMe_2 in the 400−1500 cm^{-1} range. All spectra have been scaled to a common minimum value for the transmissivity. The band at 750 cm^{-1} in the experimental spectrum of Cp_2ZrMe_2 is probably the Zr−O stretch in $(Cp_2ZrMe)_2(\mu$-O), which is caused by traces of oxygen impurities. The Cp out-of-plane vibration of $(Cp_2ZrMe)_2(\mu$-O) was found at 797 cm^{-1} in a separate experiment.

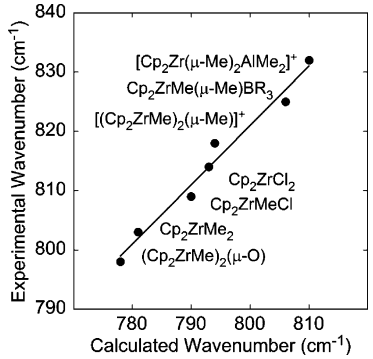

Figure 3. Comparison of measured and calculated (ADF)[25] frequencies for the out-of-plane C−H deformations of Cp. For the methyl-bridged complex with the boron cocatalyst, CF_3 model ligands on B were used: R═CF_3 (calculation), C_6F_5 (experiment). We have verified, at the G_1 and G_2 levels,[25] that calculations with R═C_6F_5 yield essentially identical band positions. Corresponding curves based on band positions calculated with Gaussian show a similar correlation, with the exception of level G_1. Deviations from the fitted line are characterized by r^2 values of 0.98 (ADF), 0.82 (G_1), 0.95 (G_2), and 0.97 (G_3).

to higher frequencies when the Cp ring becomes more strongly bound to Zr (i.e., when the attachment of remaining ligands to Zr becomes looser). The best linear fit (ν_m) to the observed band positions is given by the equations $\nu_m(\mathrm{ADF}) = 1501 + 91q - 279d$, $\nu_m(G_1) = 1561 + 65q - 326d$, $\nu_m(G_2) = 1853 + 27q - 459d$, and $\nu_m(G_3) = 1751 + 23q - 415d$, with $q = Q(\mathrm{Cp})$ in units of the elementary charge (e) and $d = d(\mathrm{Zr-Cp})$ in Å. Predicted band positions based on these models are given in Table 2. The observed trends, which are independent of the choice of density functional and basis set, may be summarized as follows: (1) Cations and compounds with bridging ligands have higher frequencies than neutral compounds. Removing a ligand completely or partly, as with a bridge, decreases the electron density in the Cp rings (i.e., q increases) and leads to a shorter Cp−Zr distance (because all cations in this study are stabilized by bridging ligands, the effect of the total charge alone is not clear). (2) Compounds with methyl ligands have lower ν values than compounds with chlorine ligands. Methyl is less electronegative than Cl, resulting in a more negative Cp ring. (3) Compounds with oxygen ligands tend to have low values of ν. The two-coordinate oxygen is a good electron donor, resulting in a more negative Cp ring. Even in a three-coordinated bridging position between Zr and two Al atoms, as in the model structure $Cp_2ZrMe(\mu_3\text{-O})Al_6O_5Me_7$,[26] oxygen forms a relatively strong bond to Zr, resulting in a fairly long Zr−Cp distance.

Table 2. Calculated Band Positions (cm^{-1}) of the Cp Out-of-Plane Deformation On the Basis of the Calculated Mulliken Charge on the Cp Ring and the Distance Between Zr and the Center of the Cp Ring[a]

	compound	ADF	G_1	G_2	G_3
A	Cp_2ZrMe_2	803	804	804	802
	$Cp_2ZrMeCl$	810	811	811	811
	Cp_2ZrCl_2	817	817	816	818
B	$(Cp_2ZrMe)_2(\mu$-O)	795	794	794	795
	$[(Cp_2ZrMe)_2(\mu$-Me)]$^+$	819	819	819	818
	$Cp_2ZrMe(\mu$-Me)BR_3	823	822	824	824
	$[Cp_2Zr(\mu$-Me)$_2AlMe_2]^+$	831	830	831	830
	calibration r^2	0.98	0.95	0.98	0.96
	validation r^2 [b]	0.91	0.80	0.89	0.78

[a] See footnotes for Table 1 and text for details. [b] Validation r^2 is based on a full leave-one-out cross-validation.

Reactions with Aluminum Alkyls. In the mixture of Cp_2ZrCl_2 and Cp_2ZrMe_2, a slow exchange takes place, and $Cp_2ZrMeCl$ is formed in good yield.[15] The reaction proceeds over several weeks. The original bands at 814 and 803 cm^{-1} diminish, and a new strong band appears at 809 cm^{-1}, characteristic of the product.

In agreement with earlier reports, $Cp_2ZrMeCl$ was obtained in a moderate yield in the reaction of TMA with Cp_2ZrCl_2.[4,5,27] No IR band attributable to Cp_2ZrMe_2 was observed. Further, no Cp_2ZrMe_2 was detected when TMA was added to $Cp_2ZrMeCl$ in a separate experiment; instead, the IR spectrum indicated the presence of a new species with the Cp out-of-plane deformation band at 815 cm^{-1}. This result suggests the formation of a chlorine-bridged adduct, $Cp_2ZrMe(\mu$-Cl)$AlMe_3$. The corresponding titanium complex is known.[28,29] The preference for a chlorine bridge over an electron-deficient methyl bridge is clearly demonstrated by the chlorine-bridged dimer of DMAC.[30,31]

No new compounds were observed in the mixture of Cp_2ZrMe_2 and TMA; hence, the double methyl bridge of the TMA dimer is preferred to a single bridge between Zr and Al. The addition of DMAC to Cp_2ZrMe_2 rapidly resulted in

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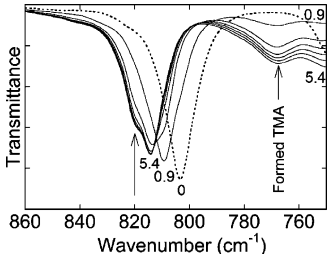

Figure 4. IR spectra acquired during the addition of DMAC to Cp_2ZrMe_2 (at Al/Zr ratios of 0, 0.9, 1.8, 2.7, 3.6, 4.5, and 5.4; initial [Zr] = 0.05 M). The region of the out-of-plane Cp deformation is shown. After the first addition of DMAC (Al/Zr = 0.9), the band position is at 809 cm^{-1} (because of $Cp_2ZrMeCl$). At Al/Zr = 5.4, the main band is at 814 cm^{-1} (because of Cp_2ZrCl_2) with a shoulder at 820 cm^{-1} (suggested to be the result of a chlorine-bridged adduct, $Cp_2ZrMe(\mu\text{-Cl})AlMe_2Cl$). The spectra were recorded 3−4 min after the additions.

$Cp_2ZrMeCl$ and TMA as the first products (Al/Zr = 0.9). The addition of more DMAC (up to Al/Zr = 5.4) gave Cp_2ZrCl_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 Figure 4. The system now contains several compounds that may form adducts, Cp_2ZrMe_2, $Cp_2ZrMeCl$, Cp_2ZrCl_2, DMAC, and TMA. No band was observed at 820 cm^{-1} in any of the binary mixtures with TMA; hence, DMAC, rather than TMA, must be involved in the formation of the new species. In another experiment, no shoulder was observed at 820 cm^{-1} when 5 equiv of DMAC was added to Cp_2ZrCl_2; hence, $Cp_2ZrMeCl$, rather than Cp_2ZrCl_2, is the component involved. When the amount of DMAC was raised 1 order of magnitude until Al/Zr = 48, a weak shoulder was observed. Likely explanations in this case are the formation of $Cp_2ZrCl(\mu\text{-Cl})AlMe_2Cl$ at a high Al/Zr ratio or a methylation of the zirconocene. The most likely cause of the shoulder at 820 cm^{-1} in the Cp_2ZrMe_2 and DMAC mixture is a chlorine-bridged adduct, $Cp_2ZrMe(\mu\text{-Cl})AlMe_2Cl$, formed by $Cp_2ZrMeCl$ and DMAC. The corresponding titanium complex has been reported.[28]

Attempts to verify the presence of $Cp_2ZrMe(\mu\text{-Cl})AlMe_3$ and $Cp_2ZrMe(\mu\text{-Cl})AlMe_2Cl$ by proton NMR spectroscopy were not successful. When Cp_2ZrCl_2 and a large excess of TMA were mixed to produce $Cp_2ZrMe(\mu\text{-Cl})AlMe_3$, the only new species identified were $Cp_2ZrMeCl$ and DMAC. However, the methyl resonance of the zirconocene at 0.45 ppm was unusually wide, 25 Hz, which indicates the presence of a dynamic process. When Cp_2ZrMe_2 and DMAC were mixed to produce $Cp_2ZrMe(\mu\text{-Cl})AlMe_2Cl$, several peaks were observed, but these could not be assigned unambiguously. Calculated frequencies support the interpretation in terms of chlorine-bridged adducts with predicted band positions of 819 ± 3 cm^{-1} for $Cp_2ZrMe(\mu\text{-Cl})AlMe_3$ and 820 ± 2 cm^{-1} for $Cp_2ZrMe(\mu\text{-Cl})AlMe_2Cl$ (based on the four DFT levels).

In summary, TMA is not able to dimethylate the zirconocene but causes the formation of $Cp_2ZrMeCl$. In systems containing chlorine, new products are formed, presumably bimetallic adducts bonded by a single chlorine bridge. None of the adducts were observed as the major component of their mixtures, consistent with the low calculated reaction energies for the formation of these adducts (1 ± 2 kcal/mol for $Cp_2ZrMe(\mu\text{-Cl})AlMe_3$ and 0 ± 5 kcal/mol for $Cp_2ZrMe(\mu\text{-Cl})AlMe_2Cl$).

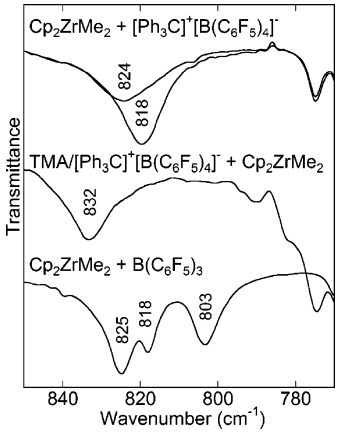

Figure 5. IR spectra of the reaction mixtures $Cp_2ZrMe_2/C(C_6H_5)_3B(C_6F_5)_4$ (band position at 818 and 824 cm^{-1} after 2 and 155 min, respectively), $Cp_2ZrMe_2/C(C_6H_5)_3B(C_6F_5)_4$/TMA, and $Cp_2ZrMe_2/B(C_6F_5)_3$. In all of the spectra, B/Zr = 1. The band at 803 cm^{-1} in the lower spectrum is *not* a result of free Cp_2ZrMe_2. The DFT calculations suggest that this is caused by a vibrational mode in the $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ complex involving B−(μ-Me) stretch and C_6F_5 in-plane and out-of-plane deformation.

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 $B(C_6F_5)_3$ and $C(C_6H_5)_3B(C_6F_5)_4$ has been investigated with in situ IR spectroscopy. The purpose of studying them in this work was to obtain experimental frequencies for their reaction products with Cp_2ZrMe_2. These cocatalysts are known to produce the cations $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ and $[Cp_2ZrMe]^+$. The latter will presumably not be present as a naked cation but will form tight and loose ion pairs with the counterions $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$, respectively. Solutions of the reagents were prepared and mixed directly in the in situ IR apparatus at room temperature. Samples were prepared for ^1H NMR with the same procedures that were used for the IR experiments, and the main products and their order of appearance during the reaction were confirmed.

When $B(C_6F_5)_3$ was added to Cp_2ZrMe_2, the first new band to appear in the 800 cm^{-1} region was detected at 818 cm^{-1} (B/Zr = 0.3). Further addition of $B(C_6F_5)_3$ resulted in a new strong band at 825 cm^{-1} (see Figure 5). Bands from free $B(C_6F_5)_3$ were not observed until the B/Zr ratio exceeded unity, and at this point the reaction seemed to be complete as no further change was observed in the spectrum of the zirconocene. When the reactants were added in opposite order, starting with excess $B(C_6F_5)_3$, the band at 818 cm^{-1} did not appear. In this system, the cation $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ is known to be formed at low B/Zr ratios, while $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ is formed at higher B/Zr ratios.[4,32] We therefore attribute the band at 818 cm^{-1} to $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ and the band at 825 cm^{-1} to $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$. The latter complex was also prepared outside the IR cell at low temperature as described by Yang et al.[16] The resulting

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IR spectrum essentially contained the same bands and an additional weak band with varying intensity and frequency between 813 and 818 cm^{-1}. It is not clear whether the latter feature is a result of $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+$ or another product.

The reactions of Cp_2ZrMe_2 with $C(C_6H_5)_3B(C_6F_5)_4$ were monitored in a similar experiment. A single band at 818 cm^{-1} was clearly observed immediately after mixing but was gradually substituted with a band at 824 cm^{-1} within a few hours. In this system, the binuclear cation $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+$ appears to be kinetically preferred and is formed even with excess cocatalyst before it is slowly converted into $[Cp_2ZrMe]^+$ (or rather weakly coordinating $[Cp_2ZrMe]^+\cdots[B(C_6F_5)_4]^-$ ion pairs).[14] The band at 818 cm^{-1} is therefore attributed to the binuclear cation and the band at 824 cm^{-1} to $[Cp_2ZrMe]^+$. The addition of TMA to this mixture immediately resulted in a new band at 832 cm^{-1}. The same band was also obtained when Cp_2ZrMe_2 was added to a mixture of TMA and boron activator. We attribute this band to the binuclear cation $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$. In Figure 5, 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 show that important intermediates can be identified by IR as well as by NMR spectroscopy. Also, the DFT calculations support the assignment of the experimentally observed IR bands (see Table 1 and Figure 3). Using the linear fit between the calculated and observed band positions, the band for the binuclear cation $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+$ is predicted to be in the 815−820 cm^{-1} range at the four computational levels (see the Overview). The band for the methyl-bridged complex, $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, is correspondingly predicted to be in the 824−829 cm^{-1} range. Somewhat surprisingly, the band position of the naked cation $[Cp_2ZrMe]^+$ is predicted to be in the 825−830 cm^{-1} range, in good agreement with the experimental value. On the basis of its low electron density on the Cp rings and small Zr−Cp distance, one might have expected a band position at higher frequency. Finally, the position of the band of the cation $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ is predicted to be in the 827−833 cm^{-1} range. As can be seen in Table 1, these are all in agreement with experimental frequencies.

Reactions with MAO. In this section, we report the results of in situ IR studies of the reactions of Cp_2ZrCl_2 and Cp_2ZrMe_2 with MAO at low Al/Zr ratios. New bands were immediately observed at 820 and 822 cm^{-1} for Cp_2ZrCl_2 and Cp_2ZrMe_2, respectively, showing that at least one new product is formed. When Cp_2ZrCl_2 was used, there was a substantial decrease in the intensity of the band attributed to the bridging methyl groups in MAO at 1257 cm^{-1}. As shown in Figure 6, the changes are similar to those produced by addition of DMAC to MAO, where MAO is chlorinated by DMAC. The top frame shows a comparison between MAO and the recovered MAO after reaction with DMAC. The bottom frame shows MAO before and after the addition of Cp_2ZrCl_2. We have previously shown that only the bridging methyls in MAO are exchangeable with the chlorine of DMAC, and even in the presence of TMA, the chlorinated

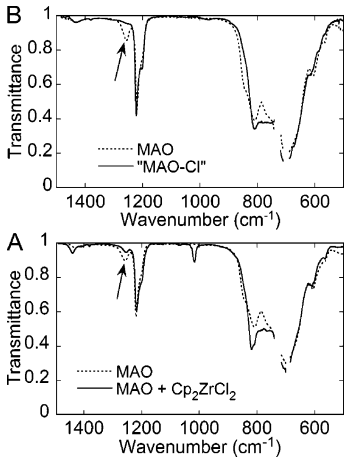

Figure 6. B: IR spectra of normal and chlorinated MAO (MAO after reaction with DMAC and subsequent workup[7]). A: Effect on the spectrum of MAO by addition of Cp_2ZrCl_2 (Al/Zr = 10, [Zr] = 0.1 M).

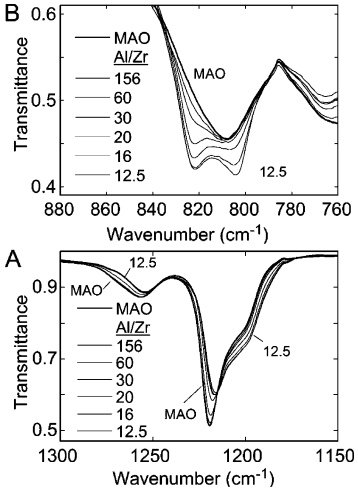

Figure 7. IR spectra of mixtures of Cp_2ZrMe_2 and MAO in toluene at progressively higher concentrations of zirconocene. A: Symmetrical deformation of methyl on Al. B: Cp out-of-plane deformation superimposed on MAO bands (initial [Al] = 0.5 M, final [Al] = 0.33 M, [Zr] = 0.027 M). The solvent component of the spectra has been removed. The spectra have been slightly scaled to compensate for the random variations in intensity caused by phase separation.

MAO was unable to activate $(Me_5C_5)_2ZrCl_2$.[7] Clearly, the methyl bridges in MAO are essential to the activation of the catalyst. In the mixture of MAO and Cp_2ZrCl_2, it was not possible spectroscopically to determine if the chlorines form Zr−Cl−Al links or go into Al−Cl−Al environments with methyl or oxygen as the bridging unit between MAO and the zirconocene. DFT calculations suggest that the combination of Al−Cl−Al and Zr−Me−Al is preferred over Al−Me−Al and Zr−Cl−Al by about 5 kcal/mol, but kinetic effects may play a role.

The subsequent studies were performed with Cp_2ZrMe_2 to exclude any ambiguity concerning the chlorine or methyl groups. In Figure 7, spectral changes upon the addition of Cp_2ZrMe_2 to MAO are shown. The series of IR spectra was recorded at progressively higher concentrations of zirconocene. Unfortunately, in concentrated samples, a phase separation takes place, and the random distribution of the two phases in the IR cell influences the intensity of the spectrum. A quantitative analysis is therefore not possible,

but a careful scaling of the spectra allows trends to be observed on the basis of the shape of the band envelope. The scaling procedure is described in the Experimental Section.

Distinct changes indicative of a reaction are observed in several regions of the IR spectrum when Cp_2ZrMe_2 and MAO are mixed. The bands in the 1150−1300 cm^{-1} region, shown in Figure 7A, are caused by the symmetric deformations of methyls on MAO. The band at 1257 cm^{-1} is assigned to the bridging methyls, while the group of bands below 1240 cm^{-1} represents different terminal methyls.[7] The Cp out-of-plane deformation bands around 800 cm^{-1} (Figure 7B) are superimposed on the strong broad Al−O stretching/methyl rock band of MAO centered at 808 cm^{-1}.[33] At the highest Al/Zr ratios, the only new band in this region is observed at 822 cm^{-1}. The absence of a sharp band at 803 cm^{-1} indicates that all or most of the zirconocene has reacted. This band was not observed until further addition of zirconocene 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 Cp_2ZrMe_2 until an Al/Zr ratio of 15−20 was reached. Further additions had no effect on these bands, consistent with the observation of free Cp_2ZrMe_2. Changes were also found in the region of C−H stretching, but the interpretation is complicated by band overlap. Except for the fluctuations caused by the phase separation, the spectrum was stable for several hours. From the described behavior, there appears to be an equivalence point at Al/Zr = 15−20. At higher Al/Zr ratios, no free Cp_2ZrMe_2 is observed while MAO is changing. At lower Al/Zr ratios, Cp_2ZrMe_2 is observed, but no changes are seen in the MAO bands.

Upon addition of excess TMA to a mixture of MAO and Cp_2ZrMe_2 ($Al_{TMA}/Zr = 11$), the band at 822 cm^{-1} disappeared, and a new band was observed at 816 cm^{-1}. In contrast to the boron-based system with $C(C_6H_5)_3B(C_6F_5)_4$, no band for $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ was detected at 832 cm^{-1}. Spectroscopic evidence for this cation has been reported but only at high Al/Zr ratios.[3] The source of the new band at 816 cm^{-1} has not been identified.

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_2ZrMe_2/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} characteristic of the vinylidene end groups of poly-1-hexene verifies catalytic activity. When MAO was added to a solution of 1-hexene and Cp_2ZrMe_2, the band at 822 cm^{-1} did not appear at all, and catalytic activity was observed. The monomer was also added to a solution of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$.[34] The band at 825 cm^{-1}, attributed to this complex, immediately disappeared followed by 1-hexene consumption. Catalytic activity at a low Al/Zr ratio with a chlorine-free system and a TMA-depleted MAO has also been reported by Pedeutour et al.[5]

Discussion

A substantial problem in the use of metallocene-based catalysts is the large excess of MAO required to obtain high polymerization activity. Although some MAO is simply consumed in the reaction with impurities and passivated by chlorination, 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 the 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 challenge is different.

The observation of a new IR band at 822 cm^{-1} in the MAO/Cp_2ZrMe_2 system, the accompanying changes in the bands around 1200 cm^{-1}, and the absence of the Cp_2ZrMe_2 band at 803 cm^{-1} indicate that an extensive reaction is taking place, even at low Al/Zr ratios. When the Al/Zr ratio is brought below 15−20 by the addition of more Cp_2ZrMe_2, the changes in the MAO bands cease, and the Cp_2ZrMe_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.[35] An association of Cp_2ZrMe_2 and MAO at a low Al/Zr ratio was also detected by Babushkin et al., but their results indicate that a slightly higher Al/Zr ratio is required to consume all of the Cp_2ZrMe_2.[3]

Bonding between MAO and the metallocene may occur through a methyl group or oxygen.[3,26,36] In the mixture of Cp_2ZrMe_2 and $B(C_6F_5)_3$, a methyl-bridged compound is formed. Similar methyl-bridged adducts are likely to form with MAO as well. On the basis of ^{13}C NMR spectroscopy, a reversible methyl-bridged adduct has been suggested by Babushkin et al.[3] Zr−O bonding has been verified for Cp_2ZrMe_2 and a *tert*-butyl aluminoxane with a strained structure and no alkyl bridges.[37] The *tert*-butyl aluminoxane cage reacts in a similar manner with TMA, forming bridging methyls while strain is released.[38] Since a significant amount of TMA is always present in commercial MAO solutions, we argue that the strained Al−O bonds are already opened, occupied by TMA, and no longer available for the metallocene. Instead, there are bridging methyl groups with reactive electron-deficient bonds. This is consistent with the reported high cocatalytic activity of the *tert*-butyl aluminoxane cage after reaction with TMA.[38]

(33) The calculations predict that deuteration of the Cp ligands will lower the Cp out-of-plane deformation to around 600 cm^{-1}, but there will still be an overlap with a MAO band of medium intensity at 605 cm^{-1} (see Figure 6).
(34) Solution of the complex prepared at low temperature.

(35) Sinn, H. *Macromol. Symp.* **1995**, *97*, 27−52.
(36) Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375−2381.
(37) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465−6474.
(38) Watanabe, M.; McMahon, C. N.; Harlan, C. J.; Barron, A. R. *Organometallics* **2001**, *20*, 460−467.

We have calculated (at the G_1 level) the IR spectrum of the two candidates, oxo-bridged $Cp_2ZrMe(\mu_3\text{-}O)Al_6O_5Me_7$ and methyl-bridged $Cp_2ZrMe(\mu\text{-}Me)Al_8O_6Me_{12}$, for the adduct responsible for the observed band at 822 cm^{-1}.[39] The former would be the result of a reaction between Cp_2ZrMe_2 and a $Me_6Al_6O_6$ MAO cage with only terminal methyl groups and Me/Al = 1.0. The latter would be the result of a reaction between Cp_2ZrMe_2 and a more realistic MAO structure, $Me_{12}Al_8O_6$, with methyl bridges and Me/Al = 1.5. In both cases, the Cp out-of-plane deformations are coupled to other vibrations of the adduct. In the calculations, several bands are present in the 760−840 cm^{-1} region, both in the MAO cage itself and in the two anticipated MAO/zirconocene adducts. For example, the methyl-bridged adduct has an almost linear methyl bridge between Zr and Al; this bridge has deformation modes coupled to Cp out-of-plane vibrations that are candidates for the observed band at 822 cm^{-1}. Furthermore, since the complexity of the real MAO solution is not fully expressed by a single structure, the experimental and calculated spectra are not easily compared in this case. It is therefore not possible to determine if the new band at 822 cm^{-1} is caused by a shift of the Cp out-of-plane vibrational mode or by changes in other characteristic modes upon adduct formation.

The question of whether the complex is linked by oxygen or methyl is not resolved by the experiments. However, we will argue that a methyl-bridged MAO/zirconocene adduct is more likely than an oxo-bridged one. First, the presence of methyl bridges in MAO is evident through the IR band at 1257 cm^{-1}. This is also clearly verified in the calculated spectrum of MAO. Second, the formation of a Zr−O bond requires that a rather strong Al−O bond be broken (assuming only three-coordinate oxygen and the absence of highly strained Al−O bonds). Presumably, the methyl bridge in MAO is the most reactive feature and will easily open up to form the new connection. The following discussion of a possible activation mechanism is, therefore, based on the methyl-bridged adduct.[40]

The rapid and extensive reaction of Cp_2ZrMe_2 with MAO at a low Al/Zr ratio has an implication on the discussion of the activation process. 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.

$$Cp_2ZrMe_2 + MAO = Cp_2ZrMe(\mu\text{-}Me)MAO \quad (1)$$

$$Cp_2ZrMe(\mu\text{-}Me)MAO = [Cp_2ZrMe]^+\cdots[Me\text{-}MAO]^- \quad (2)$$

Since MAO quickly consumes the free Cp_2ZrMe_2, the large excess of MAO is not necessary to drive eq 1 to the product side. The production of a free cation, eq 2, seems to be the limiting step. How can excess MAO help in this case? The prevailing explanation in the literature is that MAO has sites with different Lewis acidities, and only the most acidic sites are able to weaken the methyl−zirconium bond sufficiently to form ion pairs. We would like to draw attention to an alternative explanation complementary to the action of superacidic rare species.

The need for stabilization of the cation, by either the olefin, TMA, or another weak donor, has been extensively discussed in the literature.[2] The need for additional stabilization of the anion has received less attention. Marks et al.,[2] in their work on noncoordinating boron activators, have demonstrated the importance of both steric hindrance and charge dissipation at the anion to promote activation of the metallocene. A single MAO cage may not provide adequate charge dissipation, resulting in an overly strong interaction with the metallocene. With excess MAO, additional MAO cages will compete with the zirconocene cation and may form dual cage anions, $[MAO-Me-MAO]^-$, that provide better shielding of the negative charge. The second equilibrium, now with MAO on the reactant side, becomes

$$Cp_2ZrMe(\mu\text{-}Me)MAO + MAO = [Cp_2ZrMe]^+\cdots[MAO-Me-MAO]^- \quad (3)$$

Calculations, using a $Me_{12}Al_8O_6$ cage model with methyl bridges, show that the energy expense of forming a separated ion pair is lowered by as much as 20 kcal/mol with eq 3 compared to that of eq 2. A similar result was obtained by Ustynyuk and Fushman with $Al(C_6F_5)_3$.[41] This contribution to ion pair separation is of the same order as the effect of monomer coordination. The activation sequence is depicted in Figure 8. The MAO model can be described as a hexagonal cage (side view) opened at opposite sides to accommodate two $AlMe_3$ units.

For simplicity, we have not considered the formation of $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ and $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+$ in this model. It is easily expanded to include these bimetallic cations, but this part will not deviate from previous works. The failure to observe $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ when MAO and TMA were added may be a consequence of the low Al/Zr ratio, or the band may be masked by changes in the underlying shoulder at 840 cm^{-1} in the MAO spectrum.

Conclusions

Changes in the position of the out-of-plane vibration of the hydrogen atoms on the Cp ring are correlated with changes in the bonding environment around Zr in various zirconocenes and zirconocene complexes. On the basis of DFT calculations, which reproduce the experimentally observed trends, it is found that the position of this band increases with increasing electron density on the Cp ring and decreases with increasing distance from Zr to the Cp ring. In binary mixtures of Cp_2ZrMe_2, Cp_2ZrCl_2, DMAC, and TMA, new products were observed, except for TMA/Cp_2-

(39) Although the $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+$ cation has a band in roughly the right position, NMR results show that it is not generated in a high yield at this low Al/Zr ratio (ref 4).

(40) A related scheme was sketched by Kaminsky and Steiger (ref 36) using an oxygen-bridged adduct. However, the linear representation used for MAO does not reflect the real availability of unsaturated oxygen.

(41) Ustynyuk, L. Yu.; Fushman, E. A. *Russ. J. Phys. Chem.* **2004**, *78*, 936−942.

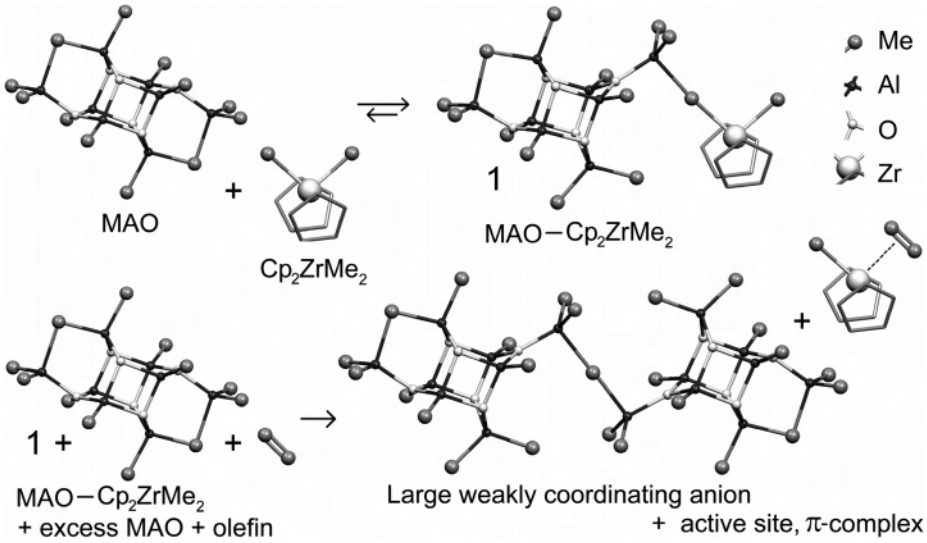

Figure 8. Ball and stick model of the suggested mechanism for zirconocene activation with MAO. A relatively small MAO cage model, $Me_{10}(\mu\text{-}Me)_2\text{-}Al_8O_6$, is used and viewed slightly tilted off its C_2 axis. Hydrogen atoms are not shown.

$ZrMe_2$ (and TMA/DMAC). The new products were $Cp_2\text{-}ZrMeCl$ and bridged hetero-bimetallic complexes. In the mixture of MAO and Cp_2ZrMe_2, a new stable complex, most likely involving a methyl bridge between Zr and Al, is observed with an IR band at 822 cm^{-1}. It is rapidly formed at low Al/Zr ratios and is proposed to be a precursor to the active catalyst. A mechanism is suggested for the activation of the metallocenes with MAO that is consistent with the need for a large excess of MAO. A key feature of this mechanism is formation of MAO cage dimers or oligomers that tend to spread out the charge of the anion and facilitate formation of the active cation.

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