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Published on Web 10/05/2002

Activation of Dimethyl Zirconocene by Methylaluminoxane (MAO)—Size Estimate for Me-MAO$^-$ Anions by Pulsed Field-Gradient NMR

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Received May 6, 2002

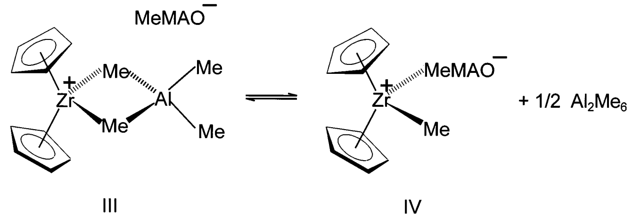
Abstract: In a study of the reaction system MAO/$(C_5H_5)_2ZrMe_2$, the size of the ion pair $[(C_5H_5)_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ $[\text{Me-MAO}]^-$ was determined by pulsed field-gradient NMR of its cationic moiety. A mean effective hydrodynamic radius of 12.2−12.5 Å, determined from diffusion rates in benzene solution at different zirconocene and MAO concentrations, indicates that the ion pair remains associated even at the lowest concentrations studied. At elevated concentrations, aggregation to ion quadruples or higher aggregates is indicated by an apparent size increase and by shifts of the C_5H_5 and Me ^{1}H NMR signals. The equilibrium constant for the reaction $[(C_5H_5)_2ZrMe^+\cdots\text{Me-MAO}^-] + {}^1/_2Al_2Me_6 \rightleftharpoons [(C_5H_5)_2Zr(\mu\text{-}Me)_2AlMe_2]^+\ [\text{Me-MAO}]^-$ changes at different Al/Zr ratios; this indicates that MAO contains various species that produce Me-MAO$^-$ anions with different Lewis basicities. The volume of the Me-MAO$^-$ anion suggests that it contains 150−200 Al atoms.

Introduction

Even though polymerization of alkenes with methylaluminoxane-activated metallocene catalysts has been the object of substantial interest for more than two decades, the structure of methylaluminoxane (MAO) and the mechanisms of its cocatalytic action are still unclear.[1] It is generally assumed that some particularly Lewis acidic sites of the MAO cluster are capable of abstracting a Cl$^-$ or Me$^-$ unit from a zirconocene chloride or methyl precursor to generate an ion pair of general type $(C_5H_5)_2ZrMe^+$ Me-MAO$^-$.[1d]

Recent studies have provided some details with regard to the structure and the nature of the zirconocene species that appear in the system MAO/$(C_5H_5)_2ZrMe_2$. Two of them, a weak Lewis acid adduct of the type $(C_5H_5)_2Zr(Me)Me \rightarrow Al(MAO)$ (type **I**) and an ion pair containing the dinuclear cation $[\{(C_5H_5)_2ZrMe\}_2(\mu\text{-}Me)]^+$ (type **II**), predominate at relatively low [Al]/[Zr] ratios but disappear when the excess of MAO is increased.[2] At ratios of Al/Zr > 200 (as are typical for active catalyst systems) only two other species are observed, an ion pair of the cation $[(C_5H_5)_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ with some Me-MAO$^-$ counteranions (type **III**)[2,3] and a species containing a $(C_5H_5)_2ZrMe^+$ cation in contact with a CH_3 group of a stable Me-MAO$^-$ anion (type **IV**),[2] from which **III** arises in an equilibrium reaction with Al_2Me_6 (Scheme 1).

Scheme 1



For an understanding of these catalyst systems, it would be highly desirable to elucidate the nature both of the MAO[4] and of the Me-MAO$^-$ species present in these equilibria. Pulsed field-gradient (PFG) NMR methods, which allow the determination of translational diffusion coefficients of a molecule or ion, would in principle be ideal to estimate the molecular dimensions of the Me-MAO$^-$ anions, which are necessarily produced when dimethyl zirconocene complexes are transformed to cationic species. Since signals of the Me-MAO$^-$ moieties cannot be identified, however, in the ^{1}H NMR spectra of these reaction systems (because of their overlap with signals of neutral MAO), we have measured the rate of diffusion of the cationic

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(4) For the molecular size of MAO, an average diameter of 19.4 ± 0.4 Å has recently been estimated from ^{1}H spin−lattice relaxation times: Hansen, E. W.; Blom, R.; Kvernberg, P. O. *Macromol. Chem. Phys.* **2001**, *202*, 2880.

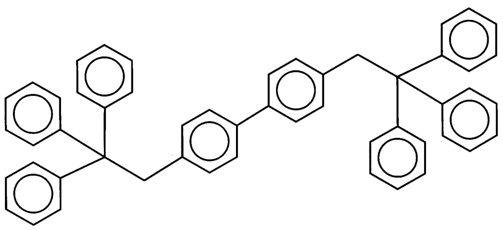
10.1021/ja020646m CCC: $22.00 © 2002 American Chemical Society

Table 1. Relative Reciprocal Diffusion Coefficients and Effective Hydrodynamic Radii of Species **III**, Chemical Shifts and Line Widths of the ^{1}H NMR Signals of Its $(C_5H_5)_2Zr(\mu\text{-}Me)_2AlMe_2^+$ Moiety, and Concentration Ratios of Species **III** and **IV** at Different Zirconocene and MAO Concentrations[a]

sample	$[Zr]_{tot}$, mmol/L	$[Al]_{tot}$, mol/L	Al/Zr	D_{ref}/D_{III}, ±0.03	R_{III}, ±0.2	δ(**III**-C_5H_5), ppm ± 0.002	δ(**III**-Me), ppm ± 0.002	Δω (**III**-C_5H_5), Hz ± 0.1	Δω (**III**-Me), Hz ± 0.1	[**IV**]/[**III**]
1	12.0	0.72	60	1.88	14.4	5.466	−0.611	1.03	1.18	5.37
2	2.6	0.72	280	1.86	14.3	5.418	−0.634	0.46	0.90	3.23
3	1.36	0.72	530	1.85	14.2	5.414	−0.637	0.42	0.89	2.28
4	0.048	0.72	15 000	1.59	12.2	5.418	−0.640	0.64		<1
5	7.17	0.43	60	1.74	13.3	5.442	−0.632	0.84	1.18	6.79
6	3.5	0.21	60	1.65	12.7	5.423	−0.647	0.65	0.94	8.71
7	1.54	0.43	280	1.67	12.8	5.405	−0.650	0.45	0.89	3.67
8	0.81	0.43	530	1.63	12.5	5.403	−0.649	0.43	0.88	2.58

[a] Measured in C_6D_6 solution at 300 K.

Chart 1



metallocene moieties. In this way, we were able to apply PFG NMR methods for the first time to MAO/metallocene reaction systems and to estimate the size of the counteranions Me-MAO$^-$ that arise in these catalytically active systems.

Experimental Section

Diffusion measurements were performed using a Bruker DRX 600 NMR spectrometer, supplied with a BGU II gradient unit and a probehead with Z-gradient. Sample solutions were prepared by dissolving weighed amounts of dry MAO[5] in C_6D_6 solutions of $(C_5H_5)_2ZrMe_2$, directly in an NMR tube, so as to give the final concentrations indicated in Table 1. Their ^{1}H NMR spectra were recorded at 600 MHz using standard 5-mm NMR tubes without spinning. Chemical shifts were calculated using the solvent signal (C_6D_5H, 7.15 ppm) as a reference. All measurements were carried out at a sample temperature of 300 K, stable within ±0.1 K and with an uncertainty of ±1 K. PFG NMR experiments were performed using a LED (longitudinal eddy current delay) pulse sequence,[6] 10 different gradient strengths from 5 to 50 G/cm, gradient pulse durations of 1.5−3 ms, diffusion times of 60−250 ms, longitudinal eddy current delays of 20−50 ms, relaxation delays of 20−60 s, and 8−32 scans. The 90° radio frequency pulse duration (about 11 μs) was calibrated for each sample within ±0.1 μs.

Quantitative integral intensity measurements for the samples were done separately at 250 MHz, using relaxation delays of 30−60 s and 20−200 scans. Spin−lattice relaxation times (T_1) corresponding to different signals were estimated by progressive saturation and were about 3−4 s for C_5H_5 protons, 1.5−2 s for Me protons of zirconocene activation products, and 0.25 s for CH_2 protons of the reference compound $C_{52}H_{42}$, (bis-α,α′(trityl)-4,4′-dimethylbiphenyl) (Chart 1). The singlet CH_2 signal of this internal reference compound at 3.80 ppm was used for all diffusion and integral intensity measurements. For this purpose, bis-α,α′(trityl)-4,4′-dimethylbiphenyl was prepared in analogy to a procedure previously described,[7] and characterized by ^{1}H NMR [(C_6D_6, δ): 3.80 (s, 4H), 6.67 (d, 4H, 7.8 Hz), 7.00 (d, 6H, 7.2 Hz), 7.04 (t, 12H, 7.2 Hz), 7.08 (d, 4H, 7.8 Hz), 7.22 (d, 12H, 7.2 Hz)] and ^{13}C NMR [($CDCl_3$, signal intensities determined with inverse gated proton decoupling, δ): 46.29 (CH_2, 2C), 58.79 (C, 2C), 125.90 (CH, 4C), 126.26 (CH, 6C), 127.91 (CH, 12C), 130.13 (CH, 12C), 131.78 (CH, 4C), 137.62 (C, 2C), 138.56 (C, 2C), 146.91 (C, 6C)]. The chemical inertness of this reference compound toward MAO and MAO/$(C_5H_5)_2ZrMe_2$ reaction mixtures in solution was confirmed by separate experiments.

The Stejskal−Tanner PFG NMR eq 1, where I = signal intensity, γ = gyromagnetic ratio, δ = duration of gradient field pulse, Δ = diffusion time, G = gradient strength, and D_t = translational self-diffusion coefficient,[8] can be simplified to eq 2 for measurements with an internal reference:

$$I = I_0 \exp\{-(\gamma\delta G)^2[\Delta - (\delta/3)]D_t\} \qquad (1)$$

$$\ln (I_X/I_{X,0}) = (D_X/D_{ref}) \ln(I_{ref}/I_{ref,0}) \qquad (2)$$

$$\ln(I_X) = A \ln(I_{ref}) + B \qquad (3)$$

Using this simplified equation, signal intensities for the reference compound (I_{ref}) and for the species of interest (I_X), measured at 10 different gradient strengths from 5 to 50 G/cm, were analyzed by least-squares linear regression of the corresponding relation (eq 3), where the regression coefficient A is the ratio of the diffusion coefficients of species X and the reference, D_X/D_{ref}. Correlation coefficients were typically 0.999−0.9999. Measurements were repeated several times with various longitudinal eddy currents and relaxation delays and with various durations of Δ and δ, keeping $\delta^2[\Delta - (\delta/3)]$ approximately constant such that I_0/I remains in the optimal range of 3−10 at $G = 50$ G/cm. Values of a diffusion coefficient ratio thus obtained were generally within a narrow range of ±2% and were then averaged.

By use of an internal reference, the effects of such experimental imperfections as gradient strength and temperature instabilities can be minimized. However, since noise and artifacts limit the useful dynamic range of signal attenuation in PFG NMR experiments, the diffusion coefficient of a reference compound should be close to that for the species under investigation, preferably within a factor of 2. This was achieved by using the reference compound $C_{52}H_{42}$ (Chart 1), which combines a large size with a suitable ^{1}H NMR spectrum (a singlet signal in an otherwise uncluttered region and other signals not overlapping signals of the species under investigation) and with chemical inertness.

For an approximately spherical particle much larger than a solvent molecule, the diffusion coefficient is given by the Stokes−Einstein equation, $D_t = kT/(6\pi\eta R)$, where k = Boltzman constant, T =

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(5) Methylaluminoxane (10% in toluene solution, total Al content 4.88 mass %, Al content as TMA 1.74 mass %, average molar mass 900) obtained as a gift from Witco-Crompton GmbH, Bergkamen, was evaporated to dryness in vacuo under stirring to yield a finely divided solid residue, which was then further exposed to a dynamic vacuum for 2−4 h at room temperature to remove most of its TMA content. As determined by ^{1}H NMR, C_6D_6 solutions of MAO samples thus obtained were free of oxidation-derived OCH_3 groups and contained ca. 5% of their Al content in form of free TMA.

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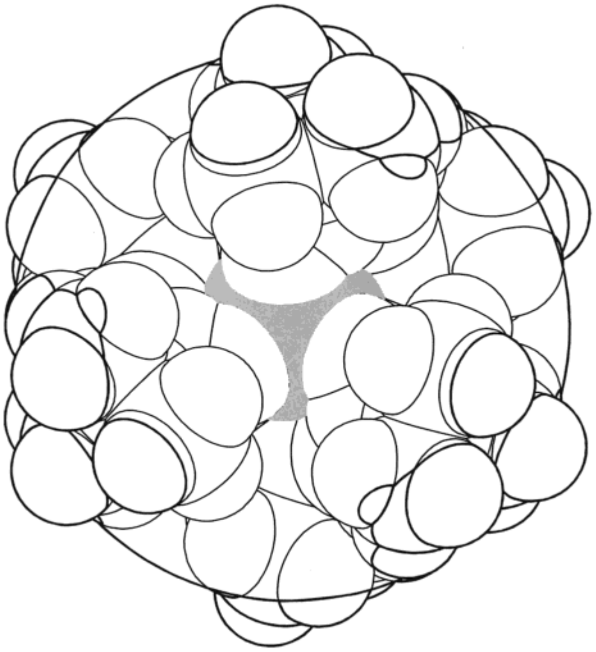

Figure 1. Schakal drawing of the van der Waals outline of $Co^{III}(DPM)_3$, modeled on the basis of the crystal structure of $Fe^{III}(DPM)_3$,[9] (projection along a C_3 axis) superimposed by a sphere with radius $r = 6.0$ Å.

temperature, η = solvent viscosity, and R = particle radius. If the shape of the reference compound can be assumed to be spherical, the effective hydrodynamic radius for species X is given by eq 4:

$$R_X = (D_{ref}/D_X)\, R_{ref} \qquad (4)$$

The molecular shape of the reference compound $C_{52}H_{42}$ is highly nonspherical, however; therefore, its effective hydrodynamic radius had to be determined by use of a primary reference. The complex $Co^{III}(DPM)_3$ (DPM = di(pivaloyl)methanate, $(CH_3)_3C{-}CO{-}CH{-}CO{-}C(CH_3)_3^-$), has a shape close to a sphere with van der Waals radius $R_{Co(DPM)_3} = 6.0$ Å (Figure 1),[9] much larger than a solvent molecule. Therefore, its diffusion coefficient can be used to determine the effective hydrodynamic radius of species X according to eq 4. Furthermore, the surface of this complex is formed by 18 methyl groups; this minimizes the probability of any π-stacking or other specific interactions with benzene solvent molecules and makes this complex an optimal primary reference for MAO and Me-MAO$^-$ particles, the surfaces of which are also thought to be lined with methyl groups. $Co(DPM)_3$ cannot be used as an internal reference, however, since it reacts with aluminum organyls. It was thus used to calibrate the diffusion coefficient of the reference compound $C_{52}H_{42}$. Measurements in C_6D_6 at 300 K gave $D_{Co(DPM)_3}/D_{ref} = 1.278$. The effective hydrodynamic radii for species X were thus determined using eq 5.

$$R_X = 1.278(D_{ref}/D_X) \times 6.0 \text{ Å} \qquad (5)$$

Results and Discussion

Of the two species (types **III** and **IV**) found in C_6D_6 solutions containing $(C_5H_5)_2ZrMe_2$ and MAO[5] at high Al/Zr ratios, species **IV** gives unsymmetrical, broad NMR signals, which are not suitable for precise PFG NMR measurements and their unequivocal interpretation, while the ion pair containing the cation $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ and the counteranion Me-MAO$^-$ (type **III**) is highly suitable for diffusion studies, since each of the ^{1}H NMR signals of their cationic parts is a sharp singlet line (Figure 2). PFG NMR measurements of the Me signal of species **III** at -0.6 ppm gave a higher diffusion coefficient than those based on its C_5H_5 signal at 5.4 ppm; in addition, the Me signal intensity deviates from the exponential decay with G^2 required by eq 1. These observations are most likely caused by the chemical exchange of Me groups between species **III** and Al_2Me_6. Measurements based on the C_5H_5 ^{1}H NMR signal of species **III** were thus used for evaluation of its diffusion rates. Diffusion coefficient ratios $D_{ref}/D_{\mathbf{III}}$ and mean effective radii $R_{\mathbf{III}}$ derived from them according to eq 5 are listed in Table 1.

For the effective radius of species **III**, values of $R_{\mathbf{III}}$ in the range of 12.2−14.4 Å are obtained at different zirconocene and MAO concentrations. This value is much larger than any reasonable estimate for the radius of the cationic part of species **III** (e.g., for $(C_5H_5)_2ZrMe_2$ we find $R \approx 3.3$ Å by PFG NMR). There can thus be no doubt that the heterodinuclear cation of species **III** diffuses, together with the Me-MAO$^-$ anion, as an associated ion pair. The fraction of time for which **III** exists as separated ions can be estimated to be so small that its contribution to the observed diffusion rates is insignificant: Almost identical values of $D_{ref}/D_{\mathbf{III}}$, obtained at zirconocene concentrations differing by a factor of 17 (samples 4 and 8), indicate a dissociation constant K of the ion pair that is substantially smaller than the lowest concentration (i.e., $K \ll 5 \times 10^{-5}$ mol/L). This result is in line with earlier reports on various alkyl zirconocene cation−borate anion pairs, which were also found to remain associated in the hydrocarbon solvent used.[10]

The $R_{\mathbf{III}}$ values obtained at different zirconocene or MAO concentrations show some minor but significant changes. As discussed above, these changes are unlikely to arise from any significant degree of ion pair dissociation. Rather, they might be caused by two concurrent effects: Increased radii might arise from formation of ion quadrupoles or higher aggregates at elevated zirconocene concentrations.[11] Such an increase in size is indeed observed when total zirconocene concentrations are increased, either at constant MAO concentrations (samples 4, 3, 2, and 1, and samples 8, 7, and 5) or at constant Al/Zr ratios (e.g., samples 6, 5, and 1).

Aggregation of two associated ion pairs to an ion quadrupole would be expected to increase the effective radius by a factor of approximately $(2)^{1/3} = 1.26$. Factors of 1.18 and 1.06, by which the effective radii of species **III** increase between samples 4 and 1 and between samples 8 and 5, respectively, are thus in a reasonable range. For decreased zirconocene concentrations, the ^{1}H NMR signals of the C_5H_5 and Me groups of species **III** move upfield to limiting values.[2] In parallel, the signals narrow significantly (Table 1). These effects are most likely due to the formation of ion quadrupoles or higher ion aggregates at elevated concentrations of **III**. The limiting values of the chemical shifts

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(9) This complex was modeled based on the crystal structure of the corresponding Fe(III) complex, $Fe(DPM)_3$ (Baidina, I. A.; Stabnikov, P. A.; Alexeev, V. I.; Igumenov, I. K.; Borisov, S. V. *Zh. Strukt. Khim.* **1986**, *27-3*, 102) by reducing metal−O distances from 1.99 to 1.89 Å, as found in the corresponding metal−acac complexes, and by minimizing intramolecular repulsions (Program HYPERCHEM). The van der Waals volume of a $Co(DPM)_3$ molecule would be equivalent to that of a sphere with radius 5.9 Å; this value is likely to underestimate the effective hydrodynamic radius, however, since the crevices between the *tert*-butyl groups appear inaccessible to solvent molecules.

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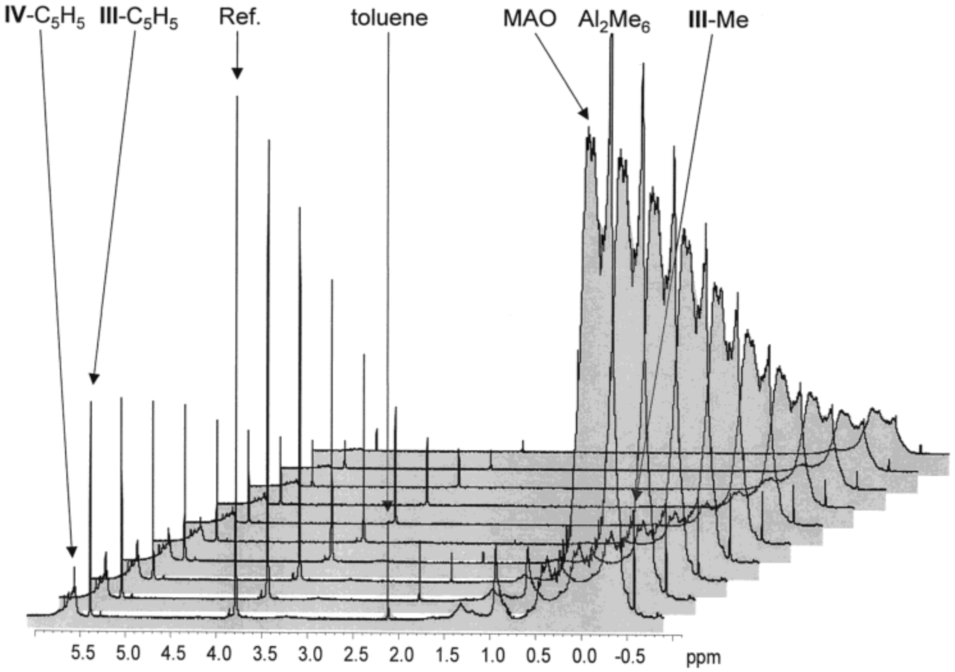

Figure 2. ^1H NMR spectra of a C_6D_6 solution containing $(C_5H_5)_2ZrMe_2$ (1.6 mmol/L) and MAO ($[Al]_{tot} = 0.7$ mol/L) at field gradients of 5 G/cm (front) to 50 G/cm (rear); duration of gradient field pulses $\delta = 2$ ms, diffusion time $\Delta = 200$ ms.

for dilute solutions can thus be considered to be those for the nonaggregated, associated ion pair **III**.

When samples with similar zirconocene concentrations (e.g., samples 3 and 7 or samples 2 and 6) are compared, R_{III} increases with MAO concentration. On the basis of the reasonable assumption that MAO molecules with different Lewis acidities differ also in their size, one would expect a gradual change of the average size of the associated ion pairs **III** with the degree of occupation of the available Lewis acidic sites of MAO. If more strongly acidic sites correspond to bigger MAO molecules, then the average size of species **III** would increase—at constant zirconocene concentration—with increasing MAO concentration, as is indeed observed. When Al/Zr ratios are changed by decreasing the zirconocene concentration at constant MAO concentration, the average degree of aggregation of ion pairs **III** and the effect of nonuniform MAO sizes described above would affect the average size of species **III** in opposite directions. This would explain why an increase of the Al/Zr ratio by a factor of 4.7 (samples 1 and 2) has only negligible effects on R_{III} while dilution with solvent by a factor of 3.4 (samples 1 and 6) diminishes R_{III} by a factor of 1.13.

Another interesting phenomenon concerns substantial changes in the concentration ratios of species **IV** and **III**, which are observed when zirconocene or MAO concentrations are changed. The interconversion between **III** and **IV** (Scheme 1) is described by the equilibrium constant K_{eq} (eq 6). Since the concentration of free Al_2Me_6 in these solutions can be assumed to be proportional to that of MAO,[12] the ratio [**IV**]/[**III**] should increase with the square root of the dilution factor when a particular sample is diluted with solvent at constant Al/Zr ratio (e.g., samples 1, 5, and 6). [**IV**]/[**III**] ratios of 6.95, 9.94, 4.18, and 2.95 are thus predicted for the diluted samples 5, 6, 7, and 8, respectively, based on the relative decrease in MAO concentrations and on the corresponding [**IV**]/[**III**] ratios of the undiluted samples, which have the same Al/Zr ratio (samples 1, 2, and 3, respectively). The experimental values of 6.79, 8.71, 3.67, and 2.58, respectively, agree surprisingly well with this prediction.

$$K_{eq} = [\mathbf{III}][\mathbf{IV}]^{-1}[Al_2Me_6]^{-1/2} \qquad (6)$$

These considerations alone are not sufficient, however, to explain the observation that the concentration ratios of species **IV** and **III** change considerably when zirconocene concentrations are decreased at constant MAO concentration. Sizable changes are observed even when all other measurable indicators—chemical shifts, signal widths, and diffusion coefficients for species **III**—remain essentially unchanged and correspond to nonaggregated, associated ion pairs (cf. samples 7 and 8). A decrease in the ratio [**IV**]/[**III**] with decreasing Zr concentrations at constant Al_2Me_6 concentration implies a change of K_{eq} in eq 6 and can be explained only by some nonuniformity in the composition and properties of the Me-MAO$^-$ anions, which causes a distribution of K_{eq} values. Our present data allow us to observe these effects of MAO nonuniformity separately from those of ion pair dissociation and aggregation and provide new evidence for conclusions made in this regard before.[2]

The surprisingly strong effects of MAO nonuniformity on K_{eq} can be qualitatively explained if we assume that at high Al/Zr ratios the MAO sites of strongest Lewis acidity give, upon abstraction of CH_3^- from $(C_5H_5)_2ZrMe_2$, a Me-MAO$^-$ anion of particularly low basicity. As a consequence, such an anion will be displaced by $AlMe_3$ more easily than more basic Me-MAO$^-$ anions formed at lower Al/Zr ratios from residual MAO molecules with lower Lewis acidity.

The effective hydrodynamic radius R_{Me-MAO} of the anion Me-MAO$^-$ itself can be assumed to be close to the values of $R_{III} =$

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[12] MAO solutions always contain some quantity of free tri(methyl)aluminum in form of the dimer (Al_2Me_6), as shown by the signals of free Al_2Me_6 in their ^1H, ^{13}C, and ^{27}Al NMR spectra: Babushkin, D. E.; Semikolenova, N. V.; Panchenko, V. N.; Sobolev, A. P.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **1997**, *198*, 3845. Compared to the zirconocene concentration range, Al_2Me_6 is always in excess.

12.2−12.5 Å, obtained for nonaggregated, associated ion pairs of type **III**, since corrections for the volume of the cation are negligible in comparison. To derive the number of Al atoms per Me-MAO$^-$ anion from these $R_{\mathrm{Me-MAO}}$ values, we have estimated, from several experimentally or theoretically determined structures of $(\mathrm{AlO}_{(3-x)/2}\mathrm{Me}_x)_n$ clusters with $n = 6-12$,[13,14] volume increments of $V_{\mathrm{Al}} \approx 40-45$ Å^3 per Al atom. This approach leads to an estimate of 150−200 Al atoms per Me-MAO$^-$ anion.

This number is higher by one order of magnitude than numbers of 10−20 Al atoms per MAO molecule, hitherto assumed on the basis of average molar masses of 600−1200 Da, determined for MAO primarily by ebullioscopy measurements.[1] This discrepancy is most likely due to the inherent weakness of colligative methods, which can provide only a number-averaged molar mass of all dissolved particles present, including variable amounts of free, dimeric trimethylaluminum, whereas our results pertain selectively to the Me-MAO$^-$ counteranions associated with alkyl zirconocene cations. Alternatively, formation of each of these anions might require more than one MAO molecule.[15]

At any rate, Al/Zr ratios of about 100−200, reported to be necessary for the conversion of a dimethyl zirconocene precursor to some marginally active complex species,[3] would thus just be sufficient to generate one Me-MAO$^-$ anion per Zr center. The question why a much greater excess of MAO—corresponding to Al/Zr ratios of 1000 or more—is generally needed for full activation of a zirconocene catalyst can now be considered in the following light: Al/Zr ratios of 1000−2000 would correspond to about 5−15 MAO molecules per Zr center, if each MAO would likewise contain 150−200 Al atoms.[15] Taking into account the nonuniform Lewis acidicity of different MAO species apparent from our results, it would appear plausible that only the most acidic 5−20% of these MAO molecules form Me-MAO$^-$ anions of sufficiently low basicity to allow their displacement from $(\mathrm{C_5H_5})_2\mathrm{ZrMe}^+$, either by TMA to form reactive species **III** or directly by an olefin to initiate polymer growth. It remains to be clarified which structural changes accompany the formation of Me-MAO$^-$ anions from their MAO precursors and how $n \approx 150-200$ $\mathrm{AlO}_{(3-x)/2}\mathrm{Me}_{x+1/n}$ units might be arranged in Me-MAO$^-$ anions of particularly low Lewis basicity.[16]

Acknowledgment. We thank Dr. Frank Schaper for help with structural modeling and for helpful comments. Gifts of MAO by Witco-Crompton and financial support of this work by INTAS (project 2000-841) and by funds of the University of Konstanz are gratefully acknowledged.

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(15) We have tried to estimate also the effective hydrodynamic radius R_{MAO} of MAO using its own ^{1}H NMR signal. While this signal is nonuniformly broadened (so as to prevent precise PFG measurements and their unequivocal interpretation) and while the Me groups of MAO exchange with much faster diffusing free $\mathrm{Al_2Me_6}$, the data obtained lead to a rough estimate of $R_{\mathrm{MAO}} \approx 12$ Å, which is somewhat larger than (but still in reasonable agreement with) that distance recently reported on the basis of ^{1}H NMR T_1 measurements.[4] Its close agreement with the mean effective radius of the Me-MAO$^-$ anion would indicate that formation of this anion requires only one MAO molecule and is not associated with any substantial enlargement of its size.

(16) For first attempts to solve this problem by means of graph theory see: Babushkin, D. E. *International Memorial K. I. Zamaraev Conference "Physical Methods for Catalytic Research at the Molecular Level"*; Novosibirsk, 1999; Abstracts, p 146.