

Toward the Identification of Dormant and Active Species in MAO (Methylaluminoxane)-Activated, Dimethylzirconocene-Catalyzed Olefin Polymerization

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Possible structural candidates for the active (**III**) and dormant (**IV**) species in dimethylzirconocene-catalyzed, MAO (methylaluminoxane)-activated olefin polymerization have been studied via density functional theory (DFT). These species are $[\text{Cp}_2\text{ZrMeAlMe}_3]^+[\text{MeMAO}]^-$ (**III**) and $[\text{Cp}_2\text{ZrMe}]^+[\text{MeMAO}]^-$ (**IV**), respectively, where $\text{Me} = \text{CH}_3$ and $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$. Relative energies in gas phase and toluene solution as well as ^1H and ^{13}C NMR chemical shifts have been calculated. These chemical shifts have been compared with ^1H and ^{13}C NMR data from new experimental investigations studying the interaction between Cp_2ZrMe_2 and MAO in toluene solution.¹ By combining experimental and theoretical results, we have been able to identify the most likely candidates for both the dormant and active species. Moreover, we are able to predict that an Al/Zr ratio of $\sim 275:1$ at 298.15 K is necessary in order for all of the Cp_2ZrMe_2 to bind to MAO as the structures we propose for **III** and **IV**. This ratio corresponds to the disappearance of the following species from solution: free Cp_2ZrMe_2 , the weak complex of Cp_2ZrMe_2 and MAO (**I**), and $[\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{Cp}_2\text{ZrMe}]^+[\text{MeMAO}]^-$ (**II**). Such a mixture would have a **IV/III** ratio of $\sim 1.8:1$.

1. Introduction

Homogeneous metallocene based precatalysts for olefin polymerization must be activated by Lewis acidic cocatalysts. The high activity imparted by MAO (methylaluminoxane) has caused it for many years to be one of the most industrially important activators in single-site olefin polymerization. Yet, despite intensive studies, MAO has remained a “black box”. First of all, the presence of multiple equilibria between different $(\text{AlOMe})_n$ oligomers has hindered experimental structural assignment of MAO. Second, without a structural model for MAO it remains nearly impossible to determine the dormant and active species present within metallocene-catalyzed, MAO-activated olefin polymerization.

Recently, we have put forward a structural model for “pure”² and trimethylaluminum (TMA)³-containing MAO. We have found that MAO consists of three-dimensional caged structures with the general formula $(\text{AlOMe})_n(\text{TMA})_m$, where n ranges between 6 and 30 and m between 0 and 4, depending upon the topology of the parent cage. A statistical approach has been used to obtain the average n and m values at different temperatures, yielding average unit formulas of about $(\text{AlOMe})_{18.08}(\text{TMA})_{0.04}$, $(\text{AlOMe})_{17.04}(\text{TMA})_{0.11}$, $(\text{AlOMe})_{15.72}(\text{TMA})_{0.17}$, and $(\text{AlOMe})_{14.62}(\text{TMA})_{0.26}$ at 198, 298, 398, and 598 K, respectively. Since the reaction between TMA and MAO is minimal, increasing the concentration of TMA has very little effect on m . This shows that most TMA is present as the free dimer and very little is actually bound to MAO. At all tem-

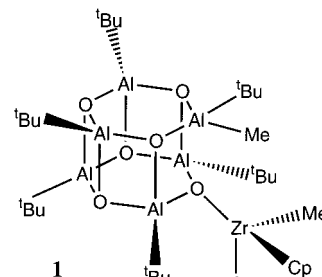


Figure 1. Structure of $[\text{Cp}_2\text{ZrMe}][(\text{tBu})_6\text{Al}_6\text{O}_6\text{Me}]$.

peratures the species of greatest abundance was found to be $(\text{AlOMe})_{12}$, with an abundance of 15.27%, 20.63%, 19.57%, and 16.56% at the aforementioned temperatures, respectively. Moreover, in an attempt to gain greater stability, most MAO structures contain very few strained, Lewis acidic bonds. For example, $(\text{AlOMe})_{12}$ has no such sites.

Within the past few years there have been several spectroscopic investigations on MAO. Here we will focus on examining the results of ^1H and ^{13}C NMR studies of mixtures of MAO and Cp_2ZrMe_2 . These are the works of Barron,⁴ Tritto,^{5,6} and most recently Babushkin et al.¹ We will also consider the work of Sinn⁷ and Barron's study on $[\text{Al}_7(\mu_3\text{-O})_6(\text{tBu})_6\text{Me}]_3$.⁸

Barron and co-workers reacted Cp_2ZrMe_2 with their *tert*-butyl analogues of MAO, $[(\text{tBu})\text{Al}(\mu_3\text{-O})]_n$ where n

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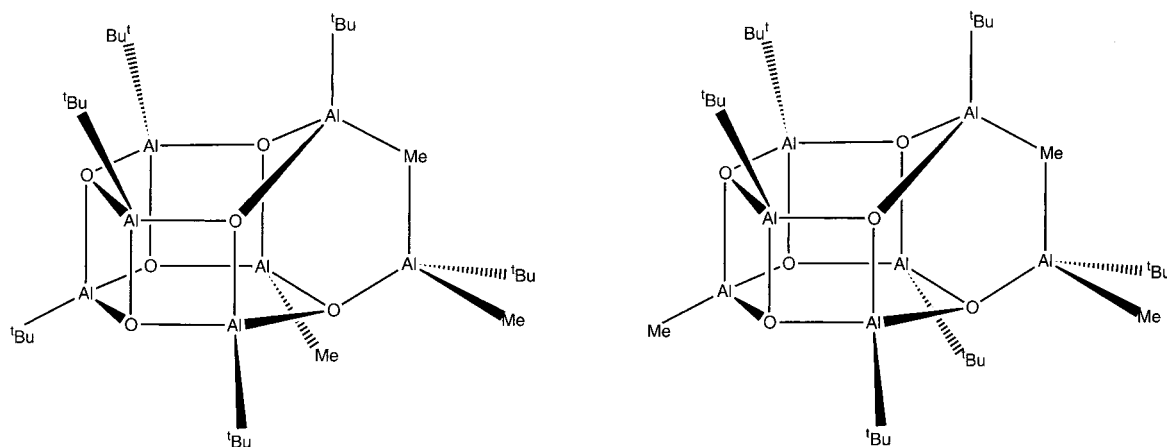


Figure 2. Isomers of $[\text{Al}_7(\mu_3\text{-O})_6(\text{tBu})_6\text{Me}_3]$.

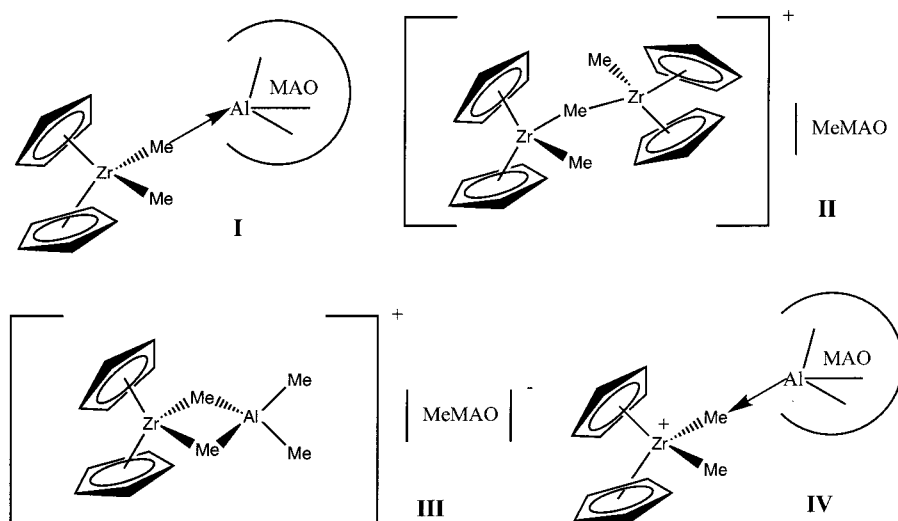


Figure 3. Proposed structures¹ for intermediates formed in a mixture of MAO and Cp_2ZrMe_2 .

= 6, 7, and 9. ^1H NMR spectroscopy was successfully used to characterize the species $[\text{Cp}_2\text{ZrMe}][(\text{tBu})_6\text{Al}_6\text{O}_6\text{Me}]$, shown in Figure 1.⁴ Separate resonances for the two Cp ligands indicated that rotation about the Zr–O bond is slow on the NMR time scale. This was attributed either to the steric interactions between the Cp ligands and *tert*-butyl groups or to an Al–Zr–Me interaction.

The work of Sinn suggests that the catalytic species in polymerization is formed only when both MAO and TMA are present in the reaction mixture.⁷ This is also evident in Barron's study on the two isomers of $[\text{Al}_7(\mu_3\text{-O})_6(\text{tBu})_6\text{Me}_3]$ shown in Figure 2.⁸ These two structures were characterized as being the products of the reaction of $[(\text{tBu})_6\text{Al}(\mu_3\text{-O})_6]$ and TMA. The polymerization of 1,5-hexadiene by $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrBz}_2]$ with different cocatalysts was examined. The following trend was found for the activity of the alumoxanes: $[(\text{tBu})_6\text{Al}(\mu_3\text{-O})_6]/(\text{AlMe}_3)_6 > \text{MAO} > [\text{Al}_7(\mu_3\text{-O})_6(\text{tBu})_6\text{Me}_3] \gg [(\text{tBu})_6\text{Al}(\mu_3\text{-O})_6]$. The first compound is thought to be a mixture of the two isomers of $[\text{Al}_7(\mu_3\text{-O})_6(\text{tBu})_6\text{Me}_3]$ where all of the *tert*-butyl substituents have been replaced with methyl groups. It has higher activity than $[\text{Al}_7(\mu_3\text{-O})_6(\text{tBu})_6\text{Me}_3]$ itself, due to the absence of the bulky *tert*-butyl groups. Barron's work not only suggests how TMA may bind to MAO but also shows that the presence of

TMA greatly enhances the catalytic activity of MAO. The presence of methyl bridges in MAO has also been suggested by other groups.^{9,10}

Tritto and co-workers have performed ^1H and ^{13}C NMR investigations on mixtures of MAO and dimethylzirconocene with different Al:Zr⁵ ratios and in the presence of ethene.⁶ They have observed the formation of three complexes, which they have identified as $[(\text{Cp}_2\text{ZrMe})_2(\mu\text{-Me})]^+[\text{MeMAO}]^-$ (**II**), $[\text{Cp}_2\text{ZrMe}]^+[\text{MeMAO}]^-$ (**IV**), and $[\text{Cp}_2\text{ZrMeAlMe}_3]^+[\text{MeMAO}]^-$ (**III**).⁵ Species **III** is noticed only at Al/Zr ratios greater than or equal to 20. It is present in very small amounts, likely due to the fact that the removal of nondeuterated toluene also removes residual TMA. An increase in Al/Zr results in the broadening of Cp and Me signals for **III**, possibly indicating fluxional equilibria, such as methyl transfer.

Recently, similar NMR investigations have been performed with Al/Zr ranging from 10 to 4000 by Babushkin and co-workers.¹ Several species that are present in a MAO/dimethylzirconocene solution at different Al/Zr ratios have been identified. Their structural assignments are given in Figure 3. Note that Tritto does not see peaks that would correspond to the weak

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complex **I**. It was found that **I**, **II**, and **IV** form at low Al/Zr ratios. As the ratio increases, **I** and **II** gradually disappear while the proportions of **III** and **IV** increase. At high Al/Zr ratios the concentration ratio of **IV/III** was found as being 1–4 depending upon the TMA content within the MAO solution.

The change in the ^1H NMR signals of the Cp rings as a function of zirconium concentration was monitored for species **III**. It led to the conclusion that **III** exists in solution as the contact ion-pair (**IIIa**) and the separated ion-pair (**IIIb**). The dissociation of **III** would form $[\text{Cp}_2\text{ZrMe}]^+$, which is the species capable of binding the olefinic substrate and hence the active species in polymerization.

Species **IV** is considered as being a “tight” ion-pair and hence the dormant state of the active site in olefin polymerization. Various groups have assumed this to be an oxygen-bound complex similar to that shown in Figure 1.^{11,12} On the other hand, Babushkin and co-workers believe it is a μ -Me bound species. They reach this conclusion from the observance of a μ -Me group in **IV**, which was only detected when a MAO sample enriched with 70% ^{13}C was used.

Within this study we will use our current knowledge of MAO, along with the clues provided by experimental NMR data, to determine possible structural candidates for **III** and **IV**, the active and dormant species in olefin polymerization. In section 3.1 we shall discuss calculations of relative energies in the gas phase and in solution for **III**. In section 3.2 we shall compare experimental and calculated NMR shifts. The relative energies of structural alternatives for **IV** will be examined in section 3.3 and the NMR data in 3.4. Section 3.5 will examine the different pathways by which **III** may be formed, along with the ion-pair formation and ion-pair dissociation energies for both **III** and **IV**. In section 3.6 we will examine the Al/Zr ratios that would be present in a MAO/TMA/ Cp_2ZrMe_2 mixture composed of structures that we propose for **III** and **IV**.

2. Computational Details

The density functional theory calculations were carried out using the Amsterdam Density Functional (ADF) program versions 2.3.3 and 2000 developed by Baerends et al.¹³ and vectorized by Ravenek.¹⁴ The numerical integration scheme applied was developed by te Velde et al.,¹⁵ and the geometry optimization procedure was based on the method of Verslius and Ziegler.¹⁶ For total energies and geometry optimizations the gradient-corrected exchange functional of Becke¹⁷ and the correlation functional of Perdew¹⁸ were utilized in conjunction with the LDA parametrization of Vosko et al.¹⁹ The electronic configurations of the molecular systems were described by a double- ζ STO basis set with one polarization function for H,

C, Al, and O, while a triple- ζ STO basis set was used for Zr. A 1s frozen core was used for C and O, while an [Ar] frozen core was used for Zr. A set of auxiliary s, p, d, f, and g STO functions centered on all nuclei were used to fit the molecular density and represent Coulomb and exchange potentials in each SCF cycle.²⁰

Solvation calculations were done using the COSMO method^{21a} as implemented in ADF.^{21b} The solvent excluding surface was used along with an epsilon value of 2.379 for the solvent toluene. Atomic radii used were 2.4, 2.3, 1.5, 2.0, and 1.16 Å for Zr, Al, O, C, and H, respectively. Geometry optimizations were performed in vacuo, and only single-point calculations were performed for the solvation effects.

Calculations of NMR chemical shifts were carried out using the implementation found in ADF 2000.²² A triple- ζ basis set with two polarization functions was used for H and C, a double- ζ basis set with one polarization function for Al and O, and a triple- ζ basis set for Zr. A 1s frozen core was used for C and O, while an [Ar] frozen core was used for Al and a [Kr] frozen core was used for Zr. Geometries optimized using the smaller basis sets for H and C were used for the NMR calculations which employed larger basis sets.

3. Results and Discussion

3.1. Energetics of Species III. Our previous calculations have shown that MAO exists as a caged structure with three-coordinate oxygen atoms and four-coordinate aluminum atoms. Despite the fact that very little $(\text{AlOMe})_6$ (~0.01%) is present at room temperature in a typical MAO solution, this is the smallest feasible structural model that may be used to represent MAO. Moreover, it contains Lewis acidic sites which are necessary for reaction with TMA or dimethylzirconocene. Within this study we perform explicit calculations on structures containing $(\text{AlOMe})_6$, which we use to model other MAO cages containing three-coordinate oxygen atoms, four-coordinate aluminum atoms, and strained Lewis acidic bonds. These cages and the acidic sites have been determined elsewhere.³

Five structural alternatives for the catalytically active species, **III**, are shown in Figure 4. In **A** a Lewis acidic site on the MAO has broken. A methyl group is transferred to an aluminum atom on the MAO cage, and $[\text{TMACp}_2\text{ZrMe}]^+$ binds to the oxygen on the MAO cage. **A** has two bridging μ -Me groups between aluminum and zirconium, whereas **C** has only one. **B** is analogous to **A** with the presence of two μ -Me's. However, the oxygen–aluminum bond between $[\text{MAOMe}]^-$ and $[\text{TMACp}_2\text{ZrMe}]^+$ has broken, forming the separated ion-pair. In **D**, the zirconocene is bound via a methyl bridge directly to an aluminum atom on the MAO cage. **E** is formed via the reaction of another $1/2(\text{TMA})_2$ with **C**. Here two bridging μ -Me groups are present as well.

The NMR data of Babushkin and co-workers show evidence for two bridging μ -Me groups, which would suggest that **A**, **B**, or **E** is the likely candidate for **III**. However, the structure **A** does not correspond to a minimum on the potential energy surface and optimizes

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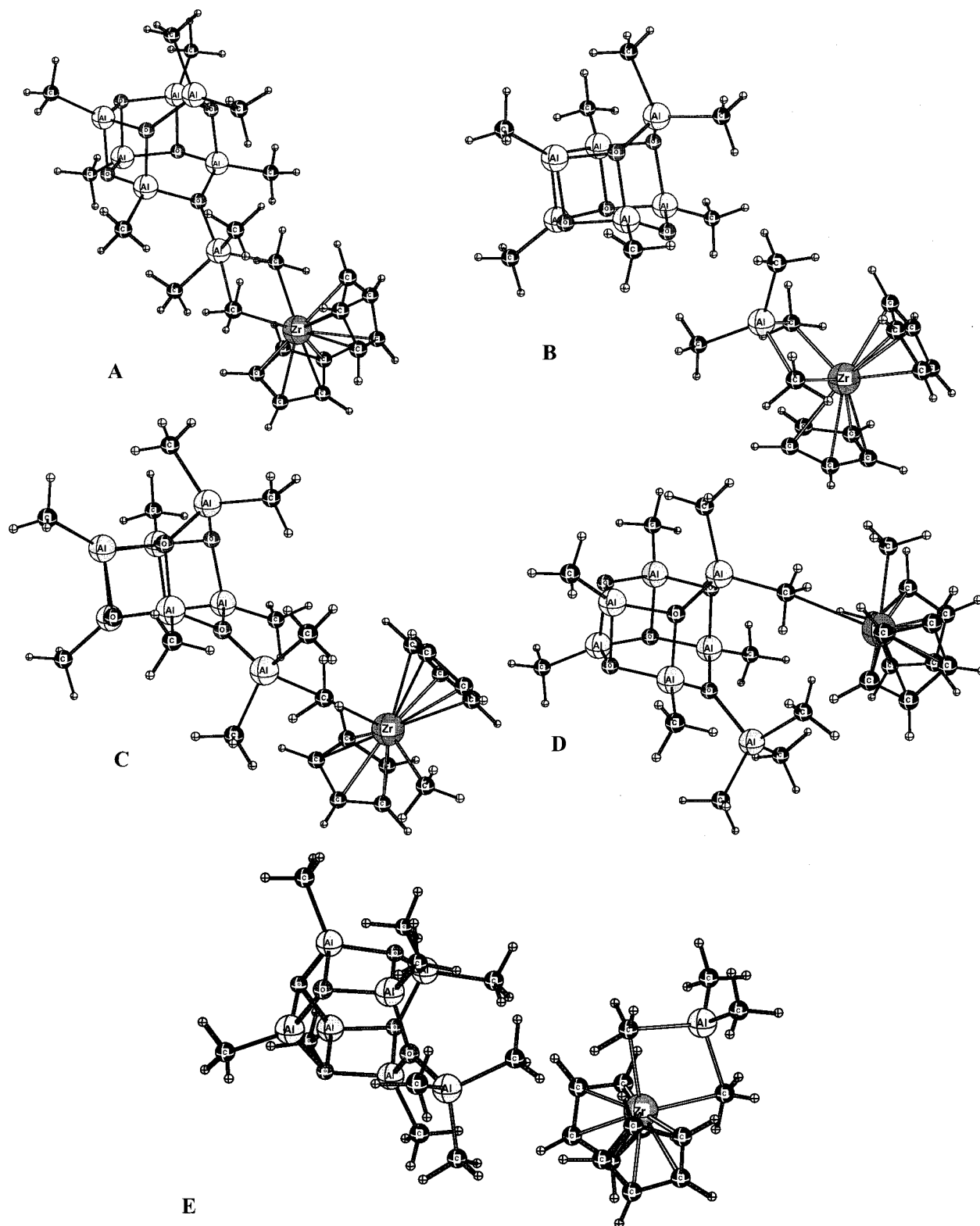


Figure 4. Possible structural alternatives for **III** (the active species).

to give **C**. This is not surprising, since aluminum does not like to be five-coordinate. The relative energies of **B** and **C** in the gas phase show that **C** is 46.80 kcal/mol *more stable* than **B**. Solvation effects ought to stabilize **B** over **C** due to the fact that in the separated ion-pair the charges are more polarized (i.e., MAOMe⁻ can be thought of as carrying the whole negative charge). However, we still find in toluene solution that **C** is 30.90 kcal/mol *more stable* than **B**. The energy difference

illustrates the fact that an aluminum–oxygen bond is much stronger than a Zr– μ Me–Al bond. ΔE for the formation of **E** (from **C** and 1/2(TMA)₂) is 15.27 and 8.02 kcal/mol in gas phase and toluene solution, respectively. This suggests that **E** will be present in only very small amounts in solution. **C** is 6.05 and 6.30 kcal/mol more stable than **D** in gas phase and solution, respectively. Different conformers of **C** may be found. Structurally, they differ in the C–Al–O–Al dihedral angle, where

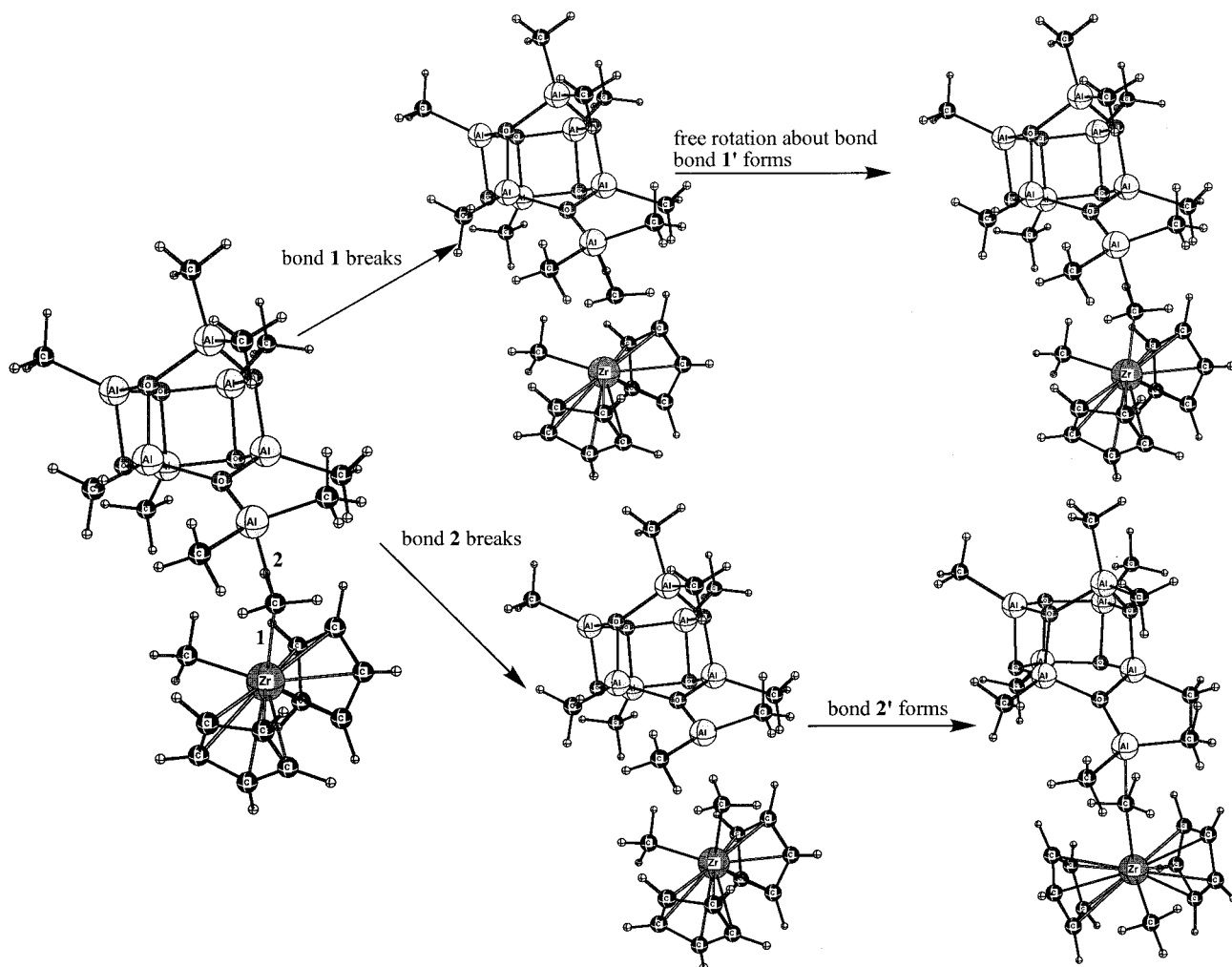


Figure 5. Breaking and re-formation of bonds in structure C.

the carbon in question is attached to zirconium. We looked at the energies of two such possible structures containing C–Al–O–Al angles of 8.8° and 75.2° . Their energies differed by ~ 0.5 kcal/mol.

Comparison of relative energies for the possible candidates for **III** suggests that **C**, with a single μ -Me, is the predominant species among **A**, **B**, **C**, **D**, and **E** in solution. It must be noted that **D** is very close in energy to **C** and will also be present in the reaction mixture, although in smaller amounts. The fact that **C** will be in greatest abundance among the candidates for **III** can be reconciled with the NMR observations of two μ -Me groups in **III** by considering the processes shown in Figure 5. In process 1 a zirconium–methyl bond is broken and regenerated after a possible rotation of the three aluminum–methyl groups around the aluminum–oxygen bond. In this case, one peak would be found as the average chemical shift value for these three Me–Al groups. Moreover, a peak corresponding to a single Me–Zr species should be present. The predictions from this process are not in line with the observed NMR spectra. In the second process, bond 2 is broken and re-formed. It is irrelevant whether there is rotation about the Al–O bond. In this scenario, the NMR peaks should integrate to give two Me groups for which the chemical shift would be the average of one μ -Me group and one zirconium–methyl. Moreover, two aluminum–methyl peaks ought

to be present as well. This second scenario fits the observed NMR data.

Energetically speaking, it is likely that this process will occur quickly on the NMR time scale. This is due to the fact that the μ -Me bond is not very strong, as can be seen from the ion-pair formation energy of **C** (from $(\text{AlOMe})_6\cdot\text{TMA}$ and Cp_2ZrMe_2). It was calculated as being -3.82 kcal/mol in the gas phase and -4.32 kcal/mol in toluene. These values correspond to the μ -Me bond strength.

3.2. NMR of Species III. For all of the NMR calculations, TMS (trimethylsilane) was used as a reference. Due to the fact that chemical shifts are temperature and solvent dependent, we have tried to gauge the inherent error present within our calculations via comparison of the calculated and experimental ^1H and ^{13}C NMR spectrum of Cp_2ZrMe_2 , shown in Table 1a. In all cases the values are slightly overestimated by ADF. These values suggest that an error of approximately 3 ppm for ^{13}C shifts and 0.5 ppm for ^1H shifts is to be expected between the calculated and experimental spectra. We have also calculated the ^1H and ^{13}C NMR spectrum of the TMA dimer and compared it with experimental data that was taken at -78°C in a solution of toluene- d_8 .²³ Table 1b shows that ADF

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Table 1. Experimental and Calculated ^1H and ^{13}C Chemical Shifts (ppm) for Cp_2ZrMe_2 (a) and the TMA Dimer (b)

a. Cp_2ZrMe_2			
	δ_{exp}^a	δ_{calc}	$\Delta\delta$
^{13}C (Cp)	109.11	111.65	2.54
^1H (Cp)	5.64	6.12	0.48
^{13}C (Me)	29.26	32.47	3.21
^1H (Me)	-0.15	-0.08	0.07
b. TMA Dimer			
	δ_{exp}^b	δ_{calc}	$\Delta\delta$
$\mu\text{-Me } ^{13}\text{C}$	-5.34	-5.80	-0.46
$\mu\text{-Me } ^1\text{H}$	-0.005	0.53	0.53
terminal ^{13}C	-8.025	-9.46	-1.44
terminal ^1H	-0.535	-0.64	-0.10

^a Reference 1. ^b Reference 23.

Table 2. Experimental and Calculated Chemical Shifts for Species III

	δ_{exp}^a	integration _{exp} ^a	δ_{calc}	integration _{calc}
^{13}C (Cp)	115.73	10C	113.60	10C
^1H (Cp)	5.5	10H	6.35	10H
^{13}C (Zr-Me)			41.7	1C
^1H (Zr-Me)			0.41	3H
^{13}C ($\mu\text{-Me}$)	38.07	2C	19.38	1C
^1H ($\mu\text{-Me}$)	-0.27	6H	0.07	3H
^{13}C (Al-Me)	-6.00	2C	-1.21	2C
^1H (Al-Me)	-0.58	6H	-0.47	6H
$^{13}\text{C}_{\text{average}}^b$	N/A	N/A	30.54	2C
$^1\text{H}_{\text{average}}^b$	N/A	N/A	0.24	6H

^a Reference 1. ^b Corresponds to average chemical shift of Zr-Me and $\mu\text{-Me}$ for ^{13}C and ^1H .

underestimates the ^{13}C shifts by up to 1.44 ppm. ^1H shifts differ from experiment by up to 0.53 ppm. The agreement is good, indicating that we should be able to reproduce the chemical shifts of Al-containing systems with $\mu\text{-Me}$ groups.

Table 2 gives the experimental results for species **III** and the calculated ones for **C**. The last two rows show the average value of the calculated ^1H and ^{13}C chemical shifts of the zirconium-methyl and $\mu\text{-Me}$ groups.

An averaging of these two values corresponds to an interchange of the two Me groups via the mechanism where bond 2 breaks, as shown in Figure 5. The average ^{13}C chemical shift of 30.54 ppm differs by 7.53 ppm from the experimental shift of 38.07 ppm, which was attributed to two $\mu\text{-Me}$ groups. However, errors of this magnitude are not uncommon for calculated ^{13}C chemical shifts. The average of the shifts corresponding to the Zr-Me and $\mu\text{-Me}$ protons was found as being 0.24 ppm, while an experimental shift of -0.27 ppm was observed for the $\mu\text{-Me}$ protons. An error of ± 0.5 ppm is not uncommon for calculated ^1H chemical shifts. The ^{13}C shifts of the Al-Me groups were calculated as being -1.21 ppm and experimentally seen at -6.00 ppm. The ^1H shifts of Al-Me agree quite closely, with a calculated value of -0.47 ppm and an experimental one of -0.58 ppm. The calculated (113.60, 6.35) and experimental (115.73, 5.5) shifts corresponding to the Cp rings agree reasonably well. Despite the fact that the different conformers of **C** have relatively the same energies, their chemical shifts may be more sensitive to changes in geometry. This may also explain the fact that calculated values deviate somewhat from experiment. Ideally, the shifts of all the conformers would be calculated and

averaged; however computationally this is not a feasible option. In general, correspondence between the shifts is very good, indicating that species **III** might have the structure suggested in **C**.

3.3. Energetics of Species IV. Three structural alternatives for **IV** are shown in Figure 6. In **F** a Me group from Cp_2ZrMe_2 binds to an aluminum atom from the MAO. In **F** a Me group from Cp_2ZrMe_2 binds to an aluminum atom of MAO forming a bridging $\mu\text{-Me}$ group. This corresponds to the structure proposed by Babushkin and co-workers. In **G** a bridging $\mu\text{-Me}$ group is present as well, along with an oxygen-bound zirconium. This is a structure analogous to the intermediate formed when TMA reacts with MAO.³ **H** is the oxygen-bound, ring-opened product, containing no $\mu\text{-Me}$ groups. Such an oxygen-bound compound has been proposed as being the dormant state for the catalyst in olefin polymerization.^{11,12}

Babushkin and co-workers have evidence for the presence of bridging $\mu\text{-Me}$ groups in structure **IV**. However, these groups were only seen when a sample enriched with 70% ^{13}C was used. Otherwise, the detection was impossible. This suggests that **H** cannot be the species seen. Yet, once again the relative energies of the different species must be taken into consideration.

The first thing to note is that **G** is not a minimum on the potential energy surface and when optimized gave **H**. When looking at the interaction of TMA and MAO, we optimized such an analogous structure. However, the fully ring-opened product corresponding to **H** was lower in energy by 5.27 kcal/mol. Perhaps, the steric bulk of the Cp rings prevents **G** from being a stable structural alternative. For the reaction shown in eq 1, ΔE was found as being -16.58 and 0.02 kcal/mol for **H** and **F**, respectively, in the gas phase. In toluene solution, these values change to -16.12 and -1.63 kcal/mol, respectively. This shows that **F** is a weakly bound species, and **H** is a tight ion-pair, in gas phase or in solution. Hence, we can conclude from comparison of relative energies that **H** is the most likely candidate for **IV**, the dormant species.



3.4. NMR of Species IV. Table 3 shows the experimental ^1H and ^{13}C chemical shifts of **IV** along with the calculated ones for **H**. For the Cp rings, the calculated ^{13}C shift of 115.78 ppm is slightly higher than the experimental value of 113.90 ppm. The calculated proton shifts of 6.40 ppm are 0.70 ppm higher than those found experimentally. The experimental ^{13}C shift of 42.00 ppm for Zr-Me is 4.77 ppm higher than the calculated value of 46.77 ppm. Experimentally, the ^1H shifts of the Zr-Me protons were not detected. We calculated them as being 0.38 ppm.

The calculated NMR values for **H** are in good agreement with those obtained experimentally for **IV**. However, **H** lacks the experimentally observed $\mu\text{-Me}$ group. Yet, it is possible that **G** is a structure lying along the reaction coordinate for other $(\text{AlOMe})_n$ cages where $n = 7, 8, 9, 10, 11, 13$. We have shown that an analogous structure is the intermediate species formed when MAO reacts with TMA.³ **G** is not stable, and hence few such

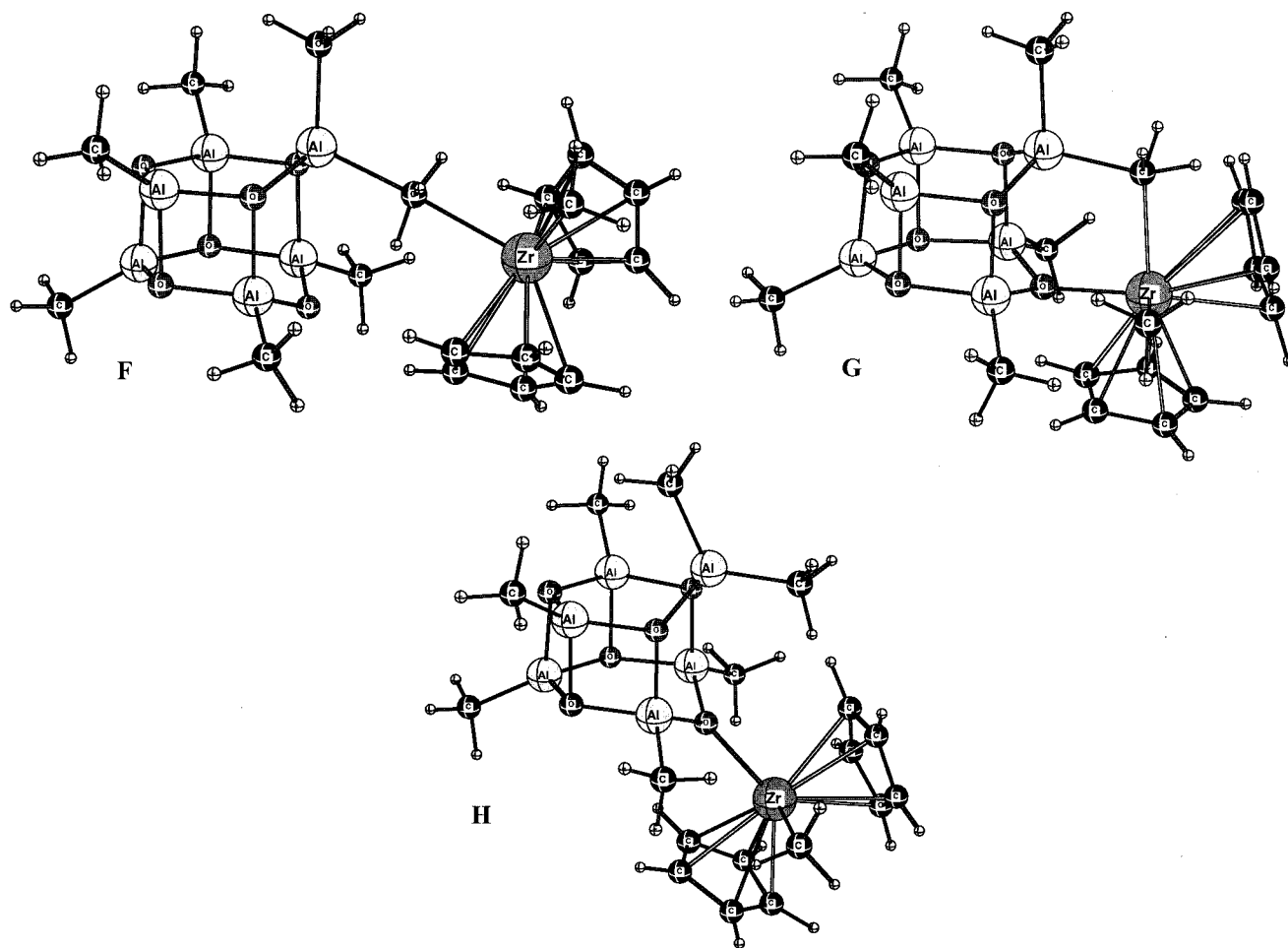


Figure 6. Possible structural alternatives for IV (the dormant species).

Table 3. Experimental and Calculated Chemical Shifts for Species IV

	δ_{exp}^a	integration _{exp} ^a	δ_{calc}	integration _{calc}
¹³ C (Cp)	113.90	10	115.78	10
¹ H (Cp)	5.70	10	6.40	10
¹³ C (Zr-Me)	42.00	1	46.77	1
¹ H (Zr-Me)			0.38	3
¹³ C (μ -Me)	9.00	1		
¹ H (μ -Me)				

^a Reference 1.

μ -Me groups would be present in solution. This would explain the fact that this signal was only visible when a sample enriched with 70% ¹³C was used. Moreover, when Barron prepared the *tert*-butyl analogue of **H**, he observed two separate resonances for the protons in the Cp groups.⁴ One explanation was the presence of an Al-Zr- μ -Me interaction. This would also indicate the formation of a species similar to **G** which lies somewhere along the reaction coordinate between products and reactants.

The NMR spectrum of **F** was also calculated and is compared with the observed spectrum for species **I**, the weakly bound species according to Babushkin et al. The results are given in Table 4. The last two rows correspond to averaging the shifts of Zr-Me and μ -Me. This corresponds to a rapid exchange between the two methyl groups. This is likely to occur due to the fact that this is a very weakly bound species. The average shift of 27.87 ppm would integrate to two carbon atoms and six

Table 4. Experimental and Calculated Chemical Shifts for Species I

	δ_{exp}^a	integration _{exp} ^a	δ_{calc}	integration _{calc}
¹³ C (Cp)	112.0	10	115.83	10
¹ H (Cp)	5.7	10	6.67	10
¹³ C (Zr-Me)	29.5 ^b	1	42.33	1
¹ H (Zr-Me)			0.66	3
¹³ C (μ -Me)	29.5 ^b	1	13.41	1
¹ H (μ -Me)			0.50	3
¹³ C _{average} ^c	N/A	N/A	27.87	2C
¹ H _{average} ^c	N/A	N/A	0.58	6H

^a Reference 1. ^b Only one band with double intensity revealed.

^c Corresponds to average chemical shift of Zr-Me and μ -Me for ¹³C and ¹H.

hydrogens. Experimentally one band with double intensity is seen at 29.5 ppm. The calculated values of (115.83, 6.67) can be compared to the experimental ones of (112.0, 5.7) for the Cp shifts. Correspondence between the calculated and experimental shifts is very good, indicating that species **I** might have the structure suggested in **F**.

3.5. Formation/Dissociation of C. The ion-pair dissociation energy for **H** is 111.72 kcal/mol in gas phase and 62.60 kcal/mol in toluene solution. This underlines that the Zr-O bond is very strong and supports the conjecture that this species is dormant during polymerization. [Tentative calculations suggest that the barrier of insertion of olefin is higher than 20 kcal/mol: T. K. Firman; internal communication.] Structure **C** can be formed in one of two ways, which are given in eqs 2

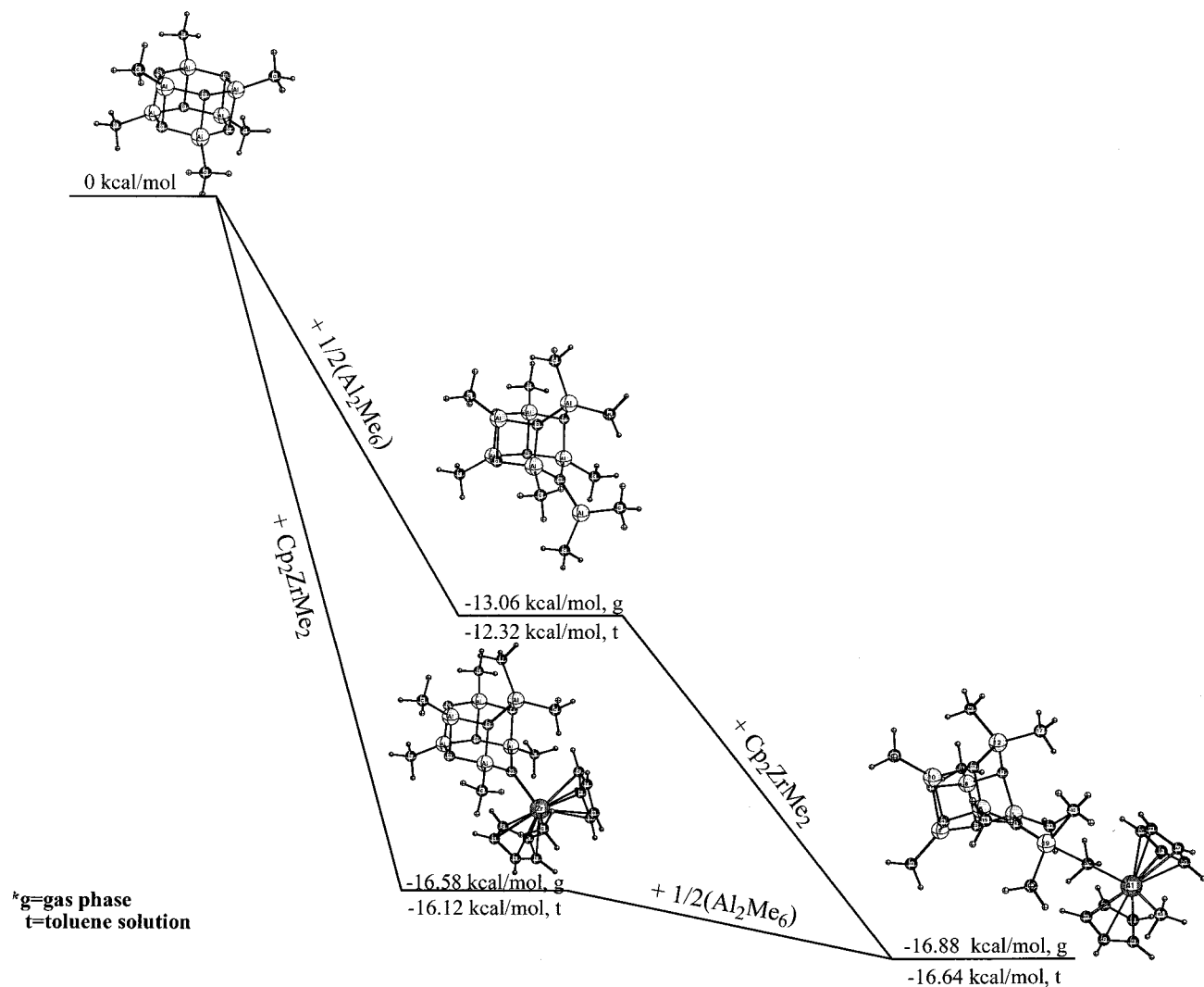
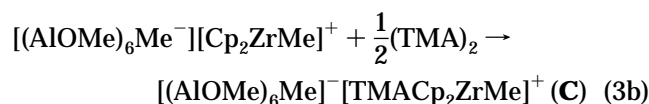
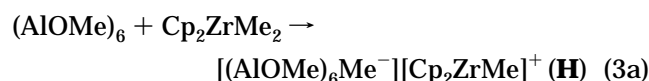
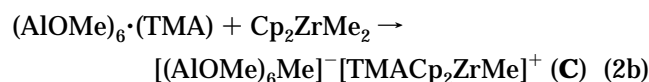
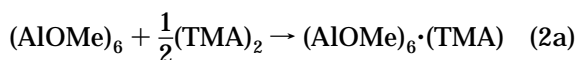


Figure 7. Energetic relationships between $(\text{AlOMe})_6$, $(\text{AlOMe})_6 \cdot (\text{TMA})$, $[\text{Cp}_2\text{ZrMe}]^+[(\text{AlOMe})_6\text{Me}]^-$ (**H**), and $[\text{Cp}_2\text{ZrMeAlMe}_3]^+[(\text{AlOMe})_6\text{Me}]^-$ (**C**) in gas phase and toluene solution.

and 3 below. The ΔE values, in gas phase as well as in toluene solution, are shown in Table 5. The process is also shown in Figure 7. Previously, we have demonstrated that **H** is the tight ion-pair. Hence, in **3a**, the ΔE values given correspond to the formation of this species.



The ion-pair dissociation energy for **C** is 92.70 kcal/mol in gas phase and 48.39 kcal/mol in toluene solution. This is lower than that of **H**, showing that this is a viable candidate for the active species in polymerization.

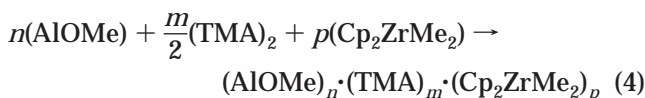
Table 5. ΔE for Eqs 2a, 2b, 3a, and 3b (kcal/mol)

reaction	$\Delta E_{(\text{gas phase})}$	$\Delta E_{(\text{solv})}$
2a	-13.06	-12.32
2b	-3.82	-4.32
3a	-16.58	-16.12
3b	-0.30	-0.52

[Tentative calculations have shown that the barrier of insertion of olefin is ~ 10 kcal/mol and hence this is a feasible process: T. K. Firman; internal communication.]

3.6. MAO/TMA/Cp₂ZrMe₂ Mixture. Consider the general process in **4** for which the Gibbs free energy per monomer unit is given in **5**. The equilibrium constant for this reaction may be found via **6**. Next **7** may be used to find the percent abundance of any species. In our first paper² on "pure" MAO, we considered the case when $m = p = 0$ and were able to calculate the percent distribution of structures with the general formula $(\text{AlOMe})_n$. In our second paper³ on "real" MAO, we considered the case when $p = 0$ and were thus able to calculate the percent distribution of structures with the general formula $(\text{AlOMe})_n \cdot (\text{TMA})_m$. We found that due to the fact that TMA hardly reacts with MAO, increasing its concentration had little effect on shifting the equilibrium. Here, we will use the thermodynamic gas-phase

data from our previous studies along with certain assumptions to examine how the equilibrium of a "real MAO" mixture is affected in the presence of zirconocene.



$$\frac{\Delta G_0(n,m,p)}{n} = \frac{G_T^0(n,m,p)}{n} - G_T^0(\text{AlOMe}) - \frac{m}{2n}G_T^0(\text{TMA})_2 - \frac{p}{n}G_T^0(\text{Cp}_2\text{ZrMe}_2) \quad (5)$$

$$K_{\text{eq}}(n,m,p) = \exp(-\Delta G_0(n,m,p)/nRT) \quad (6)$$

$$\% (\text{AlOMe})_n \cdot (\text{TMA})_m \cdot (\text{Cp}_2\text{ZrMe}_2)_p = \frac{\{(K_{\text{eq}}(n,m,p)[(\text{TMA})_2]^{m/2n}[\text{Cp}_2\text{ZrMe}_2]^{p/n})\}}{\sum_p \sum_m \sum_n \{(K_{\text{eq}}(n,m,p)[(\text{TMA})_2]^{m/2n}[\text{Cp}_2\text{ZrMe}_2]^{p/n})\}} \times 100\% \quad (7)$$

Specifically, we would like to consider a solution that contains zirconocene bound to MAO cages in the same way as in species **C** and **H**. That is, the MAO cage may be different; however the zirconocene is bound to it via either a single μ -Me or an oxygen atom at a Lewis acidic site. To examine this equilibrium, we need to know the values of $\Delta G_0(n,0,p)$ and $\Delta G_0(n,m,p)$, for species analogous to **H** and **C**, respectively. To estimate $\Delta G_0(n,0,p)$, we note that ΔE for **2a** is -13.06 kcal/mol while for **3a** it is -16.68 kcal/mol. This implies that $\Delta G_0(6,1,0)$ is similar to $\Delta G_0(6,0,1)$. Thus, we will assume that $\Delta G_0(n,0,1) = \Delta G_0(n,1,0)$ at 298.15 K. We will only consider the case when $p = 1$; thus up to one zirconocene may be attached to a MAO cage in a way analogous to that of species **H**. To estimate $\Delta G_0(n,m,p)$, we note that ΔE for **2b** is -3.82 kcal/mol and predict that ΔG at 298.15 K for this reaction ought to be ~ 2 kcal/mol. This implies that $\Delta G_0(n,m,1) = \Delta G_0(n,m,0) + 2$ kcal/mol. Again we will only consider the case when $p = 1$; that is, up to one zirconocene may be bound to a MAO cage in a way analogous to that of species **C**, irrespective of how many TMA groups are present. It is highly unlikely that species with $p \geq 2$ would be present in any significant amount due to steric effects. No other species was considered in the equilibrium. The values for $\Delta G_0(n,0,1)$ and $\Delta G_0(n,m,0)$ were obtained from our previous studies on MAO.^{2,3}

A mixture composed of only these species at 298.15 K would give a ratio of structures analogous to **H** to those analogous to **C** of 1.76 when 1 M TMA and 1 M dimethylzirconocene were used. Experimentally, it was found that at high Al/Zr ratios the molar ratio of **IV/III** varied between 1 and 4 depending upon the TMA content of the solution.¹ Also, at high Al/Zr ratios signals due to species other than **III** and **IV** were absent.¹ Thus, the value of 1.76 calculated for **H/C**-like structures agrees with experimental results.

The Al/Zr ratio of such a mixture is dependent upon the free TMA content of the solution. In the aforementioned situation we calculate the Al/Zr ratio as being 177:1. If we consider a situation with 0.009 M Cp_2ZrMe_2 and 0.5 M TMA, with about 30% of the total Al content being due to free TMA, this yields an Al/Zr ratio of 275:

1, implying that ratios of approximately this magnitude are necessary in order to guarantee that all of the Cp_2ZrMe_2 is bound to MAO in such a manner. The ratio of structures analogous to **H** to those analogous to **C** increases slightly to 1.83. In Babushkin's study this corresponds to the disappearance of NMR signals due to **I**, **II**, and free Cp_2ZrMe_2 . Weak signals corresponding to **I** and **II** are still seen at Al/Zr = 100; however the ratio at which they disappear is not given.¹

4. Conclusions

Within this study we have examined several structural candidates for the active and dormant species found in a MAO/TMA/zirconocene mixture. These have been studied by comparison of relative energies for various structural candidates in gas phase and toluene solution as well as a comparison of calculated and experimental ¹H and ¹³C NMR data.

The NMR data for species **III** showed evidence for two μ -Me groups bridging zirconium and aluminum. We found that energetically speaking such a species was either not stable (**A**) or of higher energy (**B**, **E**) than a structure with one Zr-Me and one μ -Me present (**C**). However the μ -Me bond was very weak at the Zr-Me linkage, making it possible for the Zr-Me and μ -Me methyl groups to exchange. If this process (Figure 4) were fast on the NMR time scale, the resulting spectrum would integrate to give two Me groups whose chemical shift would be the average of the one μ -Me and one Zr-Me. The calculated NMR of **C** agreed well with the experimental value for **III** when these values were averaged. The presence of conformers with very similar energies could explain the deviation between calculated and experimental chemical shift values. The ion-pair dissociation energy for **C** of 48.39 kcal/mol in toluene indicates that this is a viable candidate for the active species in polymerization. A structure (**D**) slightly higher in energy than **C** was also identified. However, very little of it should be found in the reaction mixture.

The NMR data for species **IV** showed evidence of one μ -Me group being present. However, when such a structure was considered, it was either unstable (**G**) or much higher in energy (**F**) than the oxygen-bound species with no μ -Me groups (**H**) present. The calculated NMR data agreed well with experiment, with the exception of the lacking μ -Me group. Yet, it is possible that a structure similar to **G** lies along the reaction coordinate between MAO + zirconocene and **H**. Since it is not stable, very few such μ -Me groups would be present at any given time, resulting in a weak signal. To see this signal experimentally, it was necessary to use a sample enriched with 70% ¹³C. The ion-pair dissociation energy of 62.60 kcal/mol in toluene was found for **H**. This high value shows that this is a likely candidate for the dormant species in polymerization. NMR calculations on the μ -Me bridged species **F** give close agreement with what is seen experimentally for species **I**, a weak complex between MAO and the precatalyst.

The model that we have currently proposed for MAO has the consequence that a high Al/Zr ratio, $\sim 275:1$, is necessary in order to bind all of the Cp_2ZrMe_2 to MAO as species **III** and **IV** at 298.15 K. Experimentally, the disappearance of signals due to species **I** and **II** is

observed at Al/Zr ratios of over 100. Physically, this is a result of the fact that there are very few Lewis acidic sites present in MAO. Indeed the predominant oligomer, (AlOMe)₁₂, has no acidic sites. Moreover, the reaction of TMA or Cp₂ZrMe₂ with acidic sites does not have a ΔG low enough to overcome the stability that MAO monomers gain by forming structures such as (AlOMe)₁₂.

The calculated ratio of 1.76 and 1.83 (depending upon the concentration of TMA and dimethylzirconocene) for **H/C**-like structures at 298.15 K correlates with the experimental observation that the ratio of **IV/III** varied between 1 and 4 depending upon the TMA content within the solution at high Al/Zr ratios. **H**-like structures will be more prevalent than **C**-like structures first of all due to the fact that very little TMA is actually bound to MAO and second because of the fact that the Al–Zr bond in **C**-like structures is quite weak.

In conclusion, the model which we propose explains why such a high ratio of Al/Zr is necessary in order for polymerization to occur. First of all, most MAO oligo-

mers do not contain Lewis acidic sites where TMA may bind. Next, the binding between Cp₂ZrMe₂ and (AlOMe)_{*n*}(TMA)_{*m*} is quite weak. Thus, the aluminum concentration must be much higher than the zirconium concentration in order for species such as **C** to be present in any significant amount.

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Supporting Information Available: Cartesian coordinates of optimized structures, **B**, **C**, **D**, **E**, **G**, and **H**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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