

A Density Functional Study of the Competing Processes Occurring in Solution during Ethylene Polymerization by the Catalyst (1,2-Me₂Cp)₂ZrMe⁺

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Calculations have been carried out on the reaction between the olefin polymerization catalyst (1,2-Me₂Cp)₂ZrMe⁺ (**I**) and a number of species (**D**) present in solution leading to the formation of the dormant complexes [(1,2-Me₂Cp)₂ZrMe]⁺[**D**] prior to the polymerization $\mathbf{I} + \mathbf{D} \rightarrow \mathbf{I-D} + \Delta H_{dp}$. The calculated enthalpies of dormant product formation (ΔH_{dp}) of the species **D** complexed with **I** were as follows: (**D**, ΔH_{dp} in kcal/mol): (1,2-Me₂Cp)₂ZrMe₂ (**P**), -25.8; B(C₆F₅)₃ (**C**), -9.9; C₆H₅CH₃ (**S**), -10.1; AlMe₃ (**TMA**), -25.5. The values indicate that the species **P** and **TMA** could form inhibiting complexes that would have to be dissociated before the polymerization can take place. The effect of increasing the alkyl chain length on the stability of such dormant complexes was also investigated. Also considered was the formation of the sandwiched complex **I-TMA-A** starting from the ion-pair [**I**][**A**] and **TMA** ($\mathbf{I-A} + \mathbf{TMA} \rightarrow \mathbf{I-TMA-A} + \Delta H_{sp}$) for **A** = B(C₆F₅)₃CH₃⁻ (**1**), B(C₆F₅)₄⁻ (**3**). The results (ΔH_{sp} = 4.4 kcal/mol for **I-TMA-1** and -23.5 kcal/mol for **I-TMA-3**) indicated that the formation of these sandwiched complexes was a distinct possibility in solution. The formation of the corresponding competing ethylene-sandwiched compounds **I-C₂H₄-A** was calculated for **A** = B(C₆F₅)₃CH₃⁻ (**1**), B(C₁₀F₇)₃CH₃⁻ (**2**), B(C₆F₅)₄⁻ (**3**), [(C₂B₉H₁₁)₂Co]⁻ (**4**). The stability of these complexes was compared with that of similar dormant complexes formed for the same ion pairs with the solvent toluene, C₆H₅CH₃, as the sandwiching species: **I-C₆H₅-CH₃-A**. The comparison showed that the ethylene monomer would be preferred to the solvent by the cation in forming these sandwiched complexes. Finally discussed are three possible modes of approach of the ethylene monomer toward the ion pair [(1,2-Me₂Cp)₂ZrMe]⁺[B(C₆F₅)₄]⁻ (**I-3**) and the ion pair [(1,2-Me₂Cp)₂ZrEt]⁺[B(C₆F₅)₄]⁻ (**II-3**) before the uptake of the olefin by the cation. A comparison of the ethylene π -complexes formed from the uptake of ethylene by these different approaches showed that the ethylene approaching and complexing to the cation from the side opposite to the anion **3** forms a π -complex which is more stable than the corresponding complex with the ethylene sandwiched between the two ions.

I. Introduction

Group IV metallocenes remain one of the most viable commercial catalysts for single-site olefin polymerization today, despite the introduction and development of new catalysts without cyclopentadienyl ligands. Experimental studies^{1–4} conducted on metallocenes have revealed that the active catalyst is the species Cp₂MMe⁺ (Cp = C₅H₅, M = Zr, Hf, Ti, Me = CH₃) or its metallocene derivatives. These species are formed in solution by the extraction of a methide group from the

precatalyst Cp₂MMe₂ with the help of a Lewis acidic cocatalyst, **A**, as shown in eq 1.



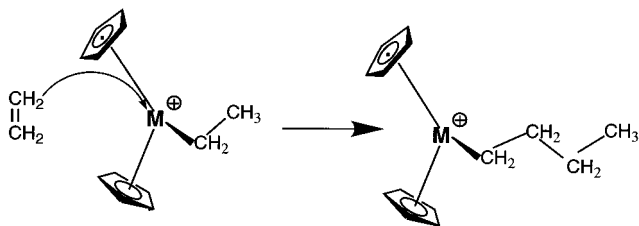
The Lewis acid cocatalysts used for this purpose have been boranes⁴ and their aluminum analogues,⁵ methylaluminoxanes (MAO),³ as well as compounds of the type [CPh₃]⁺[A]⁻.⁶ The catalytic activity has been attributed to the cationic, coordinatively unsaturated complex Cp₂MMe⁺ and its derivatives. The generally accepted polymerization scheme is shown in Scheme 1.

In an ideal situation, the cation [(Cp₂)MMe]⁺ formed would be freely accessible and would proceed to insert

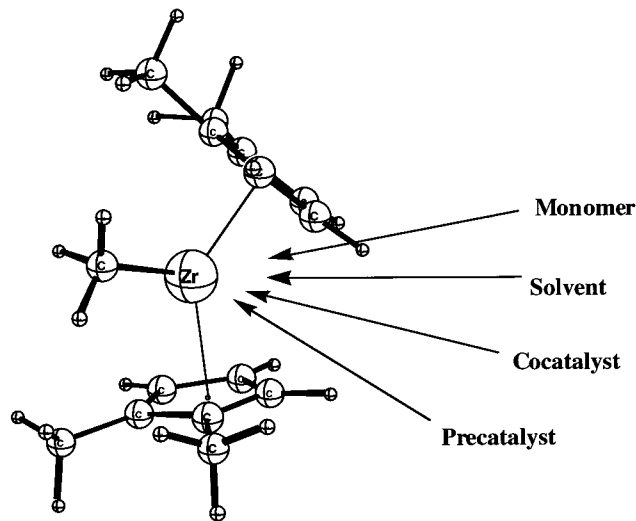
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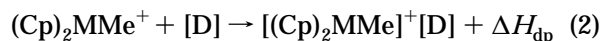
Scheme 1: Catalysis Process of Polymerization of Monomer (Ethylene) by the Metallocene Catalyst [(Cp)₂MMe]⁺



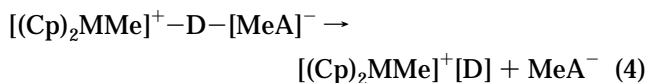
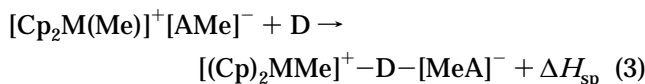
Scheme 2: Possible Competitors for the Vacant Coordination Site in the Cationic Catalyst [(1,2-Me₂Cp)₂ZrMe]⁺



the alkene monomer, leading to the formation of the polymer chain. However, the path to polymerization may be impeded in several ways. Experimental studies^{4d,7} have revealed that insertion can be inhibited by the competition for the vacant cationic site by other species present—the neutral catalyst precursor, the activator, or the solvent, as shown in Scheme 2. This could lead to dormant products that would have to be dissociated before insertion can proceed. The reaction leading to the formation of such dormant compounds is shown in eq 2, with “D” representing the species coordinating to the cation in solution and ΔH_{dp} being the enthalpy of dormant product formation.



The catalyst $[Cp_2M(Me)]^+$ might be too tightly bound to A^- to be freely accessible and react with D according to eq 2. In that case, a possible route to the formation of dormant complexes could be via the species D inserting into the ion pair and coordinating to the cation, thereby forming a sandwiched compound as shown in eq 3, with ΔH_{sp} being the enthalpy of forming the sandwiched product. The compound thus formed can then dissociate to form the separated anion and the dormant complex $[(Cp)_2MMe]^+[D]$.



Formation of dormant complexes, as discussed in eqs 2–4, could contribute to the low⁸ initial activity of the catalyst. The observed increase in the polymerization activity, after the initial dormant period, could likewise be explained by assuming that, after the insertion of one or more monomer units into the metal–alkyl bond, the dormant products formed by the various species “D” with the cation may not be as stable,^{7a} due to the larger bulk of the growing alkyl chain. Therefore, the dormant species may lose out in the competition for the vacant site with the olefin once the polymer chain has started growing.

The olefin present in solution can compete for the cationic site by forming analogous olefin-separated sandwich complexes prior to insertion of the olefin monomer into the metal–alkyl bond. A study of the enthalpy of forming such sandwiched ethylene complexes (ΔH_{es}) and a comparison of the same to the ΔH_{sp} values for the corresponding ion-pair systems can provide insight into the relative competing abilities of the different species in solution.

Theoretical work⁹ in this area has only recently begun to emerge. Klesing et al.^{9a} showed that the competition between the precatalyst and the monomer for the vacant spot in the cation is a function of the size of the ancillary ligands. Other investigations include olefin insertion into the $H_2Si(C_3H_4)(tBuN)TiMe-MeB(C_6F_5)_3$ ion pair by Lanza,^{9b} into the $Cp_2(Ti/Zr)Me-Cl_2Al[O(AlMe_3)AlHMe]_2$ ion pair by Fusco,^{9c} and into the $Cl_2TiMe(\mu-Cl)_2AlH_2$ ion pair by Bernardi.^{9d} Chan et al.^{9e} have investigated the formation of ethylene-separated ion-pair complexes for ion pairs formed between different catalysts and the counterion $B(C_6F_5)_3Me^-$.

The present study looks at the possible dormant products that can be formed in solution between the cationic species $(1,2-Me_2Cp)_2ZrMe^+$ (**I**) and the precatalyst $(1,2-Me_2Cp)_2ZrMe_2$ (**P**), the cocatalyst $B(C_6F_5)_3$ (**C**), and trimethylaluminum, $AlMe_3$ (**TMA**), both before and after insertion of an ethylene monomer into the zirconium–alkyl bond, and compares their enthalpies of dormant product formation, ΔH_{dp} . The enthalpy of formation of a dormant sandwiched ion pair (ΔH_{sp}) was studied for the ion pair $[(1,2-Me_2Cp)_2ZrMe]^+[B(C_6F_5)_3Me]^-$ (**I-1**) with **TMA** as the dormant species. The enthalpy of formation of the corresponding sandwiched olefin (ethylene) separated ion pairs (ΔH_{es}) was studied for a set of ion pairs of the type $[(1,2-Me_2Cp)_2ZrMe]^+[A]^-$, with $A^- = B(C_6F_5)_3Me^-$ (**1**), $B(C_{10}F_7)_3Me^-$ (**2**), $B(C_6F_5)_4^-$ (**3**), $[(C_2B_9H_{11})_2Co]^-$ (**4**).

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The current study also looks at the possibility of complexation of the ethylene monomer to the cation in the ion pair [(1,2-Me₂Cp)₂ZrMe]⁺[B(C₆F₅)₄]⁻ (**I-3**) and the ion pair [(1,2-Me₂Cp)₂ZrEt]⁺[B(C₆F₅)₄]⁻ (**II-3**; Et = C₂H₅), from two different directions with respect to the counterion. The total separation of the counterion after the complexation of the monomer to the cation was also studied for the **II-3** system in three different solvents: toluene ($\epsilon = 2.379$), chlorobenzene ($\epsilon = 5.71$), and dichlorobenzene ($\epsilon = 9.93$).

II. Computational Details

The density functional theory calculations were carried out using the Amsterdam Density Functional (ADF) program version 2.3.3 developed by Baerends et al.¹⁰ and vectorized by Ravenek.¹¹ The numerical integration scheme applied was developed by te Velde et al.,¹² and the geometry optimization procedure was based on the method of Versluis and Ziegler.¹³ Geometry optimizations were carried out using the local exchange-correlation potential of Vosko et al.¹⁴ without any symmetry constraints. The electronic configurations of the molecular systems were described by a triple- ζ basis set on zirconium for 4s, 4p, 4d, and 5s, augmented with a single 5p polarization function. Double- ζ STO basis were used for carbon (2s, 2p), hydrogen (1s), and nitrogen (2s, 2p) augmented with a single 3d polarization function, except for hydrogen, where a 2p polarization function was used. A set of auxiliary s, p, d, f, and g STO functions centered on all nuclei was used to fit the molecular density and represent Coulomb and exchange potentials accurately in each SCF cycle.¹⁵ The gas-phase energy difference was calculated by augmenting the local density approximation energy with Perdew and Wang's non-local correlation and exchange corrections (PW91).¹⁶ Solvent effects were not considered during the geometry optimization process. The energy difference in solution was corrected from the gas-phase energy by accounting for the solvation energy with a single-point calculation. The conductor-like screening model (COSMO), which has recently been implemented into the ADF program,¹⁷ was used for these calculations. The solvation calculations were performed with the dielectric constant 2.38 for toluene, 5.71 for chlorobenzene, and 9.93 for 1,2-dichlorobenzene. The radii used for the atoms in Å were as follows: hydrogen, 1.16; boron, 1.15; carbon, 2.0; oxygen, 1.5; fluorine, 1.2; zirconium, 2.4. These values were obtained by optimization using least-squares fitting to experimental solvation energies. The enthalpies (ΔH) reported in the following sections are potential energy differences without zero-point corrections or vibrational finite temperature corrections. Such corrections are still too expensive to calculate for the size of molecules considered here. We expect these corrections to be of the order of $\pm 2-3$ kcal/mol. For reference to the various species identified, the three cationic catalysts used will be

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identified with Roman numerals (**I-III**). The four different anions used in the study are labeled with numbers (**1-4**). The ion pairs formed between the cations and anions are identified with a dash between a Roman numeral and a number—for example, the ion pair formed from the cation [(1,2-Me₂Cp)₂ZrMe]⁺ (**I**) and the anion B(C₆F₅)₃CH₃⁻ (**1**) is labeled as **I-1**. The different species present in solution—precatalyst, cocatalyst, solvent, and AlMe₃—are labeled as **P**, **C**, **S**, and **TMA**, respectively.

III. Results and Discussion

a. Formation of Dormant Products. (i) Complexes Formed before Monomer Insertion. Dormant products between the catalyst and other species present in solution (eq 2) were studied to determine the feasibility of the formation of such compounds. Marks et al.^{4d} reported the formation of the dormant cationic (μ) complex (**I-P**) between the cation (1,2-Me₂Cp)₂ZrMe⁺ (**I**) and the precursor (1,2-Me₂Cp)₂ZrMe₂ (**P**). The crystal structure of the cationic complex was used as the starting point of our geometry optimization calculations for this complex. The optimized geometry is shown in Figure 1. The structure obtained was found to be comparable to the experimental structure obtained by Marks et al. The methyl bridging the two metal centers was found to be equidistant from the two zirconium metal centers. The Zr-C(bridging) bond length was 0.15 Å longer (2.39 Å) than the corresponding terminal Zr-C bond length (2.25 Å). Furthermore, the two Cp rings on one Zr metal center were found to be rotated approximately 90° with respect to the Zr-(μ -C)-Zr bond to avoid steric interaction with the other two Cp rings. A comparison of selected bond angles and bond lengths with the corresponding values in the crystal structure are given in Table 1.

The value of ΔH_{dp} for the formation of **I-P** was calculated to be -25.2 kcal/mol. The dormant complexes formed between the cation **I** and the cocatalyst B(C₆F₅)₃ (**C**), solvent C₆H₅CH₃ (**S**), and AlMe₃ (**TMA**), were also optimized to determine the enthalpy of formation of these complexes with the cation. The results are shown in Table 2. The values of ΔH_{dp} for **I-C** and **I-S** (-10.1 and -9.9 kcal/mol, respectively) show that the formation of these compounds would not be very favorable processes. Therefore, the cocatalyst and the solvent are not expected to be as effective in competing for the catalyst site as the counterion, precatalyst, or AlMe₃ ($\Delta H_{dp} = -25.5$ kcal/mol). The optimized complex formed with **TMA** is shown in Figure 2. In this case the four-centered bridge complex was found to be the more stable structure for the complex, instead of the μ -methyl bridged complex. This is in agreement with the structures observed experimentally^{7a} by NMR spectroscopy. The significant value of ΔH_{dp} for the formation of this compound **I-TMA** bears out the view that **TMA** can be an inhibiting agent in catalyst systems activated by MAO or in systems where it is used as a scavenger.

The enthalpy for the formation of the ion pair [(1,2-Me₂Cp)₂ZrMe]⁺[B(C₆F₅)₃CH₃]⁻ (**I-1**) from the cation **I** and the counterion B(C₆F₅)₃CH₃⁻ (**1**) was determined in a previous study¹⁸ to be -38.2 kcal/mol. This implies that for any of the other species discussed above to

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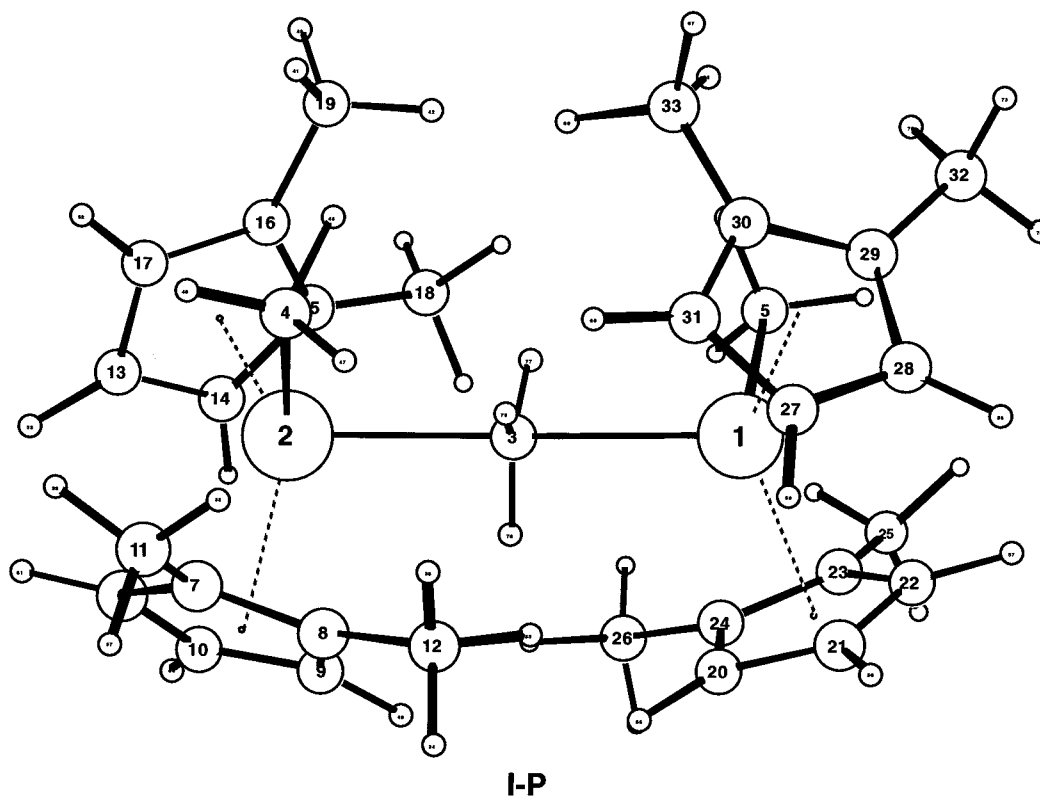


Figure 1. LDA optimized structure of the $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+ - [(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}_2]$ dormant complex.

Table 1. Selected Experimental and Calculated Bond Distances (Å) and Bond Angles (deg) for the Dormant Complex I-P

distance ^b	exptl ^a	calcd	distance ^b	exptl ^a	calcd
Zr ₁ -C ₃	2.432	2.397	Zr ₂ -C ₉	2.508	2.495
Zr ₂ -C ₃	2.405	2.377	Zr ₂ -C ₁₀	2.452	2.451
Zr ₁ -C ₅	2.235	2.257	Zr ₁ -C ₂₇	2.476	2.442
Zr ₂ -C ₄	2.255	2.260	Zr ₁ -C ₂₈	2.480	2.446
Zr ₂ -C ₆	2.451	2.453	Zr ₁ -C ₂₉	2.551	2.523
Zr ₂ -C ₇	2.574	2.534	Zr ₁ -C ₃₀	2.548	2.550
Zr ₂ -C ₈	2.574	2.535	Zr ₁ -C ₃₁	2.512	2.502
bond angle ^b	exptl ^a	calcd	bond angle ^b	exptl ^a	calcd
Zr ₁ -C ₃ -Zr ₂	170.9	171.1	C ₃ -Zr ₂ -C ₁₀	110.5	111.0
C ₃ -Zr ₁ -C ₄	92.0	92.9	C ₃ -Zr ₁ -C ₂₇	102.0	104.1
C ₃ -Zr ₁ -C ₅	93.7	93.3	C ₃ -Zr ₁ -C ₂₈	132.0	134.3
C ₃ -Zr ₂ -C ₈	84.1	83.3	C ₃ -Zr ₁ -C ₂₉	121.5	123.2
C ₃ -Zr ₂ -C ₉	81.8	81.7			

^a Reference 4d. ^b For the numbering scheme, see Figure 1.

Table 2. Enthalpy of Formation (ΔH_{dp})^a of Dormant Products, $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+ (\text{D})^b$

species D	complex formed	calcd ΔH_{dp}
$(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}_2\text{-P}$	I-P	-25.8
$\text{B}(\text{C}_6\text{F}_5)_3\text{-C}$	I-C	-9.9
$\text{C}_6\text{H}_5\text{CH}_3\text{-S}$	I-S	-10.1
$\text{AlMe}_3\text{-TMA}$	I-TMA	-25.5

^a In kcal/mol. ^b Corresponding to the process $(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}^+ + [\text{D}] \rightarrow [(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{D}] + \Delta H_{\text{dp}}$.

dislodge the anion **1** completely from the ion-pair I-1, to make the dormant species, would be thermodynamically unfavorable, given the numbers obtained in Table 2. However, the competing species D can coordinate to the cation in the presence of the anion, as shown in eq 3, forming sandwiched compounds. The possibility of formation of such a sandwiched compound with TMA is discussed later. However, in systems with larger

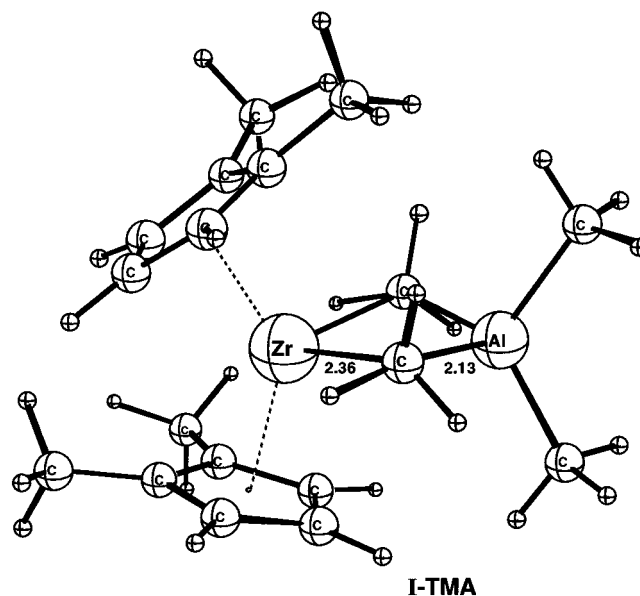


Figure 2. LDA optimized structure of the $[(1,2\text{-Me}_2\text{-Cp})_2\text{ZrMe}]^+ - \text{AlMe}_3$ dormant complex.

counterions (e.g. $\text{B}(\text{C}_6\text{F}_5)_4^-$ (**3**) etc.) where the enthalpy of formation of the ion pair from the cation I and the anion is in the range 25–30 kcal/mol, the formation of such inhibiting compounds by completely dislodging the anion from the vicinity of the ion pair may well be a possibility.

(ii) Complexes Formed after Ethylene Monomer Insertion. Compounds I-P and I-TMA had been observed, as stated earlier, by X-ray analysis, but Tritto et al.^{7a} did not observe the corresponding dormant complexes after the insertion of one, or more, monomer units into the zirconium–methyl bond. This was ex-

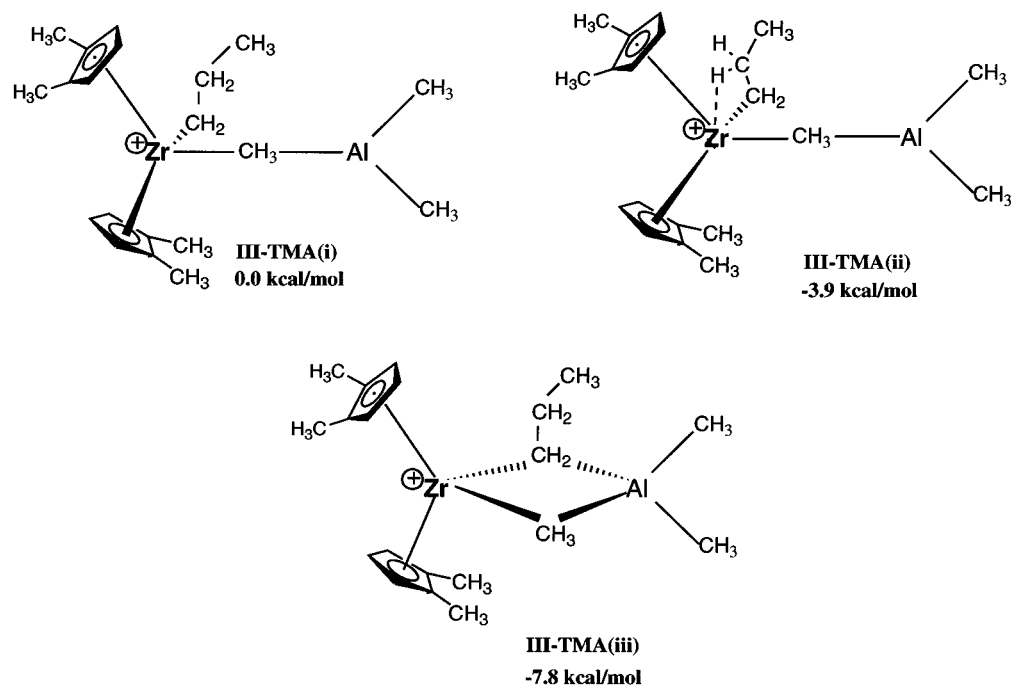


Figure 3. Possible modes of coordination of AlMe_3 to the cation $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMePr}]^+$.

plained by assuming that the dormant complexes formed after insertion of the monomer were less stable. We tested this hypothesis by optimizing the complexes **III-P** and **III-TMA** formed from the reaction between the precatalyst **P** and **TMA** with the cation $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrPr}]^+$ (**III**; $\text{Pr} = \text{C}_3\text{H}_7$) after insertion of one ethylene monomer into the zirconium-carbon bond to form the propyl chain. The other two competing species—solvent and cocatalyst—were not considered because the calculations with the dormant complexes formed with such compounds had shown that they are not strong competitors for the cationic site. For the geometry of the cationic complex **III-TMA**, three possible ways of coordination of **TMA** to the cation were considered. One mode of coordination was through the two methyl groups, forming the four-centered bridge complex **III-TMA(iii)**, similar to the structure studied earlier before monomer insertion (**I-TMA**). The other structure considered was the μ -methyl bridged complex **III-TMA(ii)**, stabilized by a β -agostic interaction, and the μ -methyl bridged complex without a β -agostic interaction, **III-TMA(i)**. The structures considered for the three possibilities are shown in Figure 3. Calculations showed that **III-TMA(iii)** was more stable by about 3.9 kcal/mol in comparison to **III-TMA(ii)** and by about 7.8 kcal/mol in comparison to **III-TMA(i)**. Hence, the enthalpy of formation of the structure **III-TMA(iii)** was used to determine the values of ΔH_{dp} . For the case of the precatalyst **P**, two structures were considered, as shown in Figure 4—the μ -methyl bridged complexes with and without a β -agostic interaction, **III-P(ii)** and **III-P(i)**, respectively. The four-centered bridge structure was not considered, as it was clear that high steric hindrance would make that a highly unstable structure. Calculations showed that the structure **III-P(i)**, without β -agostic interactions, was 8.4 kcal/mol more stable than **III-P(ii)**. Hence, the formation of the complex was considered to determine the value of ΔH_{dp} . The results are shown in Table 3. The values indicate that the

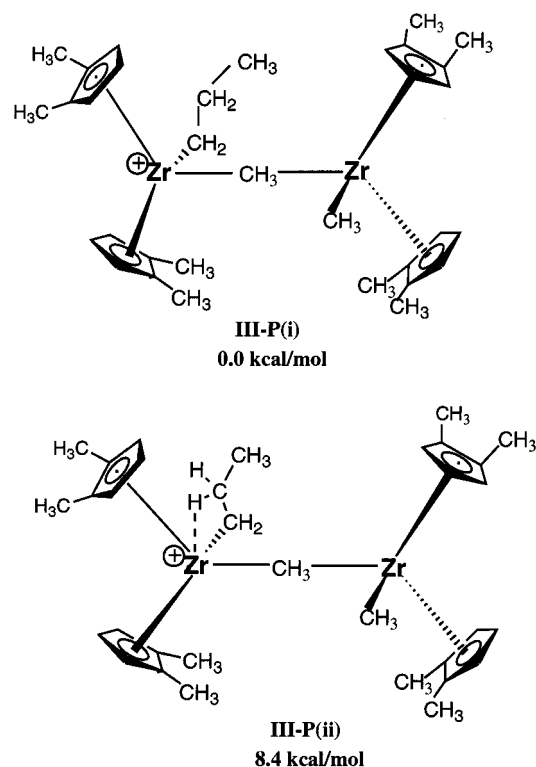


Figure 4. Possible modes of coordination of the precatalyst, $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]_2$, to the cation $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMePr}]^+$.

III-P and **III-TMA** complexes are indeed less stable than the corresponding **I-P** and **I-TMA** complexes by about 10 kcal/mol. Though it is likely that the counterion will also be bound less strongly to the cation with the larger growing chain, it is possible that with the increase in the size of the alkyl chain the stability, and hence the competing ability, of the dormant complexes formed in solution is decreased.

(iii) Formation of Sandwiched Compounds. The possibility of one of the competing species present in

Table 3. Enthalpy of Formation (ΔH_{dp})^a of Dormant Products, [(1,2-Me₂Cp)₂ZrPr]⁺ (D)^b

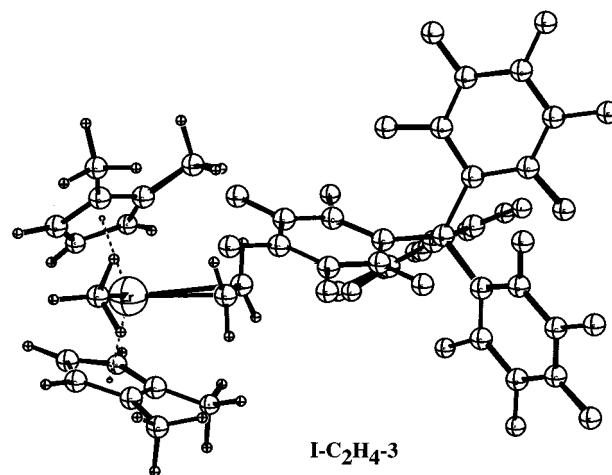
species	complex formed	calcd ΔH_{dp}
(1,2-Me ₂ Cp) ₂ ZrMe ₂ -P	III-P	-14.5
AlMe ₃ -TMA	III-TMA	-15.0

^a In kcal/mol. ^b Corresponding to the process (1,2-Me₂Cp)₂ZrPr⁺ + [D] → [(1,2-Me₂Cp)₂ZrPr]⁺[D] + ΔH_{dp} .

solution inserting between the cation and the anion to form sandwiched complexes, with the cation coordinating to the precatalyst **P**, solvent **S**, or **TMA** (eq 3), might be a feasible route to forming dormant complexes. These types of sandwiched compounds were investigated in a previous study¹⁸ involving certain ion-pair systems with the solvent toluene as the sandwiched species. From the values of ΔH_{dp} obtained and shown in Table 2, it is clear that the formation of such a compound is more likely when the sandwiched species is **TMA** or the precatalyst **P**. Naga et al.^{7b} experimentally obtained this type of complex for the ion pair **I-1** when using **TMA** as a scavenging agent. The formation of a similar complex was studied for the ion pairs [(1,2-Me₂Cp)₂ZrMe]⁺-[B(C₆F₅)₃CH₃]⁻ (**I-1**) and [(1,2-Me₂Cp)₂ZrMe]⁺[B(C₆F₅)₄]⁻ (**I-3**) with **TMA** as the sandwiched species. The enthalpy of formation of the complex [(1,2-Me₂Cp)₂ZrMe]⁺-**TMA**-[B(C₆F₅)₃CH₃]⁻ (**I-TMA-1**) (ΔH_{sp}) was determined to be 4.4 kcal/mol. The value of ΔH_{sp} for the complex [(1,2-Me₂Cp)₂ZrMe]⁺-**TMA**-[B(C₆F₅)₄]⁻ (**I-TMA-3**) was calculated to be -23.5 kcal/mol, indicating an exothermic, favorable reaction. These values indicate that the formation of sandwiched complexes is a distinct possibility in these systems. The formation of a similar complex with the precursor **P** as the sandwiched species was not studied due to size limitations, but it is clear from the similar values of ΔH_{dp} for the formation of the products **I-P** and **I-TMA**, studied earlier, that the enthalpies of formation of such compounds would be quite similar.

The marginally endothermic value of ΔH_{sp} obtained (4.4 kcal/mol) for this process shows that the formation of such compounds is a distinct possibility for ion-pair systems. Furthermore, the subsequent dissociation to form the anion **1** and the dormant complex of the cation with **TMA** (**I-TMA**) takes an additional 14.6 kcal/mol. If one takes entropic effects into account, this may be a feasible reaction and this may indicate a likely process to form dormant complexes such as **I-TMA** (and, by inference, **I-P**) in solution.

b. Ethylene-Separated Ion Pairs. The formation of dormant complexes of the type **I-TMA** in solution seems likely, judging from the value of ΔH_{sp} obtained in the previous section. In an earlier study we had looked at the formation of sandwiched species involving the solvent toluene.¹⁸ However, if the polymerization process is to proceed, then the monomer has to compete successfully with the solvent and the other species for the vacant coordinate site. That is, it should be able to complex with the cation prior to the insertion into the zirconium-carbon bond. In such a case, analogous to the solvent-, precatalyst-, and **TMA**-separated ion pairs, we would get an ethylene-separated ion-pair species. We looked at the possibility of such a competition by studying sandwiched compounds formed with ethylene as the monomer. Olefin-separated ion pairs have been studied by Chan et al.^{9e} in a previous theoretical

**Figure 5.** LDA optimized structure of the ethylene-separated ion-pair complex [(1,2-Me₂Cp)₂ZrMe]⁺-C₂H₄-[B(C₆F₅)₄]⁻.**Table 4. Enthalpy of Formation of Ethylene (ΔH_{es})^a and the Solvent-Separated Ion Pairs (ΔH_{ss})^b**

counterion A ⁻	complex formed	calcd ΔH_{es} ^{c,d}	calcd ΔH_{ss} ^c
B(C ₆ F ₅) ₃ CH ₃ ⁻ - 1	I-C₂H₄-1	14.2	18.7
B(C ₁₀ F ₇) ₃ CH ₃ ⁻ - 2	I-C₂H₄-2	11.9	18.9
B(C ₆ F ₅) ₄ ⁻ - 3	I-C₂H₄-3	-10.9	-4.2
[(C ₂ B ₉ H ₁₁) ₂ Co] ⁻ - 4	I-C₂H₄-4	-0.6	2.3

^a In kcal/mol. ^b Corresponding to the process [(1,2-Me₂Cp)₂Zr(Me)]⁺[A]⁻ + Et → [(1,2-Me₂Cp)₂Zr(Me)]⁺-Et-[A]⁻ + ΔH_{es} (Et = ethylene). ^c Corresponding to the process [(1,2-Me₂Cp)₂Zr(Me)]⁺[A]⁻ + S → [(1,2-Me₂Cp)₂Zr(Me)]⁺-S-[A]⁻ + ΔH_{ss} (S = solvent toluene). ^d Reference 18.

investigation. For reasons of comparison we studied the formation of olefin-separated ion pairs for a group of systems—two with methide bridges and two without. The geometry of the ethylene (C₂H₄) separated ion pair formed with B(C₆F₅)₄⁻ anion (**I-C₂H₄-3**) is shown in Figure 5. The enthalpies for the formation of the ethylene-separated ion-pair systems (ΔH_{es}) are shown in Table 4, along with the corresponding results for the enthalpies of formation of the solvent-separated ion pairs (ΔH_{ss}) for the same systems. The results show that the values of ΔH_{es} are smaller than the corresponding ΔH_{ss} values by about 5 kcal/mol for all the ion pairs studied. In the case of the B(C₆F₅)₄⁻ anion, the formation of the olefin-separated ion pair is actually exothermic, with the ΔH_{es} value being around -11 kcal/mol.

One can conclude from this that for all the ion pairs studied (**I-1** to **I-4**), the ethylene would “win” in the competition for the vacant site with toluene. However, in the case of **TMA** and the ion pair **I-1**, the value of ΔH_{sp} was found to be 4.4 kcal/mol, as opposed to 11 kcal/mol with ethylene for the same system. Therefore, species like **TMA** or the precatalyst **P** may form more stable sandwiched complexes than would ethylene. However, the **TMA** (as a scavenging agent in the ion-pair system **I-1**) would be present in significantly less amounts than ethylene and the concentration of the precatalyst **P** would decrease with time. Hence, it is likely that, with the passage of time, the ethylene would be the chief moiety binding to the cationic site and polymerization will not be inhibited in systems using borates as counterions. This could be a possible explanation for the enhancement in the activity of polymer-

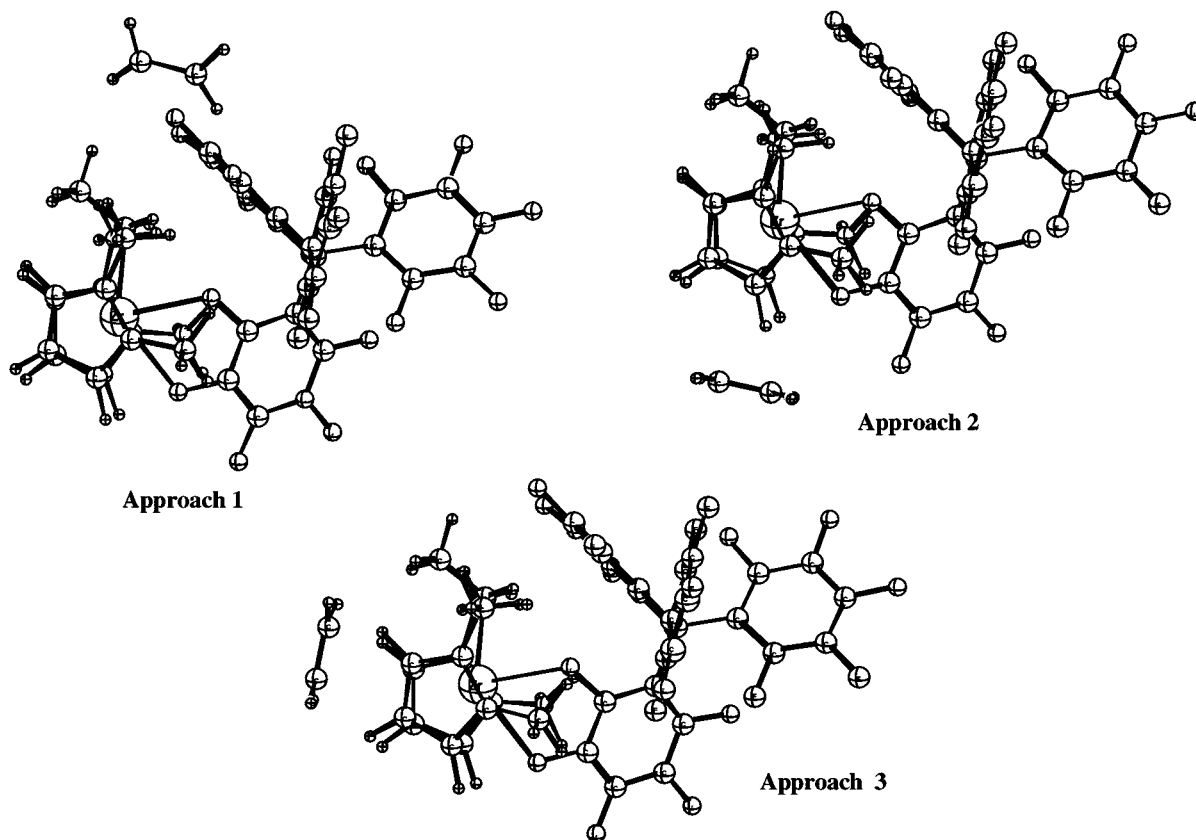


Figure 6. Different ways in which the monomer (ethylene) can approach the ion pair system $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ prior to uptake by the catalyst.

ization that occurs with the passage of time in most polymerization systems.

c. Comparison of Complexes of Ethylene Coordinated from Different Directions to the Counterion. The approach of the ethylene toward the ion pair can take place from three different directions, as shown in Figure 6. Approaches 1 and 2 would lead to the formation of the sandwiched complexes, prior to insertion. Approach 3, on the other hand, would lead to the formation of a π -complex with the ethylene coordinated to the cation on the other side of the anion. In this case the reaction would be similar to an $\text{S}_{\text{N}}2$ reaction, with the ethylene displacing the weakly bound anion from the other side and inverting the umbrella made up of the two Zr–cyclopentadienyl (Cp) bonds and one Zr–C $_{\alpha}$ bond in the process. The possibility of formation of such two different π -complexes was considered for the ion pair **I-3**: the sandwiched π -complex (**I-C₂H₄-3**) and the π -complex formed from approach 3 (**C₂H₄-I-3**). The analogous π -complexes **II-C₂H₄-3** and **C₂H₄-II-3** formed from **II-3** when the alkyl chain bound to the metal center is ethyl¹⁹ instead of methyl, i.e., the cation is $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrEt}]^+$ (**II**), was also considered.

From the values obtained, it was found that the ethylene π -complex formed from the coordination from the opposite side to the anion, i.e., **C₂H₄-I-3**, is more stable by 4.5 kcal/mol than the sandwiched complex **I-C₂H₄-3**. This implies that the coordination from the

opposite side (approach 3) may be the preferred route to olefin complexation. The extended chain (ethyl) complex **C₂H₄-II-3** is more stable than **II-C₂H₄-3** by about 3.5 kcal/mol. One might conclude on thermodynamic grounds that the coordination from the opposite side (approach 3) is the preferred route to olefin complexation. According to Lanza et al.,^{9b} this might also be the kinetically more favorable route, as a direct displacement (approaches 1 and 2) of the anion by the ethylene moiety might be difficult due to the large steric repulsion between the ethylene molecule and the aryl groups on the counterion that would have to be overcome.

A study of the structures **II-C₂H₄-3** and **C₂H₄-II-3** shows that the dihedral angle formed between the centroid **C1** of one of the cyclopentadienyl (Cp) ligands, the zirconium atom, the alpha carbon of the chain and centroid **C2** is -153.8 degrees in the complex **II-C₂H₄-3** while it is $+140.1$ degrees in the complex **C₂H₄-II-3**. This difference of 66.1 degrees in the dihedral angles for the two cases reveals the flipping of the Cp ligands in the case of Approach 3 to accommodate the ethylene molecule, showing its similarity to an $\text{S}_{\text{N}}2$ type reaction.

d. Solvent Effects on Loss of Counterion from the π -Complex. The total dissociation of the counterion **3** from the ethylene-coordinated complex, leading to the formation of the naked cationic complex **C₂H₄-(1,2-Me₂-Cp)₂ZrEt⁺** (**C₂H₄-II**) and the free anion, as shown previously in eq 4, was calculated for both the complexes **II-C₂H₄-3** and **C₂H₄-II-3**. The significance of studying this reaction is that if the enthalpy of the dissociation

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(20) Vanka, K.; Ziegler, T. Work in progress.

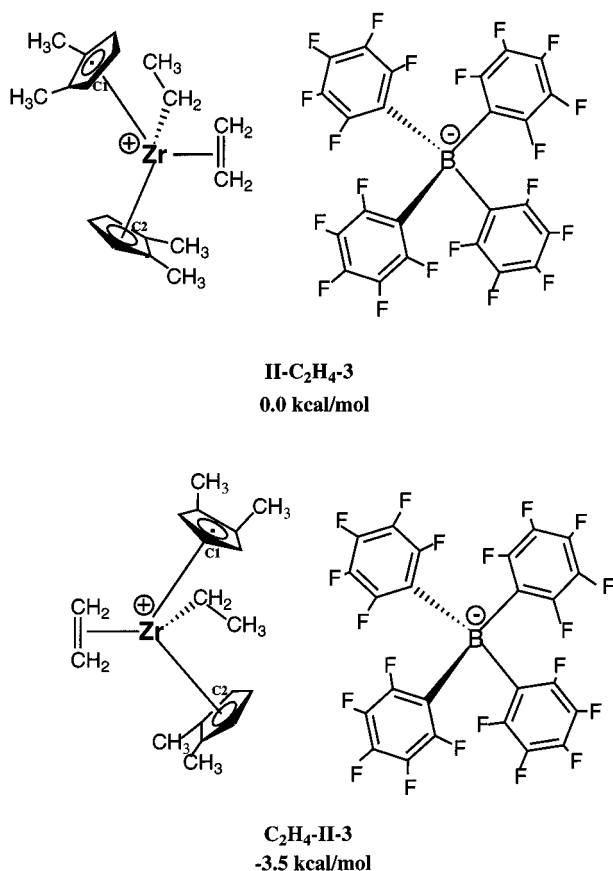


Figure 7. LDA optimized structures of the ethylene-complexed ion pairs formed by different approaches of the monomer (ethylene) to the $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion-pair system.

Table 5. Enthalpy of Total Separation (ΔH_{ts})^a of the Ethylene-Complexed Compounds in Three Different Solvents for the Complexes II-C₂H₄-3 and C₂H₄-II-3

solvent	ΔH_{ts}	
	II-C ₂ H ₄ -3	C ₂ H ₄ -II-3
C ₆ H ₅ CH ₃	14.3	16.1
C ₆ D ₅ Cl	3.2	6.7
1,2-C ₆ D ₄ Cl ₂	0.3	3.8

^a In kcal/mol. ^b Corresponding to the process $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}^+\text{Et}][\text{AME}]^- \rightarrow [(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}^+\text{Et}] + [\text{AME}]^- + \Delta H_{\text{ts}}$.

tion for this reaction is not high (i.e., in the region 10–15 kcal/mol), then entropic effects would ensure that such a reaction would be feasible and then, in such a case, the loss of the counterion from the vicinity of the cationic site would be expected to occur. The enthalpy for the dissociation was considered in three different solvents: toluene ($\epsilon = 2.379$), chlorobenzene ($\epsilon = 5.71$), and 1,2-dichlorobenzene ($\epsilon = 9.93$). The results are summarized in Table 5. For the complex II-C₂H₄-3, the value of ΔH_{ts} in toluene (14.3 kcal/mol) is at the limit where dissociation can be predicted to occur. With an increase in the dielectric constant, the enthalpy decreases so that for chlorobenzene ($\Delta H_{\text{ts}} = 3.2$ kcal/mol) and for 1,2-dichlorobenzene ($\Delta H_{\text{ts}} = 0.3$ kcal/mol), it can be said with a fair degree of confidence that dissociation would definitely occur and the counterion would dissociate itself and no longer be present near the cation during the process of polymerization. In the case of the

complex C₂H₄-II-3, the values of ΔH_{ts} are higher by about 3.5 kcal/mol, in the case of all three solvents, than for the corresponding complex II-C₂H₄-3. This is due to the slightly greater stability of the π -complex formed in this case in comparison to the sandwiched complex. From the results, it is clear that if solvents of smaller dielectric constants such as toluene or cyclohexane are considered, the counterion is likely to remain near the cationic catalytic species II during the insertion process. Hence, a study of the insertion of ethylene into the metal-alkyl bond should take the presence of the counterion into account.

IV. Conclusions

A DFT-based study was conducted on the reaction between the cation $(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}^+$ (I) and the different species that can be present in solution, forming dormant products (eq 2) that would have to be broken before catalysis can proceed with the monomer (Scheme 2). The ion-pair system that was studied for this process was $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ (I-1), and the species in solution studied that could coordinate to the cation I were the precatalyst $(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}_2$ (P), the cocatalyst $\text{B}(\text{C}_6\text{F}_5)_3$ (C), the solvent $\text{C}_6\text{H}_5\text{CH}_3$ (S), and AlMe_3 (TMA). The values of ΔH_{dp} (enthalpy of dormant product formation), obtained for the different species, showed that the precatalyst and TMA may be strong competitors for the vacant coordinate site. The value of $-\Delta H_{\text{dp}}$ for the formation of similar dormant products for these two species with the cation $(1,2\text{-Me}_2\text{Cp})_2\text{ZrPr}^+$ (III) decreased by about 10 kcal/mol, showing that the possibility of forming such complexes decreases after insertion of one or more monomer units into the zirconium-alkyl bond.

Also considered was the possibility of a separation process for the ion pair $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ (I-1), with the insertion of TMA between the ions leading to the dormant sandwiched complex $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{TMA}][\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ (I-TMA-1) with the reaction enthalpy ΔH_{sp} . The calculated value of $\Delta H_{\text{sp}} = 4.4$ kcal/mol indicates that I-TMA-1 might be present in a modest concentration. The calculated value of ΔH_{sp} for the formation of the complex I-TMA-3 $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}^+][\text{TMA}][\text{B}(\text{C}_6\text{F}_5)_4]^-$ was -23.5 kcal/mol, indicating a strong possibility of I-TMA-3 being present in solution.

The formation of the corresponding sandwiched ethylene-separated ion-pair species was considered for the ion pairs formed with the cation I and the counterions $\text{B}(\text{C}_6\text{F}_5)_3\text{CH}_3^-$ (1), $\text{B}(\text{C}_{10}\text{F}_7)_3\text{CH}_3^-$ (2), $\text{B}(\text{C}_6\text{F}_5)_4^-$ (3), and $[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}]^-$ (4) with a formation enthalpy of ΔH_{es} . A comparison between the values of ΔH_{es} and ΔH_{ss} (enthalpy of formation of the corresponding solvent (toluene)-separated complex) shows that the ethylene would be preferred to the solvent in such cases. However, a comparison between ΔH_{es} and ΔH_{sp} for the ion pair I-1 shows that TMA (and, by inference, the precatalyst) may be better coordinators to the cation in such sandwiched complexes and can inhibit the catalysis process in the initial stages of the polymerization.

Finally discussed are the possible modes of uptake of the ethylene by the cation in the presence of the counterion. The uptake leading to the sandwiched π -complex I-C₂H₄-3 and the π -complex with the eth-

ylene coordinated to the opposite side, $\text{C}_2\text{H}_4\text{-I-3}$, was considered, and a comparison of the relative stabilities of the two species shows that the ethylene complex $\text{C}_2\text{H}_4\text{-I-3}$ was more stable by about 4.5 kcal/mol in comparison to $\text{I-C}_2\text{H}_4\text{-3}$, implying that the approach of the ethylene to the cation from a direction opposite to the counterion may be the thermodynamically preferred route to uptake and subsequent insertion. The corresponding complexes with ethyl instead of methyl as the alkyl chain on the catalyst, $\text{II-C}_2\text{H}_4\text{-3}$ and $\text{C}_2\text{H}_4\text{-I-3}$, were also considered, and the complex $\text{C}_2\text{H}_4\text{-I-3}$ was found to be 3.5 kcal/mol more stable. The energy of dissociation of the anion from the π -complex was calculated in three different solvents: toluene ($\epsilon = 2.379$), chlorobenzene ($\epsilon = 5.71$), and 1,2-dichlorobenzene ($\epsilon = 9.93$). For the complexes $\text{II-C}_2\text{H}_4\text{-3}$ and $\text{C}_2\text{H}_4\text{-II-3}$, the value (around 15.0 kcal/mol) obtained for the dissociation of the anion $\text{B}(\text{C}_6\text{F}_5)_4^-$ (**3**) in toluene indicates that, in the case of nonpolar solvents such as

toluene and cyclohexane, the counterion is likely to remain near the catalyst during the process of polymerization. Hence, the influence of the counterion has to be taken into account while studying the catalysis process. On the other hand, full dissociation might occur in more polar solvents.

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Supporting Information Available: Listings giving the optimized geometries of the structures reported (Cartesian coordinates, in Å). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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