Evidence of Zircononium−Polymeryl Ion Pairs from ^{13}C NMR in Situ $^{13}C_2H_4$ Polymerization with $Cp_2Zr(^{13}CH_3)_2$-Based Catalysts

Incoronata Tritto,* Raffaella Donetti, Maria Carmela Sacchi, Paolo Locatelli, and Giulio Zannoni

Istituto di Chimica delle Macromolecole—*CNR, Via E. Bassini, 15-20133 Milano, Italy*

Received July 23, 1998; Revised Manuscript Received October 13, 1998

ABSTRACT: ^{13}C NMR spectroscopic studies of the in situ polymerization of ^{13}C-enriched ethylene ($^{13}C_2H_4$) in the presence of $Cp_2Zr(^{13}CH_3)_2$ and methylaluminoxane or $B(C_6F_5)_3$ as cocatalysts were carried out. The first direct observation of Cp_2Zr−polymeryl species was made. The in situ polymerization experiments in the presence of different concentrations of dinuclear $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ and mononuclear cation species $[Cp_2ZrMe]^+$, having $[MeB(C_6F_5)_3]^-$ or $[MeMAO]^-$ counterions, were performed. These comparisons made it possible to make the assignments of the zirconocene complexes bearing the polymeryl chain as ligands $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3MAO]^-$, $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3B(C_6F_5)_3]^-$, and $Cp_2Zr(^{13}CH_2P)(^{13}CH_3)$. They are in equilibrium with each other. Mononuclear Zr−polymeryl ion pairs such as $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3B(C_6F_5)_3]^-$ and $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3MAO]^-$ either are the propagating active species or are intermediates, closely related to the active species, in the polymer propagation.

Introduction

The past decades have seen enormous advances in the design and synthesis of "well-defined" group 4 metallocenes for α-olefin polymerization. Metallocenes need to be activated by Lewis acid cocatalysts.[1] Methylaluminoxane (MAO) has been the first and is the most frequently used cocatalyst for these new "single-site" catalysts.[2] These catalytic systems, which are going to be employed in industrial processes, require the use of large excesses of MAO. Due to multiple equilibria present in MAO solutions, metallocene−MAO systems have been considered far too complex to allow identification of the species produced. One of the roles of MAO was presumed to be the formation of 14-electron metal complexes such as $[Cp_2MR]^+$. This assumption, based on early studies[3] and on the synthesis of stabilized group 4 metallocene ionic complexes,[4] was supported by the direct synthesis of $[Cp_2MMe]^+[X]^-$, in which X^- is a "noncoordinating" counterion such as $[B(C_6F_5)_4]^-$,[5] and by the observation of the interactions between $Cp_2Zr(^{13}CH_3)_2$ and solid MAO.[6] Our interest in directly understanding the role of MAO in the polymerization activity in these homogeneous systems prompted us to make efforts to study titanocene−MAO catalysts by ^{13}C NMR spectroscopy.[7] More recently, we have undertaken the study of zirconocenes−MAO systems which because of their greater stability are more commonly used in this catalysis. Isotopically ^{13}C-enriched $Cp_2Zr(^{13}CH_3)_2$ (**1**) has been used as a probe for the reactivity of metallocenes with Lewis acids such as $AlMe_3$, $B(C_6F_5)_3$, and MAO.[8] Direct evidence of the formation in solution of the mononuclear $[Cp_2ZrMe]^+[MeMAO]^-$ (**2**), the dinuclear $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+[MeMAO]^-$ (**3**), and the $[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+[MeMAO]^-$ (**4**) cationic species, having $[MeMAO]^-$ counterions, has been provided. **3** and **4** have been proposed[1d] as possible dormant states for the active sites for olefin polymerization and, thus, as possibly responsible for catalyst deactivations according to Scheme 1.

Here we describe a study by ^{13}C NMR of the in situ polymerization of $^{13}C_2H_4$ in the presence of different concentrations of dinuclear and mononuclear cation species having either $[MeB(C_6F_5)_3]^-$ or $[MeMAO]^-$ counterions. The objective of this work is that of gaining a direct insight into the role of these species in polymerization activity. We previously reported[7d] that in in situ $^{13}C_2H_4$ polymerization in the presence of the titanocene−MAO catalytic system, the relative variations of the concentrations of the metallocene complexes detected before and after ethylene addition have given evidence of their role in the equilibria involved in the formation of active sites.

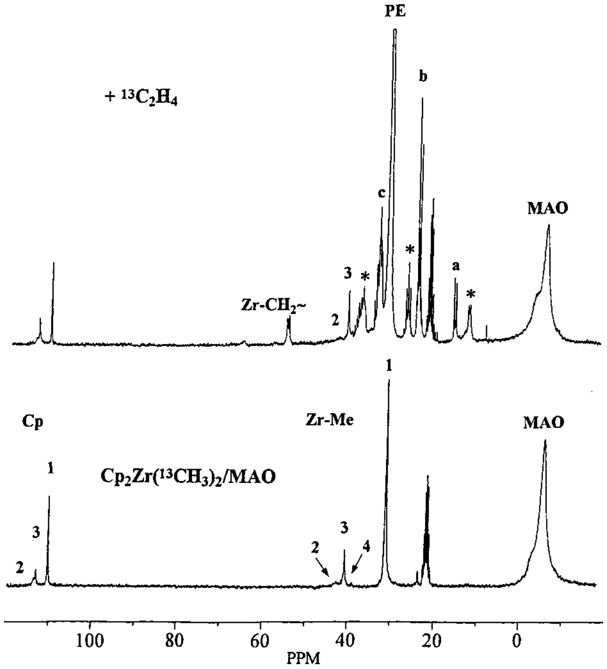
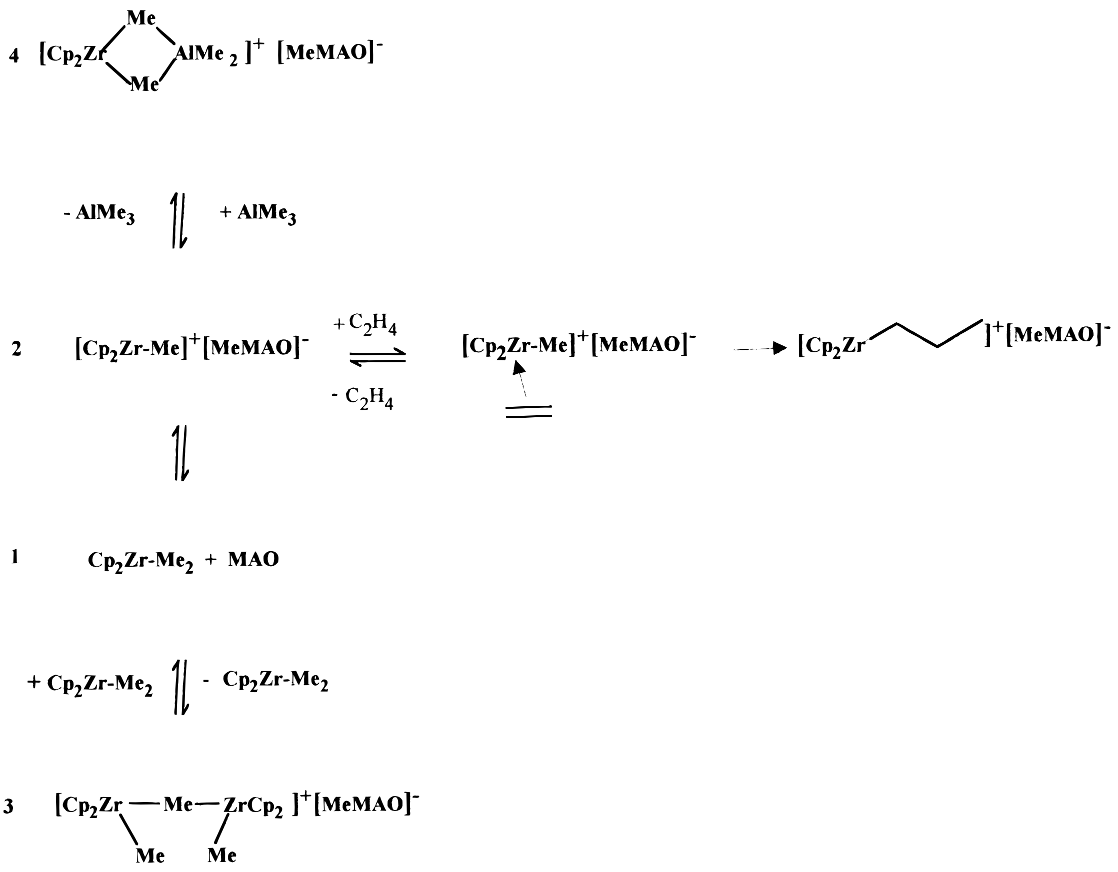


Figure 1. ^{13}C NMR spectra in toluene-d_8 at −20 °C of $Cp_2Zr(^{13}CH_3)_2$ (90% ^{13}C-enriched)/MAO (A, bottom) and of $Cp_2Zr(^{13}CH_3)_2/MAO/^{13}C_2H_4$ (90% ^{13}C-enriched) (B, top). $[Zr] = 0.07$ mol·L^{-1}, $[Al]/[Zr] = 20$, $[^{13}C_2H_4] = 0.4$ mol·L^{-1}. In B, a, b, and c indicate the multiplets which correspond to the resonances of the methyl (a) and of the methylene carbons of the ethyl (b) and *n*-propyl (c) chain end groups of the polyethylene chain, respectively. Stars (∗) indicate the signals due to the α (d, 11.24 ppm), β (m, 25.83 ppm), and γ (m, 36.40 ppm) methylene carbons of the polymer chain bound to aluminum.

10.1021/ma981164r CCC: $18.00

Scheme 1



Results

In situ Polymerization of $^{13}C_2H_4$ in the Presence of $Cp_2Zr(^{13}CH_3)_2$/MAO. NMR tube experiments involving polymerization reactions of ^{13}C-enriched ethylene were performed in the presence of **2**, **3**, and **4** to study their role in polymeric chain growth. The in situ polymerization of $^{13}C_2H_4$ in the presence of **1** and MAO was performed at Al/Zr = 20, [Zr] = 0.07 M, and −20 °C. These conditions were selected because in more diluted solutions (e.g., [Zr] = 0.01 M), reactions such as (1) and (2) are shifted too far to the left and reaction

$$\underset{\mathbf{1}}{Cp_2Zr(^{13}CH_3)_2} + MAO \rightleftharpoons \underset{\mathbf{2}}{[Cp_2Zr^{13}CH_3]^+[^{13}CH_3MAO]^-} \quad (1)$$

$$2\underset{\mathbf{1}}{Cp_2Zr(^{13}CH_3)_2} + MAO \rightleftharpoons \underset{\mathbf{3}}{[(Cp_2Zr^{13}CH_3)_2(\mu\text{-}^{13}CH_3)]^+[^{13}CH_3MAO]^-} \quad (2)$$

products are formed in low yield. On the other hand, higher Al/Zr ratios (e.g., >40) make it more difficult to observe the reaction products due to the dilution of ^{13}C enrichment caused by the scrambling reactions with aluminum methyls and due to the broadness of the signals. The ^{13}C NMR spectra in toluene-d_8 of the catalytic system before and after $^{13}C_2H_4$ addition are shown in parts A and B of Figure 1, respectively. In Figure 1A, the cationic species **2**, dinuclear **3**, and **4**, having MeMAO$^-$ counterions, are visible.[8,9] Under the experimental conditions used, that is, relatively high zirconium concentrations and low temperatures, the ion pair **2** is weakly coordinated.[9]

The $^{13}C_2H_4$ addition produces a quite complex picture (Figure 1B). Some of the features observed testify that this system is active for ethylene polymerization under the conditions used also: the most intense signal at 30.5 ppm (PE) and the multiplets indicated as a, b, and c which correspond to the CH_2 resonances of the chain and to the methyl (a) and the methylene carbons of ethyl (b) and *n*-propyl (c) chain end groups of the polyethylene chain, respectively. The appearance of multiplets is due to the $^{13}C-^{13}C$ couplings, visible because of the ^{13}C enrichment of the ethylene. All Me and Cp signals of the starting metallocenes are visible, apart from the methyl signal of **1** which is overlapped by the $(^{13}CH_2)_n$ signals of the polyethylene chain. The novelty in the ^{13}C NMR spectra of the zirconocene−methylaluminoxane system is the appearance of the doublets in the region between 55 and 65 ppm (J = 29.65 Hz). The downfield shifts of these carbons indicate that they are close to the zirconium atom, while their doublet nature reveals that they experience only one $^{13}C-^{13}C$ coupling. Thus, they are due to ^{13}C-enriched methylene carbons of the polymer chain bound to zirconium ($Zr-^{13}CH_2P$). To our knowledge, this is the first observation of zirconocene−polymeryl complexes.[10] They should arise from successive ethylene insertions into the zirconium−methyl bond of the $[Cp_2Zr^{13}CH_3]^+$ active site:

$$[Cp_2Zr^{13}CH_3]^+ + n^{13}CH_2{=}^{13}CH_2 \rightleftharpoons [Cp_2Zr^+(^{13}CH_2)(^{13}CH_2)_n{}^{13}CH_2{}^{13}CH_2{}^{13}CH_3] \quad (3)$$

The nature of the complexes, which produce the signals observed, as it will appear subsequently, has been elucidated in comparison with the in situ ethylene polymerization study carried out in the presence of $B(C_6F_5)_3$. The fact that more than one doublet is detected indicates that different $Cp_2Zr^{13}CH_2P$ species are present. It is worth noting that methylene signals of the polymer chain bound to titanium ($Ti-CH_2P$) were observed in titanocene/$AlEt_2Cl$-based catalytic systems only at a low Al/Ti mole ratio (1÷2).[11] In the course of our study of titanocene/MAO systems, we have never observed methylene signals of Cp_2Ti-CH_2P complexes unless an Al/Ti ratio lower than 5 was used.[12] The fact that these zirconium−polymeryl species are spectroscopically detectable at Al/Zr = 20 might be due to the higher stability of zirconium alkyl bonds with respect to titanium alkyl bonds. The starred signals are due to α (d, 11.24 ppm), β (m, 25.83 ppm), and γ (m, 36.40 ppm) methylene carbons of the polymer chain bound to aluminum.[13] Their presence indicates that chain-transfer reactions to aluminum occur even at −20 °C and at such a low Al/Zr mole ratio. The integrals of the Zr α methylene and Al α methylene signals indicate that about 50% of the polymer chains have been transferred to aluminum.

$$Cp_2Zr^+(^{13}CH_2)(^{13}CH_2)_n{}^{13}CH_2{}^{13}CH_2{}^{13}CH_3 + {>}Al(Me) \rightleftharpoons {>}Al^{13}CH_2(^{13}CH_2)_n{}^{13}CH_2{}^{13}CH_2{}^{13}CH_3 + Cp_2ZrMe^+ \quad (4)$$

However, it is quite difficult to obtain information on the implication of the starting ion pairs in the formation of active sites from the changes in their relative intensities due to the difficulty in evaluating these variations. Methyl resonances of **2**, **3**, and **4** are very close to the starred signals at 36.4 ppm, due to the methylenes of the polymer chain which are in the β position with regard to zirconium[14] or in the γ position with regard to aluminum. The picture observed in the in situ polymerization in the presence of the $Cp_2Zr(^{13}CH_3)_2$/MAO system differs from what we observed in the titanocene-based system which, however, contained a higher mole ratio of the ion pair $[Cp_2TiMe]^+[Cl{\cdot}MAO]^-$. This difference is due to the fact that metallocene reactivity toward MAO is in the following order: titanocenes are more reactive than zirconocenes; metallocene alkyl chlorides are more reactive than metallocene dimethyls.[15]

In situ Polymerization of $^{13}C_2H_4$ in the Presence of $Cp_2Zr(^{13}CH_3)_2/B(C_6F_5)_3$. It is well established that active zirconocene cationic complexes can be generated from the reaction of dimethylzirconocene and $B(C_6F_5)_3$, a strong Lewis acid which forms a weakly coordinating counteranion upon methide abstraction from dimethylzirconocene.[5,6] As previously reported,[8a] the NMR spectra of reactions of dimethylzirconocene and $B(C_6F_5)_3$ appear to be “neater” than those obtained in the presence of MAO as cocatalyst. This is due to the lack of Al(Me)O groups which produce adducts of a dynamic nature and enlarge the width of the signals and is due as well as to the absence of Al methyls which dilute the ^{13}C enrichment of $[Cp_2Zr(^{13}CH_3)]^+$ ion pairs. In situ polymerization of enriched ethylene has been performed in the presence of **1** and $B(C_6F_5)_3$ at three different B/Zr mole ratios between 0.5 and 2. Both dinuclear $[(Cp_2Zr^{13}CH_3)_2(\mu\text{-}^{13}CH_3)]^+[^{13}CH_3B(C_6F_5)_3]^-$ (**5**) and mononuclear $[Cp_2Zr(^{13}CH_3)]^+[^{13}CH_3B(C_6F_5)_3]^-$ (**6**) ion pairs are formed in different amounts depending on the B/Zr mole ratio, as is visible in the ^{13}C NMR spectra shown in Figure 2.[16] Actually, two close signals are observed for **5**; they were previously assigned as being due to associated and solvent-separated ion pairs.[17]

^{13}C NMR spectra of the same catalytic system after $^{13}C_2H_4$ addition are shown in Figure 2A′−C′. Under all conditions, that is, in the presence of different concentrations of dinuclear and mononuclear ion pairs, the addition of ethylene resulted in the formation of polyethylene signals (PE and chain end groups). The appearance of polyethylene signals is accompanied by a general decrease in intensities of all the starting complexes, which might be caused by catalyst precipitation induced by polyethylene formation. What is interesting to observe is the presence in the three expansions of two doublets, one around 55 ppm (Figure 2A′) and the second one at about 65 ppm (Figure 2B′ and C′). These doublets have different intensities in the three experiments. The chemical shifts of these doublets are very similar to those observed in the in situ polymerization performed in the presence of MAO as cocatalyst (Figure 1B). This confirms the general assignment of these signals to methylene carbons bonded to zirconium in the Zr−polymeryl species. A more detailed characterization of Zr−polymeryl complexes might derive from the comparison of the relative intensities of the doublet signals, which appear after ethylene addition, and of the complexes present in the experiment before ethylene addition. In the expanded spectrum of the in situ polymerization at a B/Zr mole ratio = 2, signals at 65.86 and 65.41 ppm are almost the only ones visible (Figure 2C′). Since before ethylene addition only the mononuclear ion pair **6** was present, we assign the doublet at about 65 ppm to the methylene carbons of the polymer chain bonded to the zirconium complex in the ionic mononuclear form $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3B(C_6F_5)_3]^-$ (**6P**). In Figure 2A′ at B/Zr = 0.5, the doublets at 54.17 and 53.72 ppm prevail in the same way as **1** prevails in Figure 2A before ethylene addition (only a small amount (11 mol %) of the dinuclear ion pair **5** is present); the majority of **1** is left unreacted after ethylene addition in Figure 2A′. Therefore, the signals at 54.17 and 53.72 ppm may be assigned to the methylene of the polymer chain bonded to Zr in the nonionic form $Cp_2Zr(^{13}CH_2P)(^{13}CH_3)$ (**1P**). The difference in chemical shifts of the zirconium α methylenes in **6P** and **1P** of about 10 ppm, which is approximately the difference between the methyl chemical shifts of **6** and **1**, is consistent with the above assignment. Moreover, in the in situ polymerization experiment at B/Zr = 1.0 (Figure 2B′), the chemical shifts (65.66 and 65.21 ppm) of the doublet visible in the expansion are nearly identical to the chemical shifts of those of **6P** in Figure 2C′. Since in the presence of 27 mol % of dinuclear ion pair **5** (Figure 2B′) a polymeryl ion pair complex (whose chemical shifts are identical to those of **6P**) largely prevails, it is likely that the doublet at 65.66 and 65.22 ppm is due to ionic mononuclear complex **6P** rather than to a polymeryl complex in a dinuclear form, **5P** ($[Cp_2Zr(^{13}CH_2P)_2(\mu\text{-}^{13}CH_3)]^+$). The fact that we do not observe dinuclear−polymeryl complexes such as **5P** might signify that they are less stable than dinuclear−methyl complexes. Binuclear complexes with ethyl ligands are reported to be less stable than binuclear species with methyl ligands.[18] The comparison of the relative intensities of the methyl of the ion pairs in dinuclear **5** and mononuclear **6** forms in Figure 2B and 2B′ shows that the dinuclear form

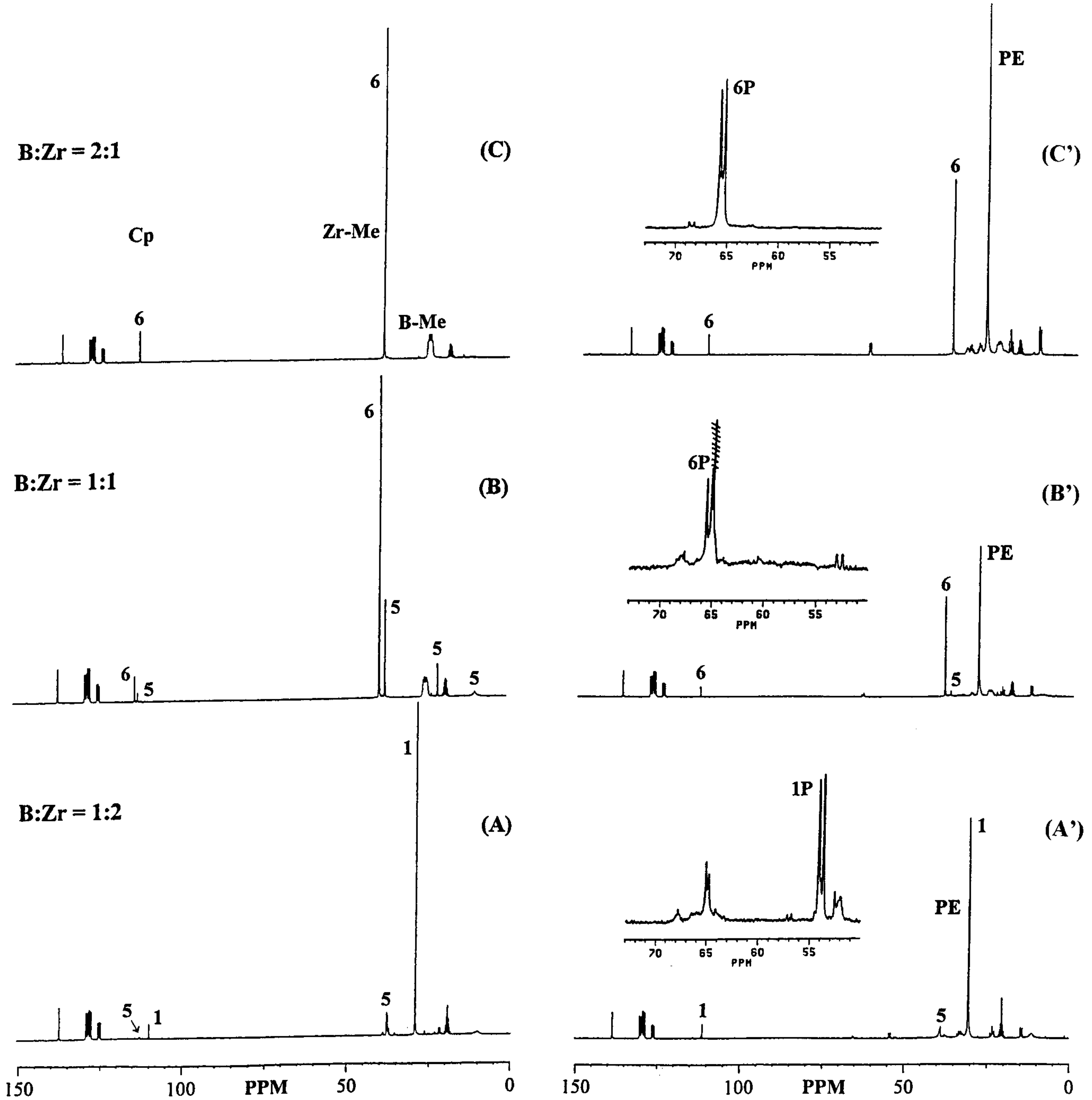


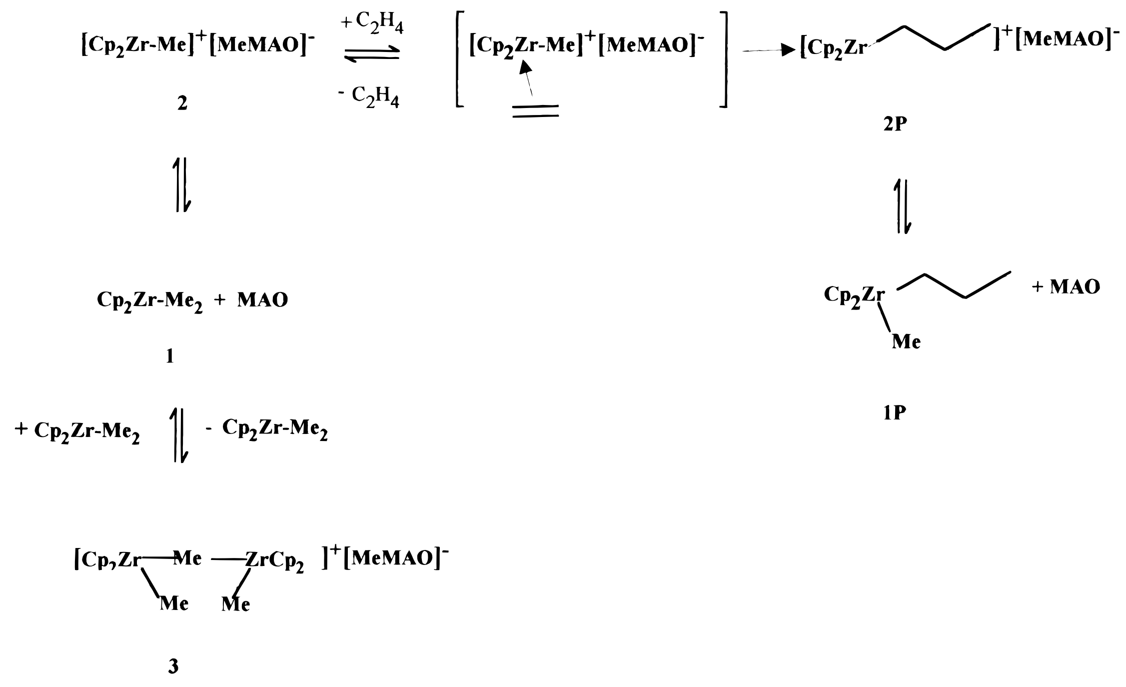
Figure 2. ^{13}C NMR spectra in toluene-d_8 at −20 °C of $Cp_2Zr(^{13}CH_3)_2/B(C_6F_5)_3$ (A, B, C) and $Cp_2Zr(^{13}CH_3)_2/B(C_6F_5)_3/^{13}C_2H_4$ (90% ^{13}C-enriched) (A′, B′, C′). [Zr] = 0.07 mol·L^{-1}, [B]/[Zr] = 0.5 (A, A′), [B]/[Zr] = 1.0 (B, B′), [B]/[Zr] = 2.0 (C, C′); [$^{13}C_2H_4$] = 0.4 mol·L^{-1}.

decreases more than the mononuclear one after the ethylene addition. This is probably due to dissociation equilibrium of **5** into **6** and **1**.

Comparison between the in situ Polymerization of $^{13}C_2H_4$ in the Presence of $Cp_2Zr(^{13}CH_3)_2$ with MAO and $B(C_6F_5)_3$ as Cocatalysts. In situ polymerizations of $^{13}C_2H_4$ performed in the presence of zirconocene alkyl cations with $[MeB(C_6F_5)_3]^-$ ([B]/[Zr] = 0.5) or $[MeMAO]^-$ ([Al]/[Zr] = 20) as counterions are compared in parts A and B of Figure 3, respectively. It is worth noting the similarities of the spectra, apart from the starred signals due to the methylene of the $Al-CH_2CH_2CH_2P$ complexes which are present in Figure 3B. Moreover, the almost complete absence in the in situ polymerization in the presence of $B(C_6F_5)_3$ of different signals due to the methylene of $B-CH_2CH_2-CH_2P$ complexes reveals that chain-transfer reactions to $B(C_6F_5)_3$ are less facile than chain-transfer reactions to MAO and to traditional aluminum alkyl cocatalysts. A comparison of the spectra in Figure 3 makes it relatively easy to assign the doublet at 64.55 ppm to a mononuclear ion pair $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3MAO]^-$ (**2P**) and the doublet at 54.41 and 53.98 ppm to the neutral complex **1P**.

The previously reported spectroscopical observation of different Zr−polymeryl species and of the neutral form **1P** indicates that an equilibrium of various Zr−polymeryl adducts exists. Scheme 2 represents the possible equilibria involved. This scheme is similar to the intermittent chain growth mechanistic scheme proposed by Fink[11b] on the basis of kinetic studies of ethylene polymerization with the $[Cp_2TiCl_2][AlR_2Cl]$

Scheme 2



catalytic system. The novelty of this study is the observation of new spectroscopically detectable complexes closely related to the propagating active species.

Conclusions

^{13}C NMR analysis of the in situ polymerization of ^{13}C-enriched ethylene in the presence of $Cp_2Zr(^{13}CH_3)_2$ and MAO or $B(C_6F_5)_3$ as cocatalyst led to the direct observation of different Cp_2Zr–polymeryl species. The in situ polymerization experiments in the presence of different concentrations of mononuclear $[Cp_2ZrMe]^+[Me\cdot B(C_6F_5)_3]^-$ (**6**) and dinuclear $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[MeB(C_6F_5)_3]^-$ (**5**) ion pairs have allowed us to make the assignments of methylene carbons next to zirconium of complexes $Cp_2Zr(^{13}CH_2P)(^{13}CH_3)$ (**1P**), $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3MAO]^-$ (**2P**), and $[Cp_2Zr^{13}CH_2P]^+[^{13}CH_3B(C_6F_5)_3]^-$ (**6P**).

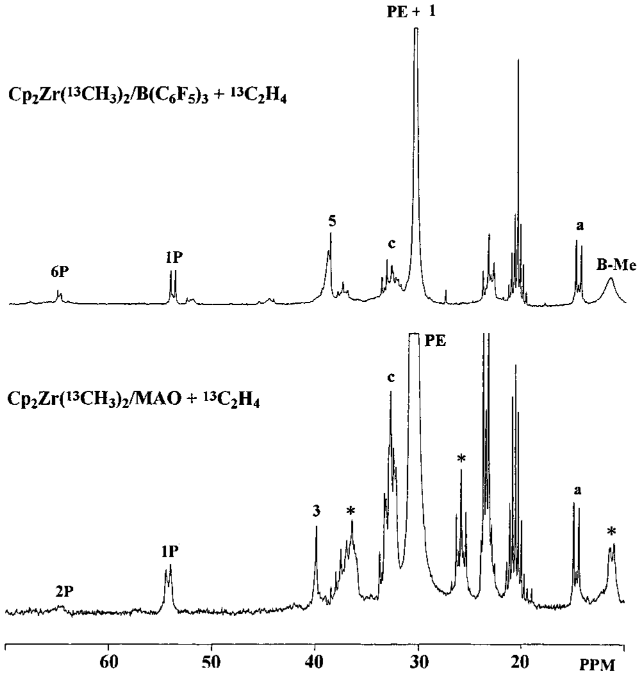


Figure 3. ^{13}C NMR spectra in toluene-d_8 at −20 °C of $^{13}C_2H_4$ in situ polymerization in the presence of the catalytic systems: $Cp_2Zr(^{13}CH_3)_2/MAO/^{13}C_2H_4$ (90% ^{13}C-enriched) (A, bottom). $[Zr] = 0.07\ mol\cdot L^{-1}$, $[Al]/[Zr] = 20$, $[^{13}C_2H_4]\ 0.4\ mol\cdot L^{-1}$; $Cp_2Zr(^{13}CH_3)_2/B(C_6F_5)_3/^{13}C_2H_4$ (90% ^{13}C-enriched) (B, top). $[Zr] = 0.07\ mol\cdot L^{-1}$, $[^{13}C_2H_4] = 0.4\ mol\cdot L^{-1}$. $[B]/[Zr] = 0.5$ (B).

The correlation between the concentration of Zr–polymeryl adducts and starting zirconium complexes leads us to conclude that the formed Zr–polymeryl adducts are in equilibrium with each other.

With respect to the intermittent chain growth mechanism proposed by Fink,[11b] this study allows us to provide evidence of new spectroscopically detectable complexes, among which the Zr–polymeryl ion pairs such as **6P** and **2P** either are the propagating active species or are intermediates closely related to the propagating active species. Finally, since we do not observe complexes containing the polymeryl ligand in a dinuclear form, we do not have evidence that dinuclear complexes are polymerization dormant states. Moreover, we do not have evidence of the existence of $AlMe_3$ adducts of Zr–polymeryl complex analogues of **4** due to the initial low concentration of **4**. However, it is possible that, analogously to the dinuclear polymeryl zirconocene species, dinuclear zirconium–aluminum polymeryl species are not stable.

Experimental Part

All manipulations were performed using standard high-vacuum techniques in Shlenk-type glassware or in a nitrogen-filled MBraun glovebox. Nitrogen was purified by passage through columns of BASF R3-11 catalyst and 4-Å molecular sieves. Air- and/or water-sensitive organometallic compounds were stored and transferred in the glovebox. Toluene-d_8 was distilled under nitrogen from sodium benzophenone ketyl. Solutions (30%) of MAO in toluene (Witco) were used after removing all volatiles and drying the resulting powder in a vacuum (12 h, room temperature, 0.1 mmHg). $Cp_2Zr(^{13}CH_3)_2$[19] and $B(C_6F_5)_3$[20] were prepared according to literature procedures.

NMR Analysis. All the ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM-270 spectrometer operating at 270

MHz (^{1}H) and at 67.89 MHz (^{13}C) in the PFT mode. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H NMR signals and to ^{13}C NMR signals of the deuterated toluene-d_8 solvent, respectively. NMR probe temperatures were measured using an anhydrous methanol sample, $\Delta\nu$(MeOH).

In all ^{1}H NMR spectra, the pulse width was 4.0 μs. The pulse repetition time was 11.72 s. A dwell time of 105 μs was used with 16K of computer memory for the interferogram. In all ^{13}C NMR spectra, the pulse width was 5.0 μs. CPD was used to remove ^{13}C−^{1}H couplings; the pulse angle was 90°. The pulse repetition time was 10.46 s. A dwell time of 28 μs was used with 16K of computer memory for the interferogram.

In situ Polymerization. In a drybox under a nitrogen atmosphere, a 5-mm NMR tube was charged with approximately 0.5 mmol of zirconocene complex and 0.5 mL of toluene-d_8. The tube was then capped with a septum rubber cap, removed from the drybox, and cooled to a given temperature. A known amount of $B(C_6F_5)_3$ or methylaluminoxane as toluene-d_8 solution was syringed into the cooled NMR tube via a gastight microsyringe and the septum wrapped with Parafilm. The tube was shaken briefly and transferred to the precooled NMR probe, and the spectra were obtained. The same sample was unloaded from the NMR probe and cooled at −78 °C. A known amount of ^{13}C-enriched ethylene, contained in a gastight syringe equipped with a 20-cm needle, was added to the cooled NMR tube containing the catalyst solution. The tube was shaken briefly and reloaded in the precooled NMR probe of the NMR instrument.

References and Notes

(1) For recent reviews, see, for example: (a) Fink, G.; Mülhaupt, R.; Brintzinger, H. H. *Ziegler Catalysts*; Springer: Berlin, 1995. (b) *Synthetic, Structural and Industrial Aspects of Stereospecific Polymerization*; Tritto, I., Giannini, U., Eds.; *Macromol. Symp.* **1995**, *89*. (c) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995,** *14*, 1145. (d) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (e) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907 and references therein.

(2) (a) Sinn, H.; Bliemeister, J.; Clausnitzer, D.; Tikwe, L.; Winter, H.; Zarnke, O. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 257. (b) Sinn, H. *Macromol. Symp.* **1995**, *97*, 27. (c) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971. (d) Barron, A. R. *Organometallics* **1995**, *14*, 3581. (e) Tritto, I.; Sacchi, M. C.; Locatelli, P.; Li, S. X. *Macromol. Chem. Phys.* **1996**, *197*, 1537 and references therein.

(3) Dyachcovskii, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci., Part C* **1967**, *16*, 2333.

(4) (a) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108,* 7410. (c) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(5) (a) Turner, H. W. Eur. Pat. Appl. 0 277 004, 1988. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (c) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (d) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (e) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(6) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112.

(7) (a) Tritto, I.; Li, S.; Sacchi, M. C.; Zannoni, G. *Macromolecules* **1993**, *26* (6), 7111. (b) Tritto, I.; Sacchi, M. C.; Li, S. *Macromol. Rapid Commun.* **1994**, *15*, 217. (c) Tritto, I.; Sacchi, M. C.; Locatelli, P.; Li, S. X. Ref 1b, p 289. (d) Tritto, I.; Li, S. X.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1995**, *28* (8), 5358.

(8) (a) Tritto I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997,** *30*, 1247. (b) Selected ^{13}C NMR data (toluene-d_8, −20 °C): $[Cp_2ZrMe]^+[Me{\cdot}MAO]^-$ (**2**) (Cp = 113.70 ppm, Zr*Me*$^+$ = 40.68 ppm q, J_{CH} = 100 Hz (the broadness of this signal makes it difficult to obtain an accurate value)); $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[Me{\cdot}MAO]^-$ (**3**) (Cp = 113.27 ppm, Zr*Me*$^+$ = 39.84 ppm, q, J_{CH} = 120.3 Hz, μ-*Me* = 22.54 ppm); and $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me{\cdot}MAO]^-$ (**4**) (Cp = 115.97 ppm, Zr*Me*$^+$ = 37.69 ppm).[8a] **2**, **3**, and **4** cations as $B(C_6F_5)_4^-$ salts have already been reported.[8c] For comparison, some of the reported data are listed here: ^{13}C NMR data (CD_2Cl_2, −60 °C $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (Cp = 113.27 ppm, Zr*Me*$^+$ = 38.81 ppm, q, J_{CH} = 120.2 Hz, μ-*Me* = 23.81 ppm); and $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (Cp = 115.96 ppm, Zr*Me*$^+$ = 38.51 ppm).[8c] (c) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(9) (a) We can exclude that **2** is coordinated to an oxygen of MAO chains since ion pairs formed from $Cp_2ZrMeCl$ and MAO have different ^{13}C NMR Zr−*Me* chemical shifts. This indicates also that the chlorine or the methyl is still coordinated to zirconium. In our opinion, in **2**, $[Cp_2ZrMe]^+$ is weakly coordinated to a $MeMAO^-$ anion since there is a strong similarity between the ^{13}C NMR data of **2** and the NMR data of the complex which has $MeB(C_6F_5)_3^-$. On the basis of crystallographic and solution dynamic NMR studies, $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$ is considered to be relatively weakly coordinated complex.[9b] (b) Marks T. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(10) (a) Evidence of zirconium−polymeryl intermediates has recently been reported.[10b] (b) Baumann, R.; Schrock, R. R *J. Orgonamet. Chem.* **1998**, *557*, 69.

(11) (a) Mynott, R.; Fink, G.; Fenzl, W. *Angew. Makromol. Chem.* **1987**, *154*, 1. (b) Fink, G.; Fenzl, W.; Mynott, R. Z. *Z. Naturfosch. B* **1985**, *40b*, 158. (c) Fink, G.; Rottler, R. *Angew. Makromol. Chem.* **1981**, *94*, 25.

(12) Unpublished results of our laboratory.

(13) Signals of the methylene of the polymer chain adjacent to aluminum are shifted downfield with respect to the Al−Me (Al−*Me* in MAO at −6.60 ppm, ^{13}C NMR data in toluene-d_8 at −20 °C) due to the additional β and γ effects of the polymer chain. Signals of the methylenes in the β and γ positions with respect to aluminum are shifted downfield with respect to the α methylenes because of the greater distance with respect to the aluminum.

(14) Signals of the methylenes in the β position with respect to zirconium are shifted highfield with respect to the α methylenes (the signals between 54 and 64 ppm). Because of the greater distance with respect to the zirconium, they have chemical shifts closer to the methylenes of the polyethylene chain. In a similar way, the signals of the methylenes in the β and γ positions with respect to titanium are reported to be shifted highfield with respect to the methylenes adjacent to titanium in ref 11.

(15) Unpublished results of our laboratory.

(16) Some relevant ^{13}C NMR data, already reported in ref 8a (toluene-d_8, −20 °C): $[Cp_2ZrMe]^+[Me{\cdot}B(C_6F_5)_3]^-$ (**6**) (Cp = 114.12 ppm, Zr*Me*$^+$ = 40.61 ppm q, J_{CH} = 122.3 Hz); $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[Me{\cdot}B(C_6F_5)_3]^-$ (**5**) (Cp = 113.20 and 113.01 ppm, Zr*Me*$^+$ = 38.91 and 38.64 ppm, q, J_{CH} = 120.7 and 118 Hz, μ-*Me* = 23.2 and 22.85 ppm).

(17) (a) Beck, S.; Prosenc, M. H.; Brintzinger, H. H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A: Chem.* **1996**, *111*, 67. (b) Haselwander, T.; Beck, S.; Brintzinger, H. H. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H., Eds.; Springer: Berlin, 1995; p 182.

(18) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1995**, *497*, 55.

(19) Samuel, E.; Rausch, M. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

(20) Massey, A. G.; Park, A. J. *Organomet. Chem.* **1964**, *2*, 245.

MA981164R