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Dimethylzirconocene−Methylaluminoxane Catalyst for Olefin Polymerization: NMR Study of Reaction Equilibria

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ABSTRACT: $Cp_2Zr(^{13}CH_3)_2$ (**1**) has been used as a probe for the reactivity of metallocene−methylaluminoxane catalysts for olefin polymerization. A ^1H and ^{13}C NMR study of the reaction equilibria between $Cp_2Zr(^{13}CH_3)_2$ and Lewis acids such as $AlMe_3$ (**2**), $B(C_6F_5)_3$ (**3**), and methylaluminoxane (MAO) (**4**) has been performed. $AlMe_3$ is always present in MAO solutions, and $B(C_6F_5)_3$ is a relatively strong Lewis acid, which has a capacity to form and stabilize ion pairs comparable to that of MAO. The use of isotopically ^{13}C-enriched dimethylzirconocene has permitted the study of these systems by ^{13}C NMR in conditions as close as possible to usual polymerization conditions, which require large excesses of MAO for reaching high activities. The comparisons of the reactivity of $Cp_2Zr(^{13}CH_3)_2$ with $B(C_6F_5)_3$ and with MAO have provided the first direct evidence of the formation in solution of monomeric $[Cp_2Zr(^{13}CH_3)]^+[Me{\cdot}MAO]^-$ (**8**), of dimeric $[Cp_2Zr(^{13}CH_3)]_2(\mu\text{-}^{13}CH_3)^+[Me{\cdot}MAO]^-$ (**7**), and of the $[(Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me{\cdot}MAO]^-$ (**9**) cationic species, having $MeMAO^-$ counterions. The influence of temperature, Al/Zr mole ratio, and zirconium concentration on the equilibria of ion pair formation has been elucidated.

Introduction

The homogeneous Ziegler−Natta catalysts based on group IV metallocenes and aluminoxanes are among those of the greatest potential industrial interest and the most highly active and selective classes of catalysts for α-olefin polymerization,[1] since they offer a unique possibility of controlling polymer structures and properties.[2] Methylaluminoxane (MAO) is the most commonly used metallocene cocatalyst.[3] However, its constitutional features are unclear and its role in giving high polymerization activities is still uncertain.[4] Group IV metallocenium ions Cp_2MR^+ have recently attracted much interest since they have been hypothesized (and are now recognized) as having a primary role in the polymerization activity of homogeneous metallocene/aluminoxane catalysts (Cp = cyclopentadienyl ligand; M = Ti, Zr, Hf; R = alkyl).[5−8] Indirect evidence for the formation of Cp_2TiCl^+ cations was provided by chemical trapping work in the $Cp_2TiCl_2/AlCl_3$ system.[5] The attempt to prove the hypothesis that the crucial role of the cocatalyst is to form Cp_2MR^+ cations led to the synthesis of model "cationic" metallocene complexes[6] and to the use of relatively strong Lewis acids based on perfluorinated organoboranes. Well-defined highly active cationic metallocene complexes[7] were synthesized, and several Cp_2ZrMe^+ model cations have been isolated and studied.[8]

As we were stimulated by the challenge of directly understanding the methylaluminoxane (MAO) role in homogeneous catalytic systems—MAO is an oligomeric species which is difficult to characterize—we have undertaken an NMR study of metallocene/MAO solutions, which has allowed us to obtain the first direct evidence of $Cp_2Ti^{13}CH_3{}^+X{\cdot}MAO^-$ formation in solution.[9] Our strategy has consisted in using isotopically ^{13}C-enriched methyltitanocene to study these systems by ^{13}C NMR in conditions as close as possible to polymerization conditions, since large excesses of MAO are usually required for reaching high activities. $Cp_2Ti^{13}CH_3Cl$ has been studied in combination with $AlMe_3$, $B(C_6F_5)_3$, and MAO. *In situ* polymerization of ^{13}C-enriched ethylene has been studied as well in order to understand the role of the observed products in the catalytic activity.[10]

In order to get a more direct insight into the formation of ion pairs in the metallocene/MAO catalytic systems and to elucidate their role in polymerization activity, in chain transfer processes, and ultimately in stereoregulation, we applied the method we have devised for the study of the titanocene/MAO system to zirconocene-based systems, since zirconocenes are more stable and

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Table 1. ^{1}H and ^{13}C NMR Spectral Parameters for the Starting Zirconocene Complex and Its Boron and Aluminum Complexes[a]

	^{1}H (δ, ppm)				^{13}C (δ, ppm)			
zirconocene	Cp	Me	μ-Me	B-Me	Cp	Me	μ-Me	B-Me
Cp_2ZrMe_2 (**1**)[b]	5.65	−0.15			110.45	30.45		
$[(Cp_2ZrMe)_2(\mu\text{-Me})]^+[MeB(C_6F_5)_3]^-$ (**5**)	5.59, 5.53	−0.19	−1.33, −1.19	1.1, 0.98	113.20, 113.01	38.91, 38.64 (q, J_{CH} = 120.7 Hz, q, J_{CH} = 118 Hz)	23.2, 22.85	11.43
$[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$ (**6**)	5.39	0.29	−0.15		114.12	40.61 (J_{CH} = 122.3 Hz)		26.84
$[(Cp_2ZrMe)_2(\mu\text{-Me})]^+[MeMAO]^-$ (**7**)[c]	n.r.	n.r.	n.r.		113.27	39.84 (q, J_{CH} = 120.3 Hz)	22.54	
$[Cp_2ZrMe]^+[MeMAO]^-$ (**8**)[c]	n.r.	n.r.			113.70	40.68 (q, J_{CH} = 100 Hz[d])		
$[Cp_2ZrMeAlMe_3]^+[MeMAO]^-$ (**9**)[c]	n.r.	n.r.	n.r.		115.97[e]	37.69[e]		

[a] ^{1}H and ^{13}C NMR spectra were recorded in toluene-d_8 at −20 °C on a Bruker AM 270 spectrometer. Chemical shifts are referenced to a residual ^{1}H NMR signal (2.08 ppm) and to a ^{13}C NMR signal (20.52 ppm) of the deuterated toluene-d_8 solvent, respectively. [b] In benzene-d_6 at 25 °C. [c] Chemical shifts were measured at Al/Zr = 20. [d] The broadness of this signal makes it difficult to obtain an accurate value. [e] At 0 °C in toluene-d_8. $[Cp_2ZrMeAlMe_3]^+[MeB(C_6F_5)_3]^-$ ^{13}C NMR in CD_2Cl_2 (−60 °C): 115.96 (Cp), 38.51 (Zr−Me−Al).[14]

more often used for producing the new polymeric products obtainable with metallocene-based catalysts. Here we are reporting on a ^{1}H and ^{13}C NMR study of $Cp_2Zr(^{13}CH_3)_2$ (**1**), used as a probe for metallocene reactivity with Lewis acids such as $AlMe_3$ (**2**), $B(C_6F_5)_3$ (**3**), and MAO (**4**). $AlMe_3$ is used since it is always present in MAO solutions, and $B(C_6F_5)_3$ is a relatively strong Lewis acid, which has a capacity to form and stabilize ion pairs comparable with that of MAO. These homogeneous comparisons will allow us to clarify equilibria of ion pair formations as well as their eventual role in the catalytic activity.

Results

Comparison between Reactions of $Cp_2Zr(^{13}CH_3)_2$ with $AlMe_3$, $B(C_6F_5)_3$, and MAO. The reaction equilibria of $Cp_2Zr(^{13}CH_3)_2$ with $AlMe_3$, $B(C_6F_5)_3$, and MAO have been studied by comparing the ^{1}H and ^{13}C NMR spectra obtained in toluene-d_8 solutions at −20 °C and [Zr] = 0.07 M. This comparison has been made at −20 °C, since at higher temperatures, as we will report in the next section, the line widths of the signals in the spectra of metallocene/methylaluminoxane systems become wider. The spectral parameters of these reactions are reported in Table 1. From the inspection of this table, it is possible to observe that ^{1}H NMR analysis of metallocene/MAO solutions is not useful, since most of the signals are not resolved. For this reason, we will report on the ^{13}C NMR study, since the wide range of ^{13}C chemical shifts and the ^{13}C enrichment of the zirconocene allow us to detect and distinguish among similar species.

In Figure 1 one can observe that $Cp_2Zr(^{13}CH_3)_2$ (**1**) apparently does not react with $AlMe_3$. Indeed, no new products are detected at −20 °C (Figure 1B). However, the scrambling of the ^{13}C enrichment of dimethylzirconocene with $AlMe_3$, revealed by the decrease of the relative intensity of the methyl peak (Figure 1B), indicates that there is a methyl exchange reaction. Similar observations were made for the same system[11] and for the $Cp_2Ti^{13}CH_3Cl/AlMe_3$ system.[9] These data confirm that $AlMe_3$ is not a good methyl acceptor toward $Cp_2Zr(^{13}CH_3)_2$.[11]

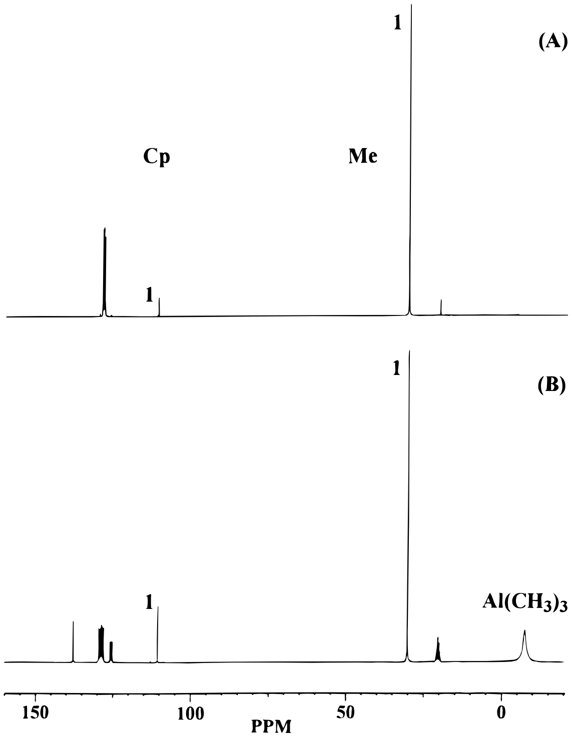


Figure 1. ^{13}C NMR spectra of $Cp_2Zr(^{13}CH_3)_2$ (^{13}C 90% enriched) in benzene-d_6 at 25 °C (A) and $Cp_2Zr(^{13}CH_3)_2/AlMe_3$ (B) in toluene-d_8 at −20 °C. [Zr] = 0.07 mol·L^{-1}, [Al]:[Zr] = 1:1 mol/mol.

The reaction equilibria between $Cp_2Zr(^{13}CH_3)_2$ and $B(C_6F_5)_3$ (**3**) have been studied at three different B/Zr mole ratios between 0.5 and 2 (Figure 2). Both dimeric **5** and monomeric **6** ion pairs are formed according to equilibria 1 and 2, as already reported.[8]

$$\underset{\mathbf{1}}{2Cp_2Zr(^{13}CH_3)_2} + \underset{\mathbf{3}}{B(C_6F_5)_3} \rightarrow \underset{\mathbf{5}}{[Cp_2Zr(^{13}CH_3)]_2(\mu\text{-}^{13}CH_3)^+[^{13}CH_3B(C_6F_5)_3]^-} \tag{1}$$

$$\underset{\mathbf{1}}{Cp_2Zr(^{13}CH_3)_2} + \underset{\mathbf{3}}{B(C_6F_5)_3} \rightarrow \underset{\mathbf{6}}{[Cp_2Zr(^{13}CH_3)]^+[^{13}CH_3B(C_6F_5)_3]^-} \tag{2}$$

Although dimethylzirconocene tends to give μ-CH_3-binuclear complexes $[(Cp_2ZrMe_2)(\mu\text{-Me})]^+$ (**5**), the monomeric ion pair $[Cp_2Zr^{13}CH_3{}^+][^{13}CH_3{\cdot}B(C_6F_5)_3]^-$ (**6**) is formed in 87.2% yield at B/Zr mole ratio = 1 (Figure 2B) and in 99.8% yield when $B(C_6F_5)_3$ is used in excess (Figure 2C). As far as the dimeric ion pair **5** is concerned, we observe two signals for the Cp (113.20 and 113.01 ppm), Me (38.91 and 38.64 ppm), and μ-Me

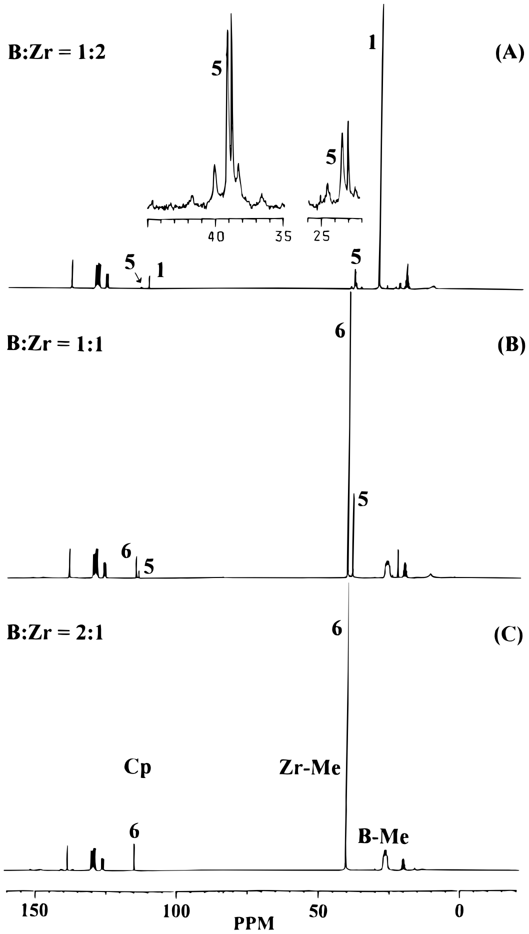


Figure 2. ^{13}C NMR spectra in toluene-d_8 at −20 °C of $Cp_2Zr(^{13}CH_3)_2$ and $B(C_6F_5)_3$: [B]:[Zr] = 0.5:1 mol/mol (A); [B]:[Zr] = 1:1 mol/mol (B); [B]:[Zr] = 2:1 mol/mol (C). [Zr] = 0.07 mol·L^{-1}.

(23.2 and 22.85 ppm) groups in the ^{13}C NMR spectra. This duality, which appears in the ^{1}H NMR spectra also, has already been observed at higher temperatures and attributed to the existence of associated and solvent-separated dimeric ion pairs.[8c]

^{13}C NMR spectra of the reactions between $Cp_2Zr(^{13}CH_3)_2$ with MAO at Al/Zr mole ratios 10 (A) and 20 (B) are displayed in Figure 3. The comparison between the chemical shifts of the $B(C_6F_5)_3$ and MAO reaction products makes the assignment of the species produced by MAO quite easy. Both binuclear $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[MeMAO]^-$ (**7**) and mononuclear $[Cp_2ZrMe]^+[MeMAO]^-$ (**8**) ion pairs are formed according to the equilibria 3 and 4.

$$\underset{\mathbf{1}}{2Cp_2Zr(^{13}CH_3)_2} + \underset{\mathbf{4}}{MAO} \rightarrow \underset{\mathbf{7}}{[Cp_2Zr(^{13}CH_3)]_2(\mu\text{-}^{13}CH_3)^+[^{13}CH_3MAO]^-} \quad (3)$$

$$\underset{\mathbf{1}}{Cp_2Zr(^{13}CH_3)_2} + \underset{\mathbf{4}}{MAO} \rightarrow \underset{\mathbf{8}}{[Cp_2Zr(^{13}CH_3)]^+[^{13}CH_3MAO]^-} \quad (4)$$

Complexes **7** and **8** exhibit methyl signal resonances shifted slightly downfield with respect to those of **5** and **6** produced by $B(C_6F_5)_3$, but remarkably downfield from the neutral zirconocene dimethyl complex **1** (Table 1). This is known to reflect the electron deficiency of the metal in these cationic species. Under these experimental conditions (relatively high concentrations and low temperatures), ion pairs **7** and **8** should be loosely associated ion pairs according to our previous studies on titanocene systems under similar conditions.[13] Moreover, the $J_{^{13}C-^1H}$ values for Zr−CH_3 for these cationic species are reported in Table 1. The values obtained for **5** and **6** are similar to those already reported, and the value obtained for **7** (120.3 Hz) is comparable to those of species **5** and gives no evidence of α-agostic interactions. The $J_{^{13}C-^1H}$ value for Zr−CH_3 of **8** seems to be quite low; unfortunately, the broadness of this signal makes it difficult to obtain an accurate value. At Al/Zr = 20 a species is also detectable, which has Cp and Me resonances at 115.97 and 37.69 ppm, respectively, assignable as the $[(Cp_2Zr(\mu\text{-}Me)_2)AlMe_2]^+[Me\cdot MAO]^-$ (**9**), similar to $[(Cp_2Zr(\mu\text{-}Me)_2)AlMe_2]^+[Me\cdot B(C_6F_5)_3]^-$, the one observed and proposed as a possible dormant state for the active sites for olefin polymerization by Bochmann.[14] However, this species is present under our reaction conditions in very small amounts, likely due to the fact that we have removed the non-deuterated toluene of the commercial MAO solution under vacuum; this process also removes some $AlMe_3$.[15] The scrambling of the ^{13}C enrichment of the zirconocene methyl with unenriched MAO methyls is indicative of the methyl exchange reaction in this case also. An increase of line widths of all Cp and Me signals with increasing Al/Zr mole ratio, which might be indicative of some fluxional equilibria such as methyl transfer, is observable also.

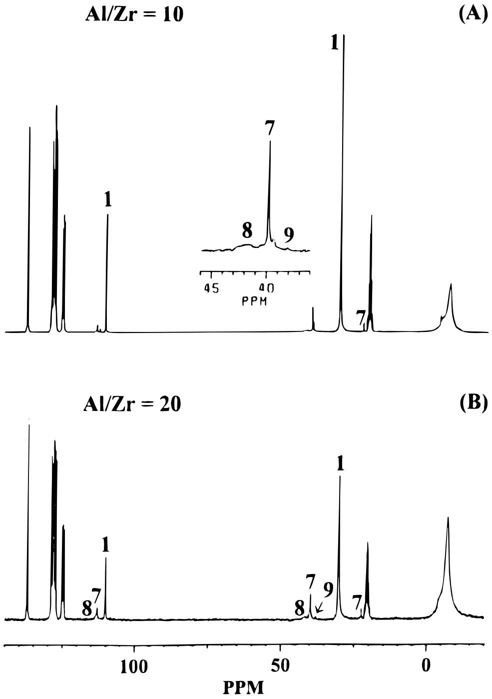


Figure 3. ^{13}C NMR spectra in toluene-d_8 at −20 °C of $Cp_2Zr(^{13}CH_3)_2$ and MAO: [Al]:[Zr] = 10:1 (A); [Al]:[Zr] = 20:1 (B). [Zr] = 0.07 mol·L^{-1}.

In order to compare the MAO and $B(C_6F_5)_3$ ability of abstracting $^{13}CH_3^-$ from Cp_2ZrMe_2 and their tendency to give monomeric (MonIP) or dimeric (DimIP) ion pairs, we have reported the data shown in Figures 2 and 3 as [DimIP][MonIP]/[Cp_2ZrMe_2] and [DimIP]/[MonIP] ratios in Table 2. The [DimIP][MonIP]/[Cp_2ZrMe_2] values indicate how far to the right both equilibria 1 and 2 and equilibria 3 and 4 lie. The [DimIP]/[MonIP] values correspond to $K_5[Cp_2ZrMe_2]$ and $K_6[Cp_2ZrMe_2]$ and

Table 2. ^{13}C NMR Data of the Reactions of $Cp_2Zr(^{13}CH_3)_2$ with MAO and $B(C_6F_5)_3$ at Different Cocatalyst/Zr Mole Ratios at −20 °C and at [Zr] = 0.07 M

cocat.	cocat./Zr	[**5**][**6**]/[**1**]^a	[**7**][**8**]/[**1**]^a	[**5**]/[**6**]^a (K_5[**1**])	[**7**]/[**8**]^a (K_6[**1**])
$B(C_6F_5)_3$	0.5	0.023		4.3	
	1	1680		0.15	
	2	n.e.^{b}		0.004	
MAO	10		0.03		0.69
MAO	20		0.20		0.60

^{a} Calculated from the integrated peak areas of the Cp and Me signals. ^{b} n.e.: not evaluable.

Table 3. ^{13}C NMR Data of the Reactions between $Cp_2Zr(^{13}CH_3)_2$ and MAO at Different Temperatures at [Zr] = 0.07 M

T (°C)	Al/Zr	[**7**][**8**]/[**1**]^a	[**7**]/[**8**]^a (K_6[**1**])
−78	10	0.005	0.29
−33	10	0.009	0.59
−20	10	0.03	0.69
0	10	0.08	0.74
+25	10	0.13	0.49

^{a} Calculated from the integrated peak areas of the Cp and Me signals.

Table 4. ^{13}C NMR Data of the Reactions between $Cp_2Zr(^{13}CH_3)_2$ and MAO at Different Al/Zr Mole Ratios and Temperatures at [Zr] = 0.07 M

T (°C)	Al/Zr	[**7**][**8**]/[**1**]^a	[**7**]/[**8**]^a (K_6[**1**])
0	20	0.35	0.79
25	20	0.78	0.41
0	40	1.52	0.52
25	40	2.78	0.12

^{a} Calculated from the integrated peak areas of the Cp and Me signals.

indicate the $B(C_6F_5)_3$ and MAO tendency to give dimeric or monomeric ion pairs.

$$\underset{\mathbf{1}}{Cp_2Zr(^{13}CH_3)_2} + \underset{\mathbf{6}}{[Cp_2Zr(^{13}CH_3)]^+[^{13}CH_3B(C_6F_5)_3]^-} \rightarrow \underset{\mathbf{5}}{[Cp_2Zr(^{13}CH_3)]_2(\mu\text{-}^{13}CH_3)^+[^{13}CH_3B(C_6F_5)_3]^-} \quad (5)$$

$$\underset{\mathbf{1}}{Cp_2Zr(^{13}CH_3)_2} + \underset{\mathbf{8}}{[Cp_2Zr(^{13}CH_3)]^+[^{13}CH_3MAO]^-} \rightarrow \underset{\mathbf{7}}{[Cp_2Zr(^{13}CH_3)]_2(\mu\text{-}^{13}CH_3)^+[^{13}CH_3MAO]^-} \quad (6)$$

From this comparison, it would seem that $B(C_6F_5)_3$ has a much greater ability to accept $^{13}CH_3^-$ than does MAO, while MAO has a greater tendency with respect to $B(C_6F_5)_3$ to stabilize binuclear ion pairs at this temperature and at these low Al/Zr ratios. However, it is worth considering that the MAO used surely has a quite high M_w with 24−25 [−Al(Me)O−] monomeric units; therefore Al/Zr = 20 should correspond to a [MAO]/Zr ratio lower than one.[15]

Reactions of $Cp_2Zr(^{13}CH_3)_2$ and MAO at Different Temperatures, Al/Zr Ratios, and Concentrations. Since polymerization activity of the MAO-cocatalyzed systems generally increases with increasing temperature, Al/Zr mole ratio, and dilution, we have studied these reactions by varying these parameters (Tables 3−5, Figures 4−6). In Table 3 and in Figure 4, the data on reaction equilibria between $Cp_2Zr(^{13}CH_3)_2$ and MAO at different temperatures (from −78 to +25 °C), Al/Zr ratio = 10, and [Zr] = 0.07 are reported. An increase of all the reaction products occurs with increase in the temperature. However, from 0 °C up, the monomeric ion pair **8** increases most. In addition, the presence of methane is observed, the development of which has been monitored by Kaminsky,[16] and it might be indicative of the formation of side products.

Table 5. ^{13}C NMR Data of the Reactions between $Cp_2Zr(^{13}CH_3)_2$ and MAO at Different Zirconium Concentrations and Al/Zr Mole Ratios at 0 °C

[Zr]	Al/Zr	[**7**][**8**]/[**1**]	[**7**]/[**8**]^a (K_6[**1**])
0.07	10	0.08^a	0.74^a
0.01	10	0.01^b	0.6^b
0.07	20	0.35^a	0.79^a
0.01	20	0.03^b	0.4^b
0.07	40	1.52^a	0.52^a
0.01	40	0.05^b	0. 3^b

^{a} Calculated from the integrated peak areas of the Cp and Me signals. ^{b} Calculated from the integrated peak areas of the Cp signals.

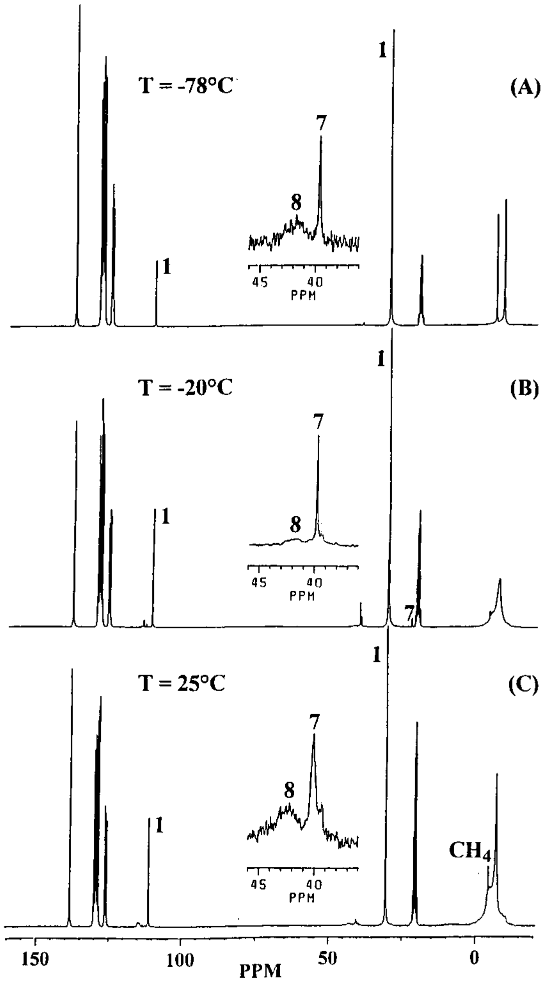


Figure 4. ^{13}C NMR spectra in toluene-d_8 of $Cp_2Zr(^{13}CH_3)_2$ and MAO: at −78 °C (A); at −20 °C (B); at 25 °C (C). [Zr] = 0.07 mol·L^{-1}; [Al]:[Zr] = 10:1.

The influence of Al/Zr mole ratio on these reaction equilibria is reported at two different temperatures in Table 4 and in Figure 5. It is observable that both monomeric and dimeric ion pairs increase along with Al/Zr mole ratio; however, it is worth observing that, at both temperatures, the monomeric ion pair **8** increases more than the dimeric one **7**. The intensity of the methyl signal relative to the Cp signal decreases further, because the methyl exchange increases along with the Al/Zr ratio (Figure 5B). Moreover, at 25 °C,

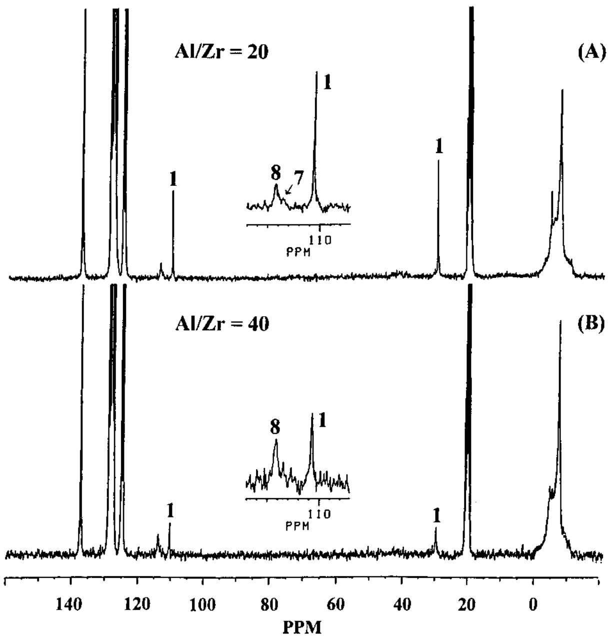


Figure 5. ^{13}C NMR spectra in toluene-d_8 of $Cp_2Zr(^{13}CH_3)_2$ and MAO at 25 °C: [Al]:[Zr] = 20:1 (A); [Al]:[Zr] = 40:1 (B). [Zr] = 0.01 mol·L^{-1}.

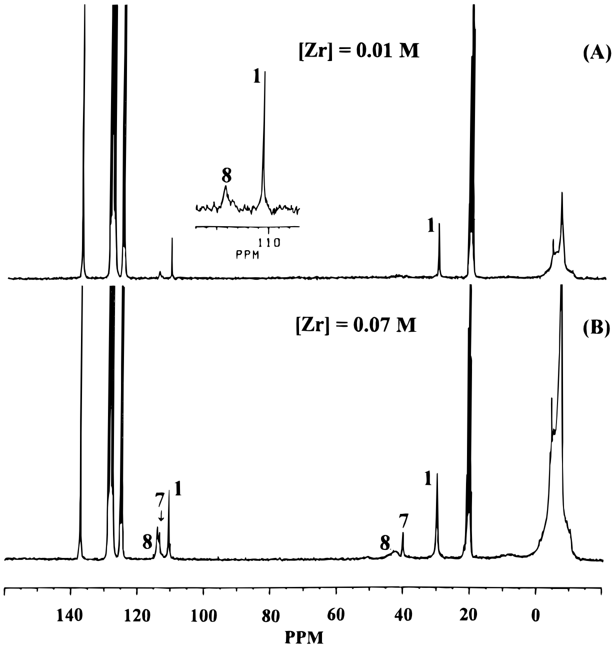


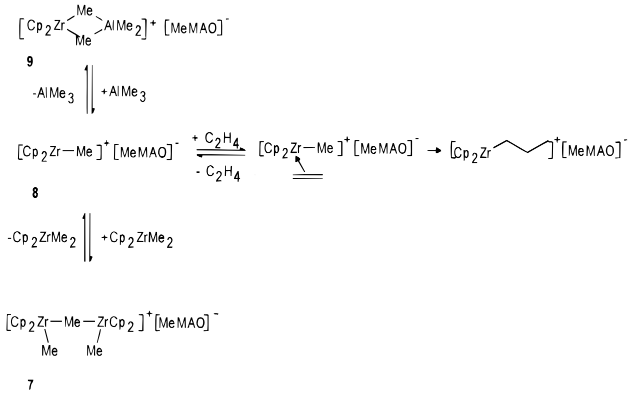
Figure 6. ^{13}C NMR spectra in toluene-d_8 of $Cp_2Zr(^{13}CH_3)_2$ and MAO at −20 °C: [Zr] = 0.01 mol·L^{-1} (A); [Zr] = 0.07 mol·L^{-1} (B). [Al]:[Zr] = 20:1.

the temperature of the spectra shown in Figure 5, ion pair methyl signals are so broad that they are hardly detectable. For this reason, the expansion of the Cp signals is shown. Metallocene-based catalysts give the maximum catalytic performance when used in very dilute solutions. A comparison at two different zirconium concentrations, 0.01 and 0.07 M, has been made, and the data are reported in Table 5 and in Figure 6. In more dilute solutions, all the reaction products are inhibited, but what seems to be most relevant is that the dimeric species decreases most.

It was not possible to study the catalytic system either to higher dilutions or to higher Al/Zr mole ratios with this method. Indeed, at higher dilutions, the reactivity decreases and ion pairs are not detectable, while, at higher Al/Zr mole ratios, the ^{13}C enrichment of the dimethylzirconocene is diluted from the exchange reactions with unenriched MAO methyls. Moreover, the quality of the spectra is reduced due to the higher viscosity of more concentrated MAO solutions.

Conclusions

The preceding analyses have provided the first evidence of the formation of monomeric $[Cp_2ZrMe]^+$, dimeric $[Cp_2Zr(^{13}CH_3)]_2{}^+$, and small amounts of the $[(Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ cationic species with MeMAO$^-$ counterions. Under these experimental conditions, that is, relatively high concentrations and low temperatures, these ion pairs should be loosely associated.[13] Methyl-bridged binuclear complexes such as $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[MeB(C_6F_5)_3]^-$ and $[(Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[MeB(C_6F_5)_3]^-$ were first observed by Bochmann by adding Cp_2ZrMe_2 or $AlMe_3$ to Cp_2ZrMe^+ obtained from Cp_2ZrMe_2 and $B(C_6F_5)_3$. They have been proposed as possible dormant states for the active sites for olefin polymerization, and thus as possibly responsible for catalyst deactivations according to the following scheme:



However, in some cases, dimeric ion pairs have also been hypothesized to be active for ethylene polymerization.[8c,17] The NMR data reported above, although obtained in conditions quite far from the usual polymerization conditions, seem to be in keeping with the scheme shown. Indeed, the monomeric ion pair produced increases with increasing temperature, Al/Zr ratio, and dilution, such as the observed trend in polymerization activity due to the variation in Al/Zr ratio, [Zr] concentration, and temperature. As to the dimeric complex, it decreases with increasing temperature, Al/Zr mole ratio, and dilution; therefore, it should not be present in significant amounts under usual polymerization conditions. In order to get a direct insight into the role of these species in the polymerization activity, we will report on an NMR study of the *in situ* polymerization of $^{13}C_2H_4$ made in the presence of different concentrations of dimeric and monomeric cation species having both $[MeB(C_6F_5)_3]^-$ and $[MeMAO]^-$ counterions.

Experimental Section

All manipulations were made using standard high-vacuum or Shlenk techniques. 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 a nitrogen filled MBraun glovebox. Toluene and diethylether were distilled under nitrogen from sodium benzophenone ketyl. 30% solutions of MAO in toluene (Witco) were used after removing all volatiles and drying the resulting powder in vacuum (12 h, room temperature, 0.1 mm Hg). $Cp_2Zr(^{13}CH_3)_2$ and $B(C_6F_5)_3$ were prepared according to literature procedures.[18−19]

Catalyst 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 the residual ^{1}H NMR signal (2.08 ppm) and to the ^{13}C NMR signal (20.52 ppm) of the deuterated methyl of toluene-d_8, respectively. NMR probe temperatures were measured by 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. Dwell time of 105 μs was used with 16 K 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 °C, the pulse repetition time was 10,46 s. Dwell time of 28 μs was used with 16 K of computer memory for the interferogram.

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 aluminum alkyl, $B(C_6F_5)_3$ or methylaluminoxane as toluene-d_8 solution was added via a gastight microsyringe and the septum wrapped with parafilm. The tube was shaken briefly and transferred to the precooled NMR probe and spectra were acquired.

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