Titanocene−Methylaluminoxane Catalysts for Olefin Polymerization: A ^{13}C NMR Study of the Reaction Equilibria and Polymerization

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ABSTRACT: The olefin polymerization catalyst based on $Cp_2Ti^{13}CH_3Cl$/MAO has been studied. Reaction equilibria and polymerization of ^{13}C-enriched ethylene were followed by ^{13}C NMR spectroscopy, and the catalytic activity was determined. Evidence has been obtained that MAO alkylates the transition metal and produces stable cationlike species $Cp_2TiMe^+Cl{\cdot}[Al(Me)O]_n^-$ (**3**). Complex **3** has been shown to be active for olefin polymerization. Two types of ion pairs have been detected for the low Al/Mt ratios. We assume that they are more or less tight ion pairs. It has also been possible to relate polymerization activity to the composition of the catalyst mixture. Temperature (−78 ÷ −20 °C), Al/Mt mole ratios (10 ÷ 40), and catalyst dilution have been shown to influence the concentration of active species such as **3** and thus to affect polymerization activity. Dilution decreases the formation of nonactive species such as $Cp_2Ti(Me)-OAl(Me)-MAO$ (**4**).

Introduction

Homogeneous catalytic systems for olefin polymerization based on group 4 metallocene complexes and aluminum alkyls (e.g., Cp_2MtX_2/AlR_nX_{3-n}, Cp = C_5H_5; Mt = Ti, Zr, Hf; X = Cl) have already been studied in the early 1960s. The interest in them was due to the fact that the homogeneity of these systems allowed mechanistic studies, which were not possible with the industrially used heterogeneous systems. The discovery in the late 1970s that methylaluminoxane $[-Al(Me)O-]_n$ (MAO) as cocatalyst in group 4 metallocene-based systems gives extremely high rates of ethylene polymerization[1] generated the development of new metallocene/alkylaluminoxane catalytic systems which make the synthesis of entirely new families of homo- and copolymers available.[2] Due to the presence of multiple equilibria in solution, the characterization of MAO is very difficult.[3] Recently, *tert*-butylaluminoxanes $[-Al(t\text{-}But)O-]_n$ with defined structures have been prepared and characterized.[4] They can be models for methylaluminoxanes. The primary function of MAO was hypothesized to be the alkylation of the transition metal and the production of cationlike d_0 14-electron alkyl complexes of the type Cp_2MtR^+ as catalytically active species. Growing indirect evidence that MAO generates metallocene cations (Cp_2MtR^+) in these systems has been furnished by works of model intermediate trapping[5] and model synthesis.[6] A few direct spectroscopic studies of Cp_2MtX_2/MAO systems are reported in the literature: (a) an X-ray photoelectron spectroscopic study,[7] which provides indications of the electronic environment at the metal; (b) an IR spectroscopic study of the interactions between MAO and Cp_2ZrCl_2;[8] (c) some ^{1}H NMR studies of Cp_2ZrCl_2/MAO.[9,10]

We have undertaken a study by ^{1}H and ^{13}C NMR analysis of the reactions of MAO with group 4 metallocenes, with the aim of getting direct information on the MAO function. We have already reported[11] on the influence of different temperatures and Al/Ti mole ratios on the products of the reactions of $Cp_2TiMeCl$ (**1**) with MAO and/or $AlMe_3$. We have furnished evidence that MAO alkylates the transition metal and produces cationlike species. In addition, we have also found that the free $AlMe_3$, if existent in MAO solutions, is not the actual cocatalyst in metallocene/MAO-based catalytic systems. With this paper we intend to supplement our previous studies by elucidating the role of the complexes observed in the catalytic activity and the influence of catalyst concentration and solvent polarity on the type of ion pairs and reaction products. The following experimental approaches have been employed: (i) an investigation by NMR of the chemistry of the equilibria of MAO with $Cp_2Ti^{13}CH_3Cl$, having 90% ^{13}C-enriched methyl ligands; (ii) a study by ^{13}C NMR of the 90% ^{13}C-enriched ethylene polymerization *in situ* in the presence of the same catalytic system; (iii) the determination of the catalytic activity of this catalyst in conditions as close as possible to those of the NMR analysis.

Results and Discussion

Influence of Temperature. We have already reported on a study of $Cp_2Ti^{13}CH_3Cl$/MAO solutions (Al/Ti mole ratio = 10) at variable temperature.[11] At −78 °C the main product is the alkylation product $Cp_2Ti(CH_3)_2$ (**2**) (86% yield) and the metallocene cationlike species $Cp_2TiMe^{\delta+}Cl{\cdot}MAO^{\delta-}$ (**3**) results in only 8% yield. In Table 1 the spectral parameters of titanocene compounds and their reaction products with MAO are reported. When the temperature was raised to −20 °C, the cationlike species increased up to 56% yield, while at higher temperatures the formation of alkylidene complexes was observed. Because of this, the following study has been made at temperatures up to −20 °C.

$$\underset{\mathbf{1}}{2Cp_2TiCH_3Cl} + 2MAO \rightarrow \underset{\mathbf{2}}{Cp_2Ti(CH_3)_2} + \underset{\mathbf{3}}{Cp_2TiCH_3^{\ +}Cl{\cdot}MAO^-} \quad (1)$$

In principle, either a partial ($Cp_2TiMe^{\delta+}Cl{\cdot}MAO^{\delta-}$) or a complete positive charge ($Cp_2TiMe^+Cl{\cdot}MAO^-$) could be generated on titanium; from a comparison of our data with those obtained through ^{27}Al NMR spectroscopy by Eisch for the $Cp_2TiCl_2/AlCl_3$ model system,[12] we can say that the downfield shift of Cp and Me signals of **3** arises

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Table 1. ^{13}C NMR Spectral Parameters for Titanocene Compounds and Titanocene–Aluminum Complexes[a]

titanocene		^{13}C, ppm Cp	^{13}C, ppm Me	solvent CD_2Cl_2 % (v/v)
Cp_2TiCH_3Cl	**1**	115.52	49.32	0
$Cp_2Ti(CH_3)_2$	**2**	113.16	46.25	0
$Cp_2Ti(CH_3)_2$	**2**	113.20	46.01	20
$Cp_2TiCH_3Cl{\cdot}MAO$	**3**	117.94	64.81	0
$Cp_2TiCH_3Cl{\cdot}MAO$	**3′**	118.0	64.68	0
$Cp_2TiCH_3Cl{\cdot}MAO$	**3**	118.05	64.63	20
$Cp_2TiCH_3Cl{\cdot}MAO$	**3**	118.12	64.41	60
$Cp_2Ti(Me)-OAl(Me){\cdot}MAO$	**4**	118.34	46.68	0

[a] Recorded at −20 °C in toluene-d_8 on a Bruker 270 spectrometer (67.89 MHz). Chemical shifts are referenced to the methyl signals of toluene-d_8: 20.52 ppm ^{13}C NMR.

Table 2. Ethylene Polymerization Activities of $Cp_2TiMeCl/MAO$ Systems[a]

run	CH_2Cl_2 %	Al/Ti	T/°C	activity/[g of PE/(g of Ti·h)]
1	0	10	−78	trace
2	0	10	−33	545
3	0	10	−20	1920
4	0	10	−20	400[b]
5	0	20	−20	3970
6	0	30	−20	5270
7	0	40	−20	8170
8	0	20	−20	3970
9	10	20	−20	4240
10	40	20	−20	4300
11	60	20	−20	4530

[a] Polymerization conditions: [Ti] = 5.0 × 10^{-4} mol/L; solvent = toluene, 80 mL; ethylene pressure = 1 atm; t = 30 min. [b] [Ti] = 5.0 × 10^{-3} mol/L.

from the fact that a complete positive charge ($Cp_2TiMe^+Cl^•MAO^-$) is generated. The $J_{C\alpha-H}$ value of the cationic complex **3** (129.2 Hz, at −20 °C) is the expected one for three hydrogens not involved in α-agostic interactions, although β-agostic interactions have been observed for $Cp'_2Zr(CH_2CH_2R)(L)^+$ complexes,[6a] which may be models for metallocene-based Ziegler–Natta olefin polymerization systems, and evidence for the existence of α-agostic interactions in the transition state of α-olefin polymerization with metallocene catalysts has been provided.[6a]

We have also observed that the polymerization activity rises from trace amounts to 1920 g of PE/(g·T·h) from −78 to −20 °C (Table 2).

To probe the polymerization activity of the cationlike species **3**, we have added a known amount of enriched ethylene to the NMR tube containing the catalyst solution frozen at −78 °C with a method similar to the one Fink first used in his elegant studies.[14] Ethylene has been dosed through a gas-tight syringe, equipped with a long needle (20 cm), and then the ^{13}C NMR spectrum at −20 °C has been recorded. It is worth saying that due to the high polymerization activity of these catalytic systems even at low temperature and Al/Ti mole ratio = 10, it is not possible to make ethylene addition through a gas buret connected to a high vacuum line. Our attempts resulted in very fast polymerizations on the walls of the NMR tube or on the solution surface.

In Figure 1 the spectra of the catalytic system (Al/Ti = 20; [Ti] = 0.026 mol·L^{-1}) before (Figure 1A) and after ethylene addition (Figure 1B) are reported. It is possible to observe the features at 30.51 ppm assignable to the $(CH_2)_n$ resonances of the polyethylene chains. The resonances at 14.61 (a), at 23.13, (b) and 32.57 ppm (c) assignable to the methyl and methylene carbons of chain end groups are visible as well.

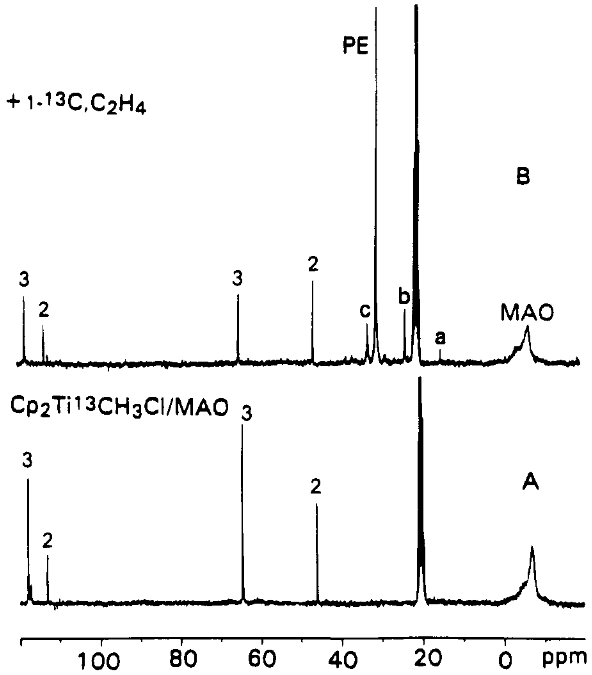

Figure 1. ^{13}C NMR spectra in toluene-d_8 at −20 °C of the systems $Cp_2Ti^{13}CH_3Cl$ (90% ^{13}C-enriched)/MAO (A) and $Cp_2Ti^{13}CH_3Cl/MAO/1\text{-}^{13}C_2H_4$ (90% ^{13}C-enriched) (B). [Ti] = 0.026 mol·L^{-1}, [Al]:[Ti] = 10:1 mol/mol, $[C_2H_4]$:[Ti] = 10:1 mol/mol. PE = polyethylene.

$$\underset{\mathbf{3}}{Cp_2TiCH_3^+Cl^•MAO^-} + nC_2H_4 \rightarrow Cp_2Ti(CH_2CH_2)_{n-1}\underset{c}{CH_2}\underset{b}{CH_2}\underset{a}{CH_3}{}^+Cl^•MAO^- \quad (2)$$

It is worth observing that the intensity of the methyl resonance of the chain end group is lower than those of b and c methylene resonances of the same chain end group due to the fact that the methyl comes from the titanocene methyl ligand whose initial enrichment has been scrambled with unenriched MAO methyls, while b and c methylene come from the constantly enriched ethylene.[15] However, what is most important is that while the polyethylene features have grown, those of cationic species **3** have diminished. These findings are direct evidence that **3** is the species active for olefin polymerization. This evidence which parallels that obtained by Marks for the solid $Cp_2Zr(^{13}CH_3)_2/MAO$ system[16] is the first, to our knowledge, obtained for the soluble catalytic system which shows that these cationlike species are active for olefin polymerization.

In addition, since the increase in polymerization activity observed when the temperature is raised to −20 °C parallels the increase in active species, we can conclude that the higher polymerization activity observed at higher temperatures, within the range of temperatures we have studied, is due to an increase of the number of active sites as well as to the normal increase of the propagation rate.[17]

Influence of the Al/Ti Ratio. It is well-known that one of the requirements for obtaining the exceptionally high polymerization activity typical of metallocene/MAO-based catalytic systems is the use of a high Al/Mt mole ratio. MAO is usually used at Al/Mt mole ratios of 10^3–10^4.[1,2] In our previous study we have already shown that by increasing the Al/Ti mole ratio species **3**, which is the active species, increases.[11] In

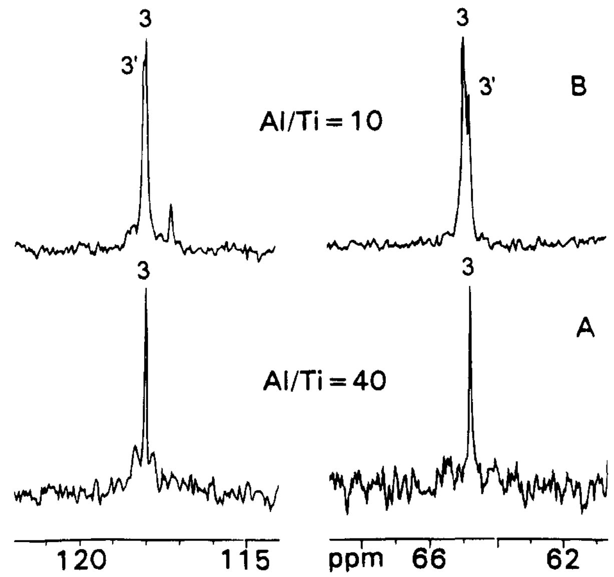

Figure 2. ^{13}C NMR spectra in toluene-d$_8$ at −20 °C of Cp$_2$Ti^{13}CH$_3$Cl and MAO: [Ti] = 0.01 mol·L^{-1}, [Al]:[Ti] = 40:1 mol/mol (A); [Ti] = 0.07 mol·L^{-1}, [Al]:[Ti] = 10:1 mol/mol (B).

Figure 2 the expansion of the Cp and Me regions of the spectra of Cp$_2$Ti^{13}CH$_3$Cl/MAO solutions at two Al/Ti mole ratios is shown. It is possible to see that at a mole ratio Al/Ti = 10 (Figure 2B) we have in fact two slightly different species **3** (117.94 ppm (Cp), 64.8 ppm (Me)) and **3′** (118.0 ppm (Cp) and 64.68 ppm (Me)). When increasing the Al/Ti ratio, we do not see the methyl at higher field and the Cp at lower field. Since the presence of a positive charge produces downfield shifts of the methyl resonances in toluene-*d*$_8$ (compare **1** and **3** in Table 1), we tentatively interpret these data as the existence of two different types of ion pairs **3** and **3′** and that **3′**, which has the methyl at higher field and is visible at a lower Al/Ti mole ratio, is a little tighter than **3**.

$$\underset{\mathbf{3'}}{Cp_2TiCH_3^{+}\cdots Cl^{\cdot}MAO^{-}} \quad \underset{\mathbf{3}}{Cp_2TiCH_3^{+}\cdots\cdot Cl^{\cdot}MAO^{-}}$$

Therefore, we can conclude that the increase of species **3** explains the increase of polymerization activity observed when raising the Al/Ti ratios (polymerization runs 3, 5, 6, and 7 in Table 2).

Influence of Titanium Concentration. The metallocene concentration is a variable which like the Al/Mt mole ratio has clearly been shown to have a remarkable influence on polymerization activity. At high Al/Mt mole ratios the more the catalytic system is diluted, the higher is the catalytic activity obtainable (e.g., compare polymerization runs 3 and 4 in Table 2). In order to study the influence of dilution with our method, we have studied our system at various metallocene concentrations. Eisch in his variable-temperature ^{1}H and ^{13}C NMR study of Cp$_2$TiCl$_2$/AlCl$_3$ in CD$_2$Cl$_2$ solutions has evidenced the presence of contact and solvent solvated ion pairs in different amounts depending on the catalyst concentration.[12]

In Figure 3 the spectra obtained at two different titanium concentrations ([Ti] = 0.07 M in Figure 3B and [Ti] = 0.01 M in Figure 3A) of Cp$_2$Ti^{13}CH$_3$Cl/MAO (Al/Ti mole ratios = 20) in toluene-*d*$_8$ solutions are compared. A small amount of species **4** (in the expansion of Figure 3B) having Cp and Me signals at 118.34 and 46.68 ppm, respectively, at [Ti] = 0.01 M is clearly observable. At [Ti] = 0.07 M the ratio of the species observed changes to favor **4**. We have previously observed that these features also appear as the Al/Ti ratio increases and increase in the presence of a polar solvent such as CD$_2$Cl$_2$.[11a] Because of this, we have tentatively assigned **4** as a solvent-separated ion pair. However, the new finding that species **4** increases with the concentration allows us to exclude that **4** has features characteristic of either SSIP (solvent-separated ion pair) or SCAP (solvated-cation ion pair).[13] They should both increase along with dilution. A comparison of the chemical shifts of this species with those obtained by Marks for some zirconocene-supported systems[16] allows us to assign **4** as Cp$_2$Ti(Me)−OAl(Me)−MAO.

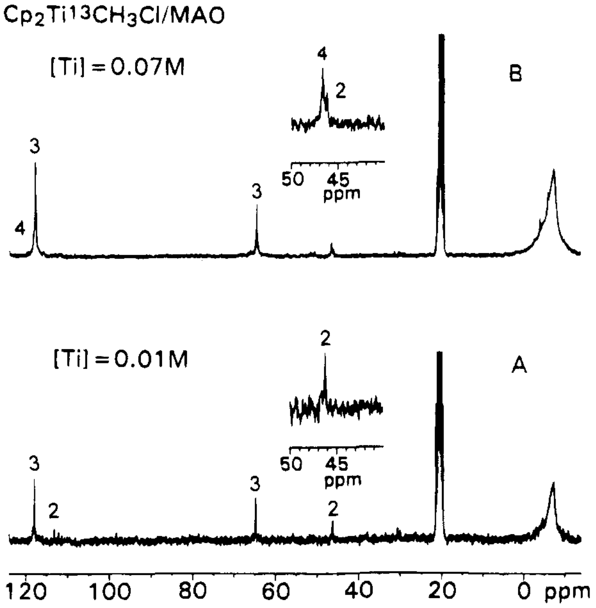

Figure 3. ^{13}C NMR spectra in toluene-*d*$_8$ at −20 °C of Cp$_2$Ti^{13}CH$_3$Cl and MAO: [Ti] = 0.01 mol·L^{-1} (A); [Al]:[Ti] = 20:1, [Ti] = 0.07 mol·L^{-1} (B).

$$\underset{\mathbf{1}}{Cp_2TiMeCl} + Me_2Al\text{-}O[\text{-}Al(Me)O\text{-}]_nAlMe_2 \xrightleftharpoons{-AlMe_2Cl} \underset{\mathbf{4}}{Cp_2TiMeO[\text{-}Al(Me)O\text{-}]_nAlMe_2} \quad (3)$$

Moreover, from the study of ^{13}C-enriched ethylene polymerization *in situ* we have found that species **4** does not seem to be active for olefin polymerization (Figure 4). Indeed, the appearance of polyethylene peak PE (Figure 4B) is accompanied by a decrease of the ratio between the intensity of signals of species **3** and **4**. This apparent inactivity is in keeping with the structure assigned to **4**, which does not have any easily accessible coordination sites. However, it is conceivable that, since the species we observe are in dynamic equilibria with each other, the Ti-O bond can be broken and **4** can be transformed into an active species. In conclusion, it is likely that at the high Al/Ti mole ratios normally used dilution becomes very important and that the higher activity observed when dilution increases is due to the fact that dilution impedes the formation of nonactive species, such as **4**, which may be formed at higher concentrations when the Al/Ti mole ratio increases.

Influence of Solvent. Olefin polymerizations with metallocene/MAO catalytic systems are usually carried out in toluene or hydrocarbon solutions, however, solvent polarity has been shown to affect the catalytic performance. In addition, in the case of a syndiospecific

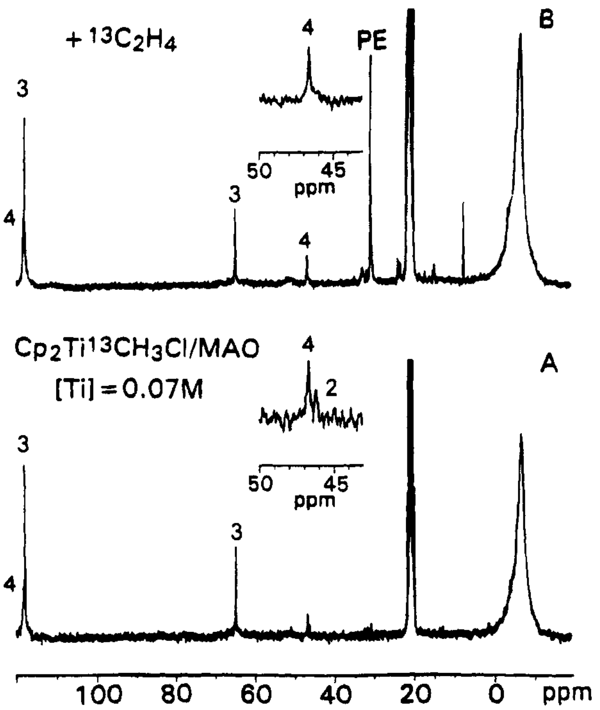

Figure 4. ^{13}C NMR spectra in toluene-d_8 at −20 °C of the systems $Cp_2Ti^{13}CH_3Cl$/MAO (A) and $Cp_2Ti^{13}CH_3Cl$/MAO/^{13}C 90% C_2H_4 (B). [Ti] = 0.07 mol·L^{-1}, [Al]:[Ti] = 40:1, [C_2H_4]:[Ti] = 4:1.

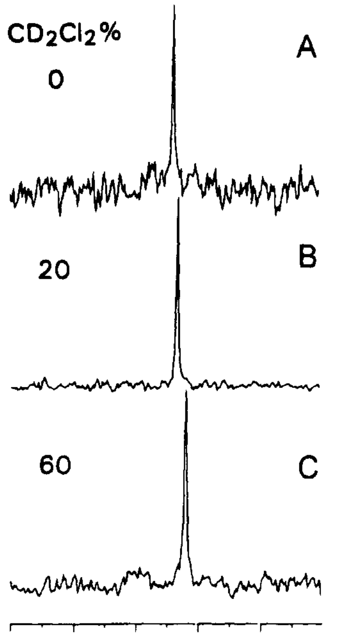

Figure 5. ^{13}C NMR spectra in toluene-d_8 at −20 °C of $Cp_2Ti^{13}CH_3Cl$ and MAO in the presence of 0 (A), 20 (B), and 60% (C) of CH_2Cl_2 (v/v). [Ti] = 0.07.

catalytic system, the solvent polarity has been shown to affect the stereospecifity of the polypropylene product also.[20] We have attempted to obtain more information on the kind of ion pairs produced in metallocene/MAO systems by monitoring the ^{13}C NMR spectra of the reactions of $Cp_2Ti^{13}CH_3Cl$ and MAO in solution of toluene-d_8 containing 0, 20, and 60% of CD_2Cl_2 (v/v). Figure 5 shows the $Ti-CH_3^+$ region of the spectra. Apart from the slight increase of **4** already reported,[11a] it is evident from the inspection of this region of the spectrum that apparently there are no big changes, but only a gradual variation of chemical shifts either of Cp and Me resonances (Table 1). Slight shifts of Cp and Me signals in the same directions have also been observed for Cp_2TiMe_2 in the presence of CD_2Cl_2 (Table 1). Two different $Cp_2Ti^+Cl/AlCl_4^-$ species have been detected by "freezing out" the $Cp_2TiCl_2/AlCl_3$ system at −20 °C;[12] the species with high-field signals has been shown to be favored by CD_2Cl_2, and thus it has been assigned as the less tight ion pair. However, since we do not observe the simultaneous presence of different features, the changes we have observed could be due only to the change of solvent and not to less tight ion pairs. The polymerization runs 8−11 (Table 2) have been carried out in the presence of 0, 10, 40, and 60% of CH_2Cl_2 (v/v), respectively. A moderate increase of polymerization activity is observed when the amount of the polar solvent is increased. This might be in keeping with the slight changes in NMR spectra. Greater increases in polymerization activities at higher temperatures and in the presence of different catalytic systems are reported.[20] It is likely that at higher temperatures the action of loosening ion pairs by a polar solvent such as CD_2Cl_2 is more effective. However, as already mentioned, we have limited this study to low temperatures because at higher temperatures the formation of interfering new species has been observed.

Conclusions

In conclusion, the method that we have used, that is, the combination of ^{13}C NMR analysis of equilibria involved in the $Cp_2Ti^{13}CH_3Cl$/MAO catalytic system, the ^{13}C NMR study of polymerization *in situ* of ^{13}C-enriched ethylene, and the determination of the polymerization catalytic activity, has allowed us to obtain direct evidence (i) of the MAO ability to alkylate the transition metal and to produce and stabilize cationlike species **3** ($Cp_2TiMe^+Cl{\cdot}[AlMeO]_n^-$ and (ii) that species **3** is active for olefin polymerization. It has also been possible to relate the polymerization activity and the reaction products observed. The increase in activity obtained when the temperature (up to −20 °C) and Al/Ti mole ratios (from 10 to 40) are increased is due to the increase of active species such as **3**. The increase in activity observed when increasing the dilution may be ascribed to the fact that dilution impedes the formation of nonactive species such as **4**. The NMR data in toluene/dichloromethane solvent mixtures do not give clear-cut evidence of the effect of solvent polarity, while the polymerization activity obtained by us and others suggests that the polarity of a solvent such as dichloromethane has the effect of loosening the active ion pairs.

Experimental Part

All operations and manipulations were carried out under a dry nitrogen atmosphere by using glovebox or Schlenk line techniques. MAO (30 wt % as toluene solution, Witco) was used after removing all volatiles and drying the resulting powder in vacuum (12 h, room temperature, 0.1 mmHg). Toluene-d_8 was dried and vacuum transferred from a solution of sodium diphenylketyl. $Cp_2Ti^{13}CH_3Cl$[21] and $Al(^{13}CH_3)_3$ (90% ^{13}C-enriched)[22] were prepared according to the literature.

NMR Analysis. ^1H and ^{13}C NMR were recorded on a Bruker 270 spectrometer (270-MHz ^1H, 67.89-MHz ^{13}C). Probe temperatures were calculated by measuring $\Delta\nu$ (MeOH). Chemical shifts are reported in δ and referenced to the methyl signals of toluene-d_8: 2.08 ppm ^1H NMR, 20.52 ppm ^{13}C NMR. A typical sample was prepared in a glovebox by loading the titanocene complex (ca. 0.5 mmol in 0.5 mL of toluene-d_8) into a 5-mm NMR tube. The tube was capped with a septum rubber cap. The solution was cooled at a given temperature, and a known amount of aluminum alkyl or methylaluminoxane as a toluene-d_8 solution was added via a gas-tight microsyringe.

***In Situ* Polymerization.** A known amount of ^{13}C-enriched ethylene was added to the NMR tube, which was precooled at −78 °C, via a gas-tight syringe equipped with a 20-cm needle.

Polymerizations. Ethylene polymerizations were performed in a 150-mL round-bottomed Schlenk flask, which was charged with titanocene and 80 mL of toluene. A known amount of $AlMe_3$ or MAO as a toluene solution was syringed into the solution through a gas-tight syringe. The catalyst components were left to react for 5 min at the polymerization temperature, and then after evacuation of the system ethylene was introduced at atmospheric pressure. Polymerizations were quenched by adding C_2H_5OH. Polymers were precipitated in $C_2H_5OH{\cdot}HCl$, washed with C_2H_5OH, and dried in vacuo. Polymerization activities reported in Table 2 represent the result of the average values of at least three polymerization runs.

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(15) The measured ratio between the integrals of "a" methyl and "b" or "c" methylene resonances is $^1/_3$, which is the one expected. Indeed, the ^{13}C enrichment of the methyl, which derives from **1** after scrambling with MAO methyls, measured from the ratio between the integrals of Me and Cp resonances of **3** in Figure 1A, is about 15%. The $1\text{-}^{13}C,C_2H_4$ used in this experiment is 90% enriched and thus the average enrichment of each methylene of the polyethylene formed is 45%.

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(17) Low E_a should be expected for the cationlike species **3**. Recently calculations on ethylene insertion into $CH_3TiCl_3^+$ have shown that the formation of a positive charge on the metal leads to a decrease in the activation energy from 11−14 to 4 kcal/mol.[18] Assuming a constant number of active sites and E_a of about 4 kcal/mol, the increase in productivity due to an increase of temperature of 13 °C is 2.9 times. In this temperature range we observe a productivity increase of 3.5 times. However, it is worth considering that we cannot expect quantitative comparisons between NMR tube and batch experiments. Polymerization runs with these systems are usually made at Al/Mt ratios = 10^3-10^4. At the Al/Ti ratio used (10−20) possible solvent impurities (80 and 0.7 mL respectively in the batch and NMR tube polymerization) can have a strong influence.

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(19) Mt-Me: δ 41.3 ($Cp_2ZrCH_3^+CH_3[Al(Me)O]_n^-$ in $Cp_2Zr(CH_3)_2$/MAO solid system); 36.0 (Cp_2ZrCH_3OAl- in $Cp_2Zr(CH_3)_2$ supported on dehydroxylated alumina); 31.4 ($Cp_2Zr(CH_3)_2$).[6b]

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