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^1H and ^{13}C NMR Spectroscopic Study of Titanium Metallocene–Aluminoxane Catalysts for Olefin Polymerizations[†]

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ABSTRACT: In order to study the formation and the nature of Ti/Al adducts that play a role in the olefin polymerization activity of the group 4 metallocene–methylaluminoxane catalytic systems, the reactions of $AlMe_3$ and/or methylaluminoxane with $Cp_2TiMeCl$ and Cp_2TiMe_2 have been monitored by ^1H and ^{13}C NMR spectroscopy. Temperatures between 203 and 283 K and Al/Ti ratios from 1 to 40 have been used. The change in ^{13}C NMR signals has been found the most diagnostic. Several adducts have been observed and identified. The kind of adducts changes both with the reaction temperature and the Al/Ti ratio. By comparing the MAO and $AlMe_3$ reactions with $Cp_2TiMeCl$ it is possible to deduce that, with respect to $AlMe_3$, MAO is a better alkylating agent and it has a greater capacity for producing and stabilizing cation-like complexes. At the Al/Ti ratio of 40 a complex that we tentatively assign as a solvent separated ion pair prevails. The fact that, after the addition of CH_2Cl_2 to the toluene solution, this complex is present in greater amounts is consistent with this assignment.

Introduction

Metallocene complexes such as Cp_2MtCl_2 (Mt = Ti, Zr, Hf) in the presence of aluminum alkyl reagents constitute a class of homogeneous catalysts for Ziegler–Natta olefin polymerization.[1] Since their discovery they have been studied mainly because, with respect to the heterogeneous industrially used catalysts, they are more amenable to mechanistic studies.[2] The discovery that the substitution of aluminum alkyls with methylaluminoxane (MAO)[3] produces extremely high catalytic activity has stimulated a great new interest in this field. New metallocene complexes,[4] which make the synthesis of homopolymers with novel microstructures[5] and new homopolymers[6] with narrow molecular weight distribution possible, have been developed. However, despite its peculiar characteristics and importance, the role of MAO, an oligomeric species $[-Al(Me)O-]_n$ obtained by partial hydrolysis of $AlMe_3$,[7] is still little understood. Various lines of evidence based on early conductivity and electrodialysis investigations[8] and on more recent theoretical[9] and spectroscopic[10] studies, intermediate trapping[11] and model synthesis[12] suggest that cation group 4 metal alkyl complexes of the type Cp_2MtR^+ are the catalytically active species and that the primary role of MAO is to produce this cation-like active center:

$$Cp_2MtR_2 + [-Al(Me)O-]_n = Cp_2MtR^+[R[-Al(Me)O-]_n]^- \quad (1)$$

As to the role of MAO an alternative hypothesis has been advanced which is based on the similarity of the microstructures of the polymers produced using MAO and $AlMe_3$ as cocatalysts.[13] $AlMe_3$, which to some extent always remains bound to MAO even after removal of all volatiles under vacuum, has been proposed to give the following equilibrium (2) in solution:

$$[-Al(Me)O-]_n \cdot xAlMe_3 = [-Al(Me)O]_n \cdot (x-y)AlMe_3 + (y/2)Al_2Me_6 \quad (2)$$

According to this hypothesis the "free" $AlMe_3$, and not $MAO \cdot xAlMe_3$, might be the actual cocatalyst in metallocene–MAO based systems.

With the aim of getting direct information on the reactions of MAO with group 4 metallocenes we have undertaken an investigation by NMR of the basic interactions of titanocene complexes in homogeneous solutions. We have studied by ^1H and ^{13}C NMR spectroscopy at different temperatures and different Al/Ti ratios the following titanocene complexes and aluminum compounds:

[†] In memory of Prof. Piero Pino.

[•] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

Table I. ^{13}C NMR Data for Reactions between Titanocene Compounds and $AlMe_3$[a]

titanocene reagent	T, K	ratio Al/Ti	^{13}C signals (δ, ppm) Cp	Me	titanocene product	mol %[b]
Cp_2TiCH_3Cl	253		115.52	49.32	1	100
$Cp_2Ti(CH_3)_2$	253		113.16	46.25	2	100
Cp_2TiCH_3Cl	253	1	113.19	46.21	2	11
			117.08	60.22	3	89
Cp_2TiCH_3Cl	253	2	113.19	46.21	2	15
			117.07	60.14	3	85
Cp_2TiCH_3Cl	253	15	113.08	46.16	2	19
			116.98	60.41	3	81
Cp_2TiCH_3Cl	203	10	113.03	46.30	2	2
			116.84	60.56	3	98
$Cp_2Ti(CH_3)_2$	253	1	113.16	46.25	2	100
$Cp_2Ti(CH_3)_2$	253	2	113.15	46.23	2	100
$Cp_2Ti(CH_3)_2$	253	15	113.06	46.17	2	100

[a] ^{13}C NMR have been recorded at 67.89 MHz in toluene-d_8. Chemical shifts are referenced to the toluene CD_3 signal at 20.52 ppm. [b] Molar fractions of titanocene compounds calculated by the integrated peak areas of the Me signals.

$$Cp_2TiCH_3Cl, Cp_2Ti(CH_3)_2, Cp_2Ti^{13}CH_3Cl, Al(CH_3)_3, [Al\text{-}(CH_3)O]_n$$

The change of electron density at the metal center upon treatment of the titanocene complexes with the aluminum compounds will cause a shift in NMR signals, providing information on the reaction products and on the nature of the active sites in these polymerization systems.

Results

Reactions of the Titanocene Compounds with $AlMe_3$. In order to have a better understanding of the role of MAO in yielding high polymerization activities when combined with group 4 metallocenes, we have begun an investigation by ^1H and ^{13}C NMR of toluene-d_8 solutions of these catalysts. All the reactions have been first monitored by ^1H NMR spectroscopy, which requires shorter accumulation times with respect to ^{13}C NMR. We will report mainly on ^{13}C NMR spectroscopic studies because the wide ^{13}C chemical shift range has made it possible to distinguish among species which have very similar chemical shifts in the proton spectrum. Initially, to clarify the actual role of the "free" $AlMe_3$ in MAO solutions in the catalytic activity of metallocene–MAO based systems and to easily assign the spectra at the same time, we have studied by ^{13}C NMR spectroscopy the reactions of $Cp_2TiMeCl$ (1) and $AlMe_3$ in toluene-d_8 at 253 K (Table I, Figure 1). One equivalent of $AlMe_3$ reacts rapidly with $Cp_2TiMeCl$. Indeed, the Ti–Cp (115.52 ppm) and Ti–Me (49.32 ppm) signals of the starting metallocene have completely disappeared (Table I). Two new Cp and Me signals appear, indicating the presence of two different species. Cp_2TiMe_2 (2) (113.16 ppm (Ti–Cp), 46.25 ppm (Ti–CH_3)) is easily assigned by comparison with the spectrum of the independently synthesized compound. As to the second species one can observe that this has downfield Ti–Cp (117.08 ppm) and Ti–CH_3 (60.22 ppm) displacements similar to those observed by Fink in the $Cp_2TiMeCl/AlMeCl_2$ system;[14] therefore these signals are assigned to the complex $Cp_2TiMeCl{\cdot}AlMe_3$ (3). Interestingly, in all the spectra the prevailing product is 3. Further addition of $AlMe_3$ up to 15 equiv did not result in an appreciable change of the ratio between species 3 and 2. It is worthwhile to note that at 253 K Cp_2TiMe_2 at Al/Ti ratios within the range 1–15 is not complexed by $AlMe_3$ (Table I). This fact confirms that Ti–Cl bonds can be polarized more easily than Ti–Me bonds.

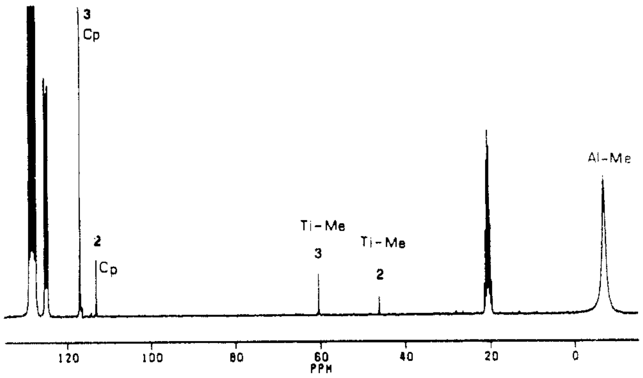


Figure 1. ^{13}C NMR spectrum of $Cp_2TiMeCl$ and $AlMe_3$ in toluene-d_8 recorded at 253 K and at 67.89 MHz. [Ti] = 0.1 mol·L^{-1}, [Al]:[Ti] = 15:1.

Reactions of Titanocene Compounds with MAO. It has been shown that the polymerization activity of group 4 metallocene complexes with MAO as cocatalyst is affected by temperature, the Al/Ti ratio, and catalyst concentration and that great catalytic activity is reached at high Al/Ti ratios and at high catalyst dilutions. In order to understand the role of these parameters in the formation and activity of the catalytic species, we have measured our NMR spectra of $Cp_2TiMeCl$/MAO solutions at different temperatures and at different Al/Ti ratios. To study the reactions of titanocene compounds with MAO at titanium concentrations as dilute as possible, we have used $Cp_2Ti^{13}CH_3Cl$ having 90% ^{13}C enriched methyl ligands. However NMR spectroscopy of MAO solutions is complicated by the fact that, at the $Cp_2Ti^{13}CH_3Cl$ concentration that we need to use in order to have a good signal/noise ratio in the ^{13}C NMR spectra, the MAO solutions become viscous when the Al/Ti ratio approaches 40, especially at temperatures as low as 240 K.

(a) Effect of Temperature. In Figure 2 and Table II the ^{13}C NMR spectra of $Cp_2Ti^{13}CH_3Cl$ and MAO (Al/Ti = 10) at different temperatures are reported. At 203 K (Figure 2A), in addition to the solvent resonances, the splitting of MAO signals, that in the proton NMR spectrum has been attributed by Resconi to the Al_2Me_6 dimer (equilibrium 2), is visible.[13] Even at a temperature as low as 203 K, with MAO at this Al/Ti ratio, $Cp_2TiMeCl$ has reacted to give Cp_2TiMe_2 in an 86% yield. The titanocene alkylation is a typical alkylaluminum reaction; however, at the same temperature and Al/Ti ratio, $AlMe_3$ gives Cp_2TiMe_2 in only a 2% yield (Table I). Therefore the alkylation reaction is faster with MAO than with $AlMe_3$. From the integrals of Cp and Me signals it is possible to observe that the ^{13}C methyl is scrambled with the MAO methyls. At 240 K new Cp and Me resonances at lower field are visible. The species which is in greater quantity has Cp and Me signals at 117.96 and 64.6 ppm, respectively, that is, at even lower field than the previous complex 3. We can assign this species as $Cp_2TiMe^{+\delta}Cl{\cdot}MAO^{-\delta}$ complex 4, the further downfield shift of NMR signals indicating a further decrease of electron density at the metal center. It is worthwhile to note that the same complex is obtained when we add MAO to the $Cp_2TiMeCl{\cdot}AlMe_3$ complex (Al/Ti = 10). At 253 K in Figure 2B the signals increase in

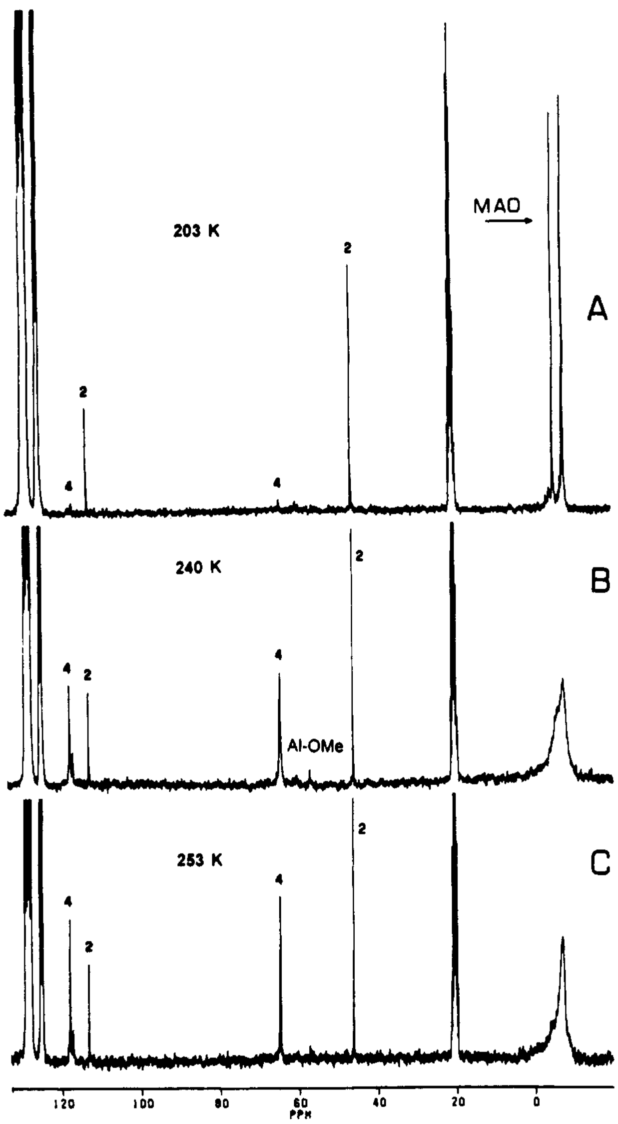
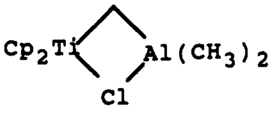


Figure 2. ^{13}C NMR spectra of $Cp_2Ti^{13}CH_3Cl$ (^{13}C 90% enriched) and MAO in toluene-d_8 recorded at 67.89 MHz and at 203 K (Figure 2A), 240 K (Figure 2B), 253 K (Figure 2C). [Ti] = 0.07 mol·L^{-1}, [Al]:[Ti] = 10:1.

intensity for this complex.[15] In Figure 3 the ^{13}C NMR spectra of the $Cp_2Ti^{13}CH_3Cl$/MAO system at Al/Ti = 10 at 253 K (Figure 3A), 273 K (Figure 3B), and 283 K (Figure 3C) are shown. By comparing Figure 3B,C, it is possible to observe that by further increasing the temperature new species have appeared. The signals at 187.89 ppm (μ-CH_2), 112.25 ppm (Cp), and −6.80 ppm ($AlMe_2Cl$) are due to the so-called "Tebbe" reagent **5**.[16] The resonance at



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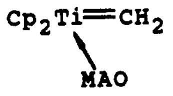

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178.96 ppm is also in the region of a methylidene carbon. Since in the ^1H NMR spectrum of the same solution the features of this last methylidene species consist of two doublets at 7.66–7.63 and 7.33–7.30 ppm (2H), two singlets at 5.49 ppm (5H) and 5.45 ppm (5H), and a singlet at −2.24 ppm (3H), we tentatively assign the given structure to complex **6**.[17] The AX pattern in the proton spectrum of the methylidene protons and the appearance of two Cp signals both in proton and carbon spectra imply an asymmetry of this adduct.

Table II. ^{13}C NMR Data for Reactions between $Cp_2Ti^{13}CH_3Cl$ and MAO at Different Temperatures and at Al/Ti = 10[a]

	^{13}C signals (δ, ppm)					
T, K	μ-CH_2	Cp	Me	Al–Me	compd	mol %[b]
203		117.94	64.94		4	8
		117.12	60.51		3	6
		113.07	46.34		2	86
240		117.96	64.63		4	44
		117.12	60.51		3	15
		113.16	46.23		2	41
253		117.94	64.68–64.81		4	56
		117.15	60.51		3	11
		113.19	46.24		2	33
273		118.10	64.87		4	29
		113.24	46.21		2	16
	187.89	112.25			5	45
	178.96	111.97		−10.8	6	10
283		118.18	64.95		4	6
		113.24	46.19		2	2
	188.06	112.28		−4.11	5	49
	178.98	112.05		−10.73	6	43

[a] ^{13}C NMR spectra have been recorded at 67.89 MHz in toluene-d_8. Chemical shifts are referenced to the toluene CD_3 signal at 20.52 ppm. [b] Molar fractions of titanocene compounds calculated by the integrated peak areas of Cp and Me signals.

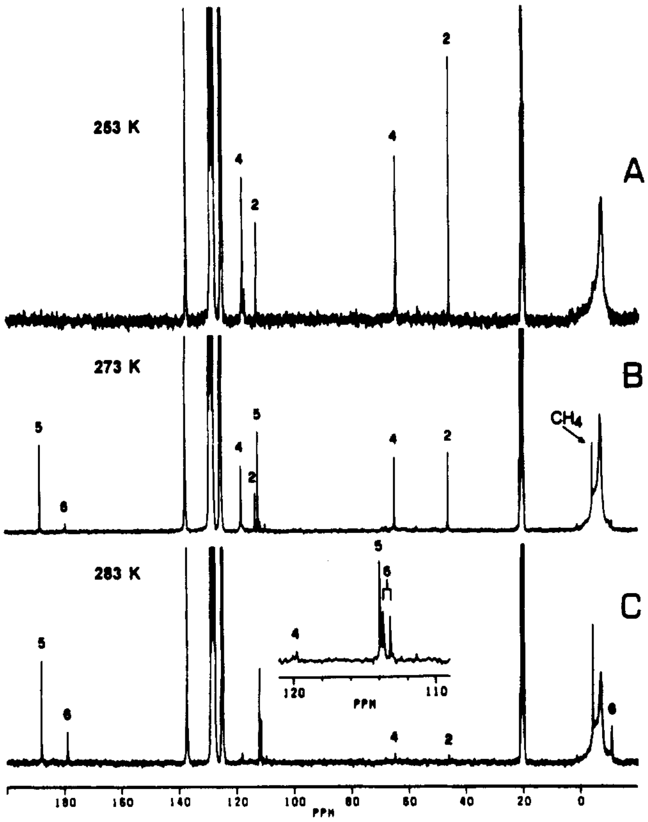

Figure 3. ^{13}C NMR spectra of $Cp_2Ti^{13}CH_3Cl$ (^{13}C 90% enriched) and MAO in toluene-d_8 recorded at 67.89 MHz and at 253 K (Figure 3A), 273 K (Figure 3B), 283 K (Figure 3C). [Ti] = 0.07 mol·L^{-1}, [Al]:[Ti] = 10:1.

(b) Effect of Al/Ti Ratios. In Figure 4 the ^{13}C NMR spectra at 253 K of $Cp_2Ti^{13}CH_3Cl$ and MAO at various Al/Ti ratios (Al/Ti = 10 (A); Al/Ti = 20 (B); Al/Ti = 40 (C)) are shown. Chemical shifts of the titanocene products are reported in Table III. These spectra have been monitored at 253 K, that is, at a temperature lower than the one at which the methylidene complexes **5** and **6** are formed. By comparing Figure 4A,B, it is possible to observe that at Al/Ti = 20 a great amount of Cp_2TiMe_2

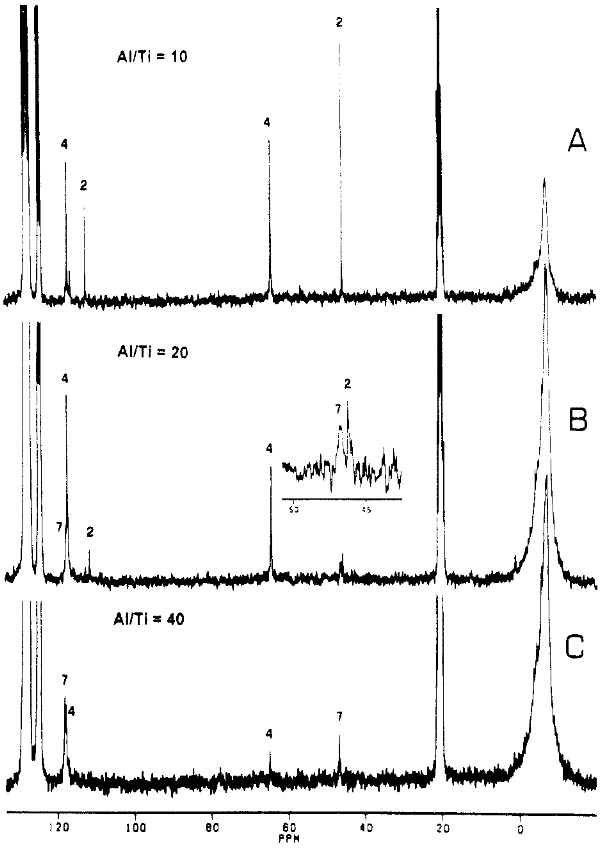

Figure 4. ^{13}C NMR spectra of $Cp_2Ti^{13}CH_3Cl$ (^{13}C 90% enriched) and MAO in toluene-d_8 recorded at 253 K and at 67.89 MHz: (A) [Al]:[Ti] = 10:1, [Ti] = 0.07 mol·L^{-1}; (B) [Al]:[Ti] = 20:1, [Ti] = 0.14 mol·L^{-1}; (C) [Al]:[Ti] = 40:1, [Ti] = 0.07 mol·L^{-1}.

Table III. ^{13}C NMR Data for Reactions between $Cp_2Ti^{13}CH_3Cl$ and MAO at Different Al/Ti Ratios[a]

sample	T, K	Al/Ti	^{13}C signals (δ, ppm) Cp	Me	compd	mol %[b]
1	253	10	117.94	64.68–64.81	4	56
			117.15	60.51	3	11
			113.00	46.24	2	33
2	253	20	118.00	64.79	4	82
			118.34	46.69	7	10
			113.07	46.21	2	8
3	253	40	118.01	64.77	4	43
			118.34	46.68	7	57
4		20[c]	118.01	64.91	4	84
			118.41	46.80	7	16

[a] ^{13}C NMR spectra have been recorded at 67.89 MHz in toluene-d_8. Chemical shifts are referenced to the CD_3 of the toluene at 20.52 ppm. [b] Molar fractions of titanocene compounds calculated by the integrated peak areas of Cp and Me signals. [c] In toluene-d_8/CD_2Cl_2 (4:1).

has disappeared by giving the cation-like $Cp_2TiMe^{+\delta}Cl \cdot MAO^{-\delta}$ complex 4. In the expansion of the methyl region it is possible to observe the appearance of a small amount of a new species, having Cp and Me signals at 118.34 and 46.68 ppm, respectively. As the Al/Ti ratio increases up to 40, these features increase at the expense of those of the $Cp_2TiMe^{+\delta}Cl \cdot MAO^{-\delta}$ complex 4. They prevail at Al/Ti = 40 (Figure 4C). It is possible to observe that the Cp resonance has a chemical shift similar to that of the cation-like species, while the methyl resonance is only shifted slightly downfield with respect to the Cp_2TiMe_2 methyls. This feature is reproducible and it is the only one present if the Al/Ti ratio increases. It could be assigned to a solvent separated ion pair (7), due to the existence of the following equilibrium (eq 3):

$$Cp_2TiMe^+[-Al(Me)O-]^-_n = Cp_2TiMe^+S[-Al(Me)O-]_n^- \;(7) \quad (3)$$

$$S = \text{solvent}$$

An equilibrium between the contact ion pair and the solvent separated ion pair has been studied by Eisch in the $Cp_2TiCH_2SiMe_3Cl/AlCl_3$ model system.[18] He has shown that this equilibrium is shifted to the right by polar solvents. To verify that this is the right assignment, we have studied the reaction of $Cp_2TiMeCl$ and MAO in solutions of toluene-d_8/CD_2Cl_2 (4/1) at Al/Ti = 20, that is, at the ratio at which 7 is present in a small amount. The fact that complex 7 increases by adding a polar solvent such as CD_2Cl_2 (compare samples 2 and 4 in Table III) is consistent with the assignment of complex 7 as a solvent separated ion pair.

Conclusions

From our NMR studies of the reactions of $Cp_2TiMeCl$ with $AlMe_3$ and MAO it is possible to draw the following conclusions about the role of $AlMe_3$ and MAO in producing the catalytically active species in these systems under the experimental conditions used: (i) MAO is a better alkylating agent; (ii) MAO has a greater capacity for producing and stabilizing cation-like complexes. Indeed, only MAO gives the complex 4 that has characteristics closer to a cation-like species.[10] As to the adducts observed in solution at different Al/Ti ratios and at different temperatures, they should coexist in dynamic equilibria. Each adduct concentration depends on the Al/Ti ratio and the temperature. As to the alkylidene complexes such as 5 and 6, formed at temperatures as high as 273 K, it is quite interesting to note that (a) at Al/Ti = 10 Tebbe reagent formation is much faster with MAO than with $AlMe_3$,[19] (b) structures such as 6 have never been observed in the presence of $AlMe_3$,[20] and (c) at Al/Ti = 40 complex 6 prevails since the MAO methyls compete with the only chlorine present in 1.

Preliminary NMR experiments, in which the toluene solutions of $Cp_2TiMeCl$/MAO were exposed to ethylene, indicate that at all the temperatures and Al/Ti ratios studied, this system is active for olefin polymerization. Further work is necessary to relate the complexes observed to the catalytic activity of these systems, and some work will be specially devoted to elucidating the role of the alkylidene complexes, that are metathesis active catalysts, in the addition polymerization and mechanism. It is known, to the contrary, that the $Cp_2TiMeCl/AlMe_3$ system hardly shows any polymerization activity. All these findings (a) are inconsistent with the hypothesis that "free" $AlMe_3$ is the actual cocatalyst in the metallocene–MAO based catalytic systems and (b) furnish further evidence that the active center is a cation-like species produced by MAO. In addition, taking into account reports that the catalytic activity increases with the Al/Ti ratios, that is, as complex 7 increases, we propose as a working hypothesis that complex 7 is likely to be the most active species in the MAO based catalytic system.

Experimental Section

All operations and manipulations have been carried out under dry nitrogen atmosphere by using glovebox and standard high vacuum or Schlenk line techniques. Nitrogen used was purified by passage through columns of BASF RS-11 (Fluka) and Linde 4-Å molecular sieves. $AlMe_3$ and Cp_2TiCl_2 (Aldrich) were used as received. MAO (30% w/w toluene solution, Schering) was used after removing all volatiles and drying the resulting white powder in vacuum (12 h, room temperature, ≈0.1 mmHg). $Cp_2TiMeCl$,[21] Cp_2TiMe_2,[22] $^{13}CH_3Li$,[23] and $Al(^{13}CH_3)_3$[24] (^{13}C 90% enriched) were synthesized by known procedures. $Cp_2Ti^{13}CH_3Cl$[21] and $Cp_2Ti(^{13}CH_3)_2$[22] (^{13}C 90% enriched) were prepared with the same procedures by using $^{13}CH_3Li$ and $Al(^{13}CH_3)_3$, respectively. Toluene-d_8 was dried and vacuum transferred from a solution of sodium benzophenone ketyl.

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 dν (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 toluene-d_8 solution was added via a gastight microsyringe. The tube was shaken to effect dissolution and then loaded into the precooled NMR probe.

^1H NMR data at 253 K in toluene-d_8: (1) δ 5.66 (10H, Cp), 0.80 (3H, Me); (2) δ 5.61 (10H, Cp), 0.04 (6H, Me); (3) δ 5.63 (10H, Cp), 0.85 (3H, Me); (4) δ 5.59–5.58 (10H, Cp), 0.85 (3H, Me); (5) δ 8.26 (μ-CH_2), 5.56 (Cp), 0.10 (Al-Me); (6) δ 7.66–7.63 (d 1H), 7.33–7.30 (d 1H), 5.49 (5H, Cp), and 5.45 ppm (5H, Cp), −2.24 (3H); (7) δ 5.56 (10H, Cp), 0.07 (3H, Me).

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