¹H and ¹³C NMR Spectroscopic Study of Titanium(IV) Species Formed by Activation of Cp₂TiCl₂ and [(Me₄C₅)SiMe₂N^tBu]TiCl₂ with Methylaluminoxane (MAO)

Konstantin P. Bryliakov,^{*,†,‡} Evgenii P. Talsi,[†] and Manfred Bochmann^{*,§}

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, and Department of Natural Science, Novosibirsk State University, 630090 Novosibirsk, Russian Federation, and Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, United Kingdom

Received July 8, 2003

Summary: Using ¹³C and ¹H NMR spectroscopy, the products of the reaction of *Cp*₂*TiCl*₂ with methylaluminoxane (MAO) at Al: Ti ratios of 5:1 to 300:1 have been identified as Cp₂TiMeCl, Cp₂TiMe₂, [Cp₂TiMe(μ -Cl)Cp₂-TiCl]⁺[Me-MAO]⁻ (**II**₁), [$Cp_2TiMe(\mu - Cl)Cp_2TiMe$]⁺[Me- $MAO^{+}(\mathbf{II}_{2}), [Cp_{2}TiMe(\mu - Me)Cp_{2}TiMe]^{+}[Me-MAO]^{-}(\mathbf{II}_{3}),$ the heterobinuclear ion pair $[Cp_2Ti(\mu-Me)_2AIMe_2]^+$ [Me-MAO⁻ (III), and a "zwitterion-like" intermediate, formulated as $Cp_2TiMe^+ \leftarrow Me-AI^- \equiv MAO$ (IV). In contrast, $[(Me_4C_5)SiMe_2N^tBu]TiCl_2/MAO$ gives only zwitterionlike, not heterobinuclear, species.

Methylaluminoxane (MAO) remains the most widely used cocatalyst for metallocene-based catalysts.¹⁻⁴ Information on the structure of "cation-like" species formed upon activation of group 4 metallocenes with MAO is crucial in the understanding of polymerization activities. Within the last 5 years, important data were obtained on the solution structure of "cation-like" species formed upon activation of various zirconocenes with MAO. For the catalytic system Cp₂ZrMe₂/MAO, four different types of zirconium(IV) species were identified: Cp₂MeZr-Me \rightarrow Al \equiv MAO (**Zr-I**), [Cp₂ZrMe(μ -Me)- Cp_2ZrMe]⁺[Me-MAO]⁻ (**Zr-II**), [$Cp_2Zr(\mu-Me)_2AlMe_2$]⁺- $[Me-MAO]^-$ (**Zr-III**), and $Cp_2ZrMe^+ \leftarrow Me-Al^- \equiv MAO$ (Zr-IV).^{5,6} The solution structures of the cationic parts of ion pairs Zr-II to Zr-IV were unambiguously determined by ¹H and ¹³C NMR spectroscopy.⁶ It was shown that complexes Zr-I and Zr-II are observed in the reaction solution only at low Al:Zr ratios (<100:1), while at high Al:Zr ratios, complexes Zr-III and Zr-IV are the

major species. In complexes Zr-II and Zr-III, the perturbing [Me-MAO]⁻ anion is in outer-sphere contact to the coordinatively saturated zirconocene cation. Thus, Zr-II and Zr-III are not strongly influenced by the nonuniform nature of the [Me-MAO]⁻ counteranions, and consequently Zr-II and Zr-III display sharp NMR signals. The complex Zr-IV gives rise to a broadened NMR resonance due to the nonuniformity of tightly bound [Me-MAO]⁻ anions. Very recently, it was shown that at Al:Zr > 500:1 complexes of the type **Zr-III**, [L₂- $Zr(\mu-Me)_2AlMe_2]^+[MeMAO]^-$, strongly dominate in the reaction mixture for most L_2ZrCl_2/MAO systems ($L_2 =$ various cyclopentadienyl, indenyl, and fluorenyl ligands).⁷

The situation for titanocene/MAO systems is far less clearly determined. Tritto and co-workers observed the formation of sharp ¹³C NMR resonances upon activation of Cp_2TiMe_2 and $Cp_2TiMeCl$ with MAO (Al:Ti = 10-40), and some of these were tentatively assigned to the ion pairs [Cp₂TiMe]⁺[Cl-MAO]⁻ and [Cp₂TiMe]⁺[Me-MAO]^{-.8,9} However, it is natural to expect that similar ion pairs of types II-IV can be formed in the related Cp2TiMe2/MAO and Cp2ZrMe2/MAO systems. This background prompted us to reinvestigate the classical Cp₂-TiCl₂/MAO system in a wider range of Al:Ti ratios. In this work, using ¹H and ¹³C NMR spectroscopy and ¹³Cenriched MAO, cationic species formed in the system Cp₂TiCl₂/MAO were characterized for the first time.

Results and Discussion

The System Cp₂TiCl₂/MAO. The ¹H and ¹³C NMR spectra (Figures 1 and 2) of Cp₂TiCl₂/MAO solutions in toluene at Al:Ti ratios of 5-300 show that five different types of titanium(IV) species could be identified in this system. They are the methyl complexes Cp₂TiMeCl (existing mainly as adducts with AlMe₃ and MAO) and Cp_2TiMe_2 , the homobinuclear ion pairs $[Cp_2TiMe(\mu-Cl)-$

[†] G. K. Boreskov Institute of Catalysis and Novosibirsk State University.

[‡] Fax: +7 3832 34 3766, E-mail: bryliako@catalysis.nsk.su.

⁺ Fax: +7 3832 34 3760, E-mail: bryllako@catalysis.nsk.su.
[§] University of East Anglia.
(1) Chen, E.; Marks, T. J. Chem. Rev. 2000, 100, 1391.
(2) Kaminsky, W., Ed. Metalorganic Catalysts for Synthesis and Polymerization: Recent Results by Ziegler-Natta and Metallocene Investigations, Springer-Verlag: Berlin, 1999.
(3) Bochmann, M. J. Chem. Soc., Dalton Trans. 1996, 255.
(4) Distribution: U. H. Einshen D. Metheward B. Distribution, D. Wallow

⁽³⁾ Bochmann, M. J. Chem. Soc., Datton Trans. 1996, 255.
(4) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. Angew. Chem., Int. Ed. Engl. 1995, 34, 1143.
(5) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. Macromolecules 1997, 30, 1247.
(6) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. Macromol. Chem. Phys. 2000, 201, 558.

⁽⁷⁾ Talsi, E. P.; Bryliakov, K. P.; Semekolenova, N. V.; Zakharov, V. A.; Ystenes, M.; Rytter, E. *Mendeleev Commun.* **2003**, 48.

⁽⁸⁾ Tritto, I.; Sacchi, M.; Li, S. Macromol. Rapid Commun. 1994, 15, 217.

⁽⁹⁾ Tritto, I.; Sacchi, M.; Locatelli, P.; Li, S. Macromol. Symp. 1995, 89 289



Figure 1. ¹H NMR spectra of $Cp_2TiCl_2 + MAO$ in toluene at -15 °C ([Al] = 0.75 M), in the range of Cp carbon signals, with Al:Ti ratios of (a) 10, (b) 20, (c) 40, (d) 90, and (e) 300.

Cp₂TiCl]⁺[Me-MAO][−] (**II**₁), [Cp₂TiMe(μ -Cl)Cp₂TiMe]⁺-[Me-MAO][−] (**II**₂), and [Cp₂TiMe(μ -Me)Cp₂TiMe]⁺[Me-MAO][−] (**II**₃), the heterobinuclear ion pair [Cp₂Ti(μ -Me)₂AlMe₂]⁺[Me-MAO][−] (**III**), and the "zwitterion-like" intermediate Cp₂TiMe⁺←Me-Al[−]≡MAO (**IV**) (Chart 1). Their NMR signals are shown in Figures 1 and 2, and the NMR parameters are collected in Table 1.

In contrast to the Cp₂ZrMe₂/MAO system,⁶ with Cp₂-TiCl₂/MAO at Al:Ti ratios of 40-90, three homobinuclear complexes of type II (either Cl- or Me-bridged) could be observed in Figures 1c,d and 2c. Complex II₁ could be detected only at very low Al:Ti ratios (e.g. at Al:Ti = 10, $[II_1]$: $[II_2] \approx 1$), while at higher ratios (20– 40) the homobinuclear species II_2 and II_3 appear. As in the related Zr system, complexes II display sharp ¹³C NMR Ti-CH₃ signals, shifted downfield with respect to Cp₂TiMe₂ and Cp₂TiMeCl due to their cationic nature. The chemical shift of II₂ is only slightly affected by the outer-sphere anion, as shown by comparison with the ion pair $[Cp_2TiMe(\mu-Cl)Cp_2TiMe]^+[B(C_6F_5)_4]^-$ synthesized by reacting a mixture of Cp₂TiMeCl and Cp₂-TiMe₂ (ca. 1:1) with $[CPh_3][B(C_6F_5)_4]$ in a Ti:B ratio of 2:1 (toluene, -15 °C), which displays very similar chemical shifts (Table 1).

When the Al:Ti ratio is increased, the Cl bridge in II_2 is replaced by a methyl bridge, and II_2 is converted to II_3 (Figures 1b-d and 2c). It was confirmed that Ti species formed at Al:Ti ratios of ≥ 90 contain no chlorine (Figures 1d and 2c): in a separate experiment, Cp₂-



Figure 2. $(a-c)^{13}C$ NMR spectra of $Cp_2TiCl_2 + MAO$ in toluene at -15 °C ([AI] = 0.75 M), in the ranges of Cp, Ti–Me, and μ -Me carbon signals (arbitrary scale), with Al:Ti ratios of (a) 20, (b) 40, and (c) 90. (d) ¹³C NMR spectrum of $Cp_2TiCl_2 + MAO$ in toluene at -15 °C ([AI] = 0.75 M) with Al:Ti = 90, in the ranges of Ti–Me and μ -Me carbon signals. Asterisks mark admixtures in toluene.

TiMe₂ was reacted with MAO (Al:Ti = 100) to afford the same species II_3 , III, and IV.

It is seen that at Al:Ti ratios approaching those typically employed under olefin polymerization conditions (Al:Ti = 300, Figure 1e), complexes **III** and **IV** dominate in the reaction mixture, as was the case in the Cp₂ZrMe₂/MAO system. To support our assignment of the NMR peaks of **III**, the related complex [Cp₂Ti(μ -Me)₂AlMe₂]⁺[B(C₆F₅)₄]⁻ was prepared in situ by mixing of Cp₂TiMe₂, AlMe₃, and [CPh₃][B(C₆F₅)₄] in a 1:50:1 ratio (toluene, -15 °C). The chemical shifts of the corresponding peaks of [Cp₂Ti(μ -Me)₂AlMe₂]⁺[B(C₆F₅)₄]⁻ and **III** were very similar (Table 1).

The assignment of the NMR signals of the tight ion pair **IV** was simplified by their characteristic broadening (Figures 1 and 2, Table 1). Like the related Zr system,⁶ the proposed structure of compound **IV** is supported by the detection of a ¹³C NMR signal near δ

Fable 1.	¹³ C and ¹ H NMR Chemica	al Shifts (ppm), Line	• Widths $\Delta v_{1/2}^{a}$ (Hz)	, and <i>J</i> I _{CH}	Coupling (Constants	(Hz)
	for Comp	lexes II–IV and Ref	erence Complexes	in Toluene			

			Т,	¹³ C	¹ H	¹³ C	¹ H	¹³ C	¹ H
no.	species	Al:Ti	°C	(Ср)	(Cp)	(Ti-Me)	(Ti-Me)	(µ-Me)	(Al-Me)
1	Cp2TiClMe Cp2TiClMe	5 10	$-20 \\ -15$	116.03^b 117.06^b	5.62^{b} 5.60^{b}	53.06 ^b ($\Delta v_{1/2} = 30$) 59.56 ^b ($\Delta v_{1/2} = 80$)	0.83 ^b 0.85 ^b		
2	Cp ₂ TiMe ₂	20	-15	112.07	5.50	46.25 ($\Delta v_{1/2} = 80$) ($J^1_{CH} = 123$)	-0.21		
3	$[Cp_2TiMe(\mu-Cl)Cp_2TiCl]^+$ MeMAO ⁻ (II ₁) ^c	10	-15	117.9	5.55	64.38 ($\mathcal{J}^{1}_{CH} = 128$)	0.79		
	$[Cp_2TiMe(\mu-Cl)Cp_2TiMe]^+$ MeMAO ⁻ (II ₂) ^c	20-40	-15	117.9	5.55	64.67 ($J^1_{\rm CH} = 128$)	0.79		
	[Cp ₂ TiMe(µ-Me)Cp ₂ TiMe] ⁺ MeMAO (II ₃) ^c	90	-15	117.62	5.71	68.81 ($\mathcal{J}^{1}_{CH} = 128$)	0.34	NF^d	
4	$[Cp_2Ti(\mu-Me)_2AlMe_2]^+ \\ MeMAO^- (III)^c$	90	-15	118.20	5.20			46.48^d ($J^1_{CH} = 119$)	-0.74
5	Cp ₂ TiMe ⁺ ←Me-Al≡MAO ⁻ (IV) ^c	40-300	-15	117.9 ($\Delta v_{1/2} = 100$)	5.6 ($\Delta v_{1/2} = 75$)	66 ($\Delta v_{1/2} = 150$)	NF^d	$13^d (\Delta v_{1/2} = 150)$	
6	$Cp_2TiCl_2^c$		25	119.50	5.86				
7	Cp ₂ TiClMe ^{c,e}		-20	115.45	5.66	49.31 ($J^{1}_{CH} = 129$)	0.78		
8	Cp ₂ TiMe ₂ ^{c,e}		-20	113.10	5.60	46.20 ($J^1_{\rm CH} = 124$)	0.01		
9	$\begin{array}{l} [Cp_2TiMe(\mu\text{-}Cl)Cp_2TiMe]^+ \\ [B(C_6F_5)_4]^{-\ c} \end{array}$		-15	117.7	5.50	63.6	0.69		
10	$[Cp_2Ti(\mu-Me)_2AlMe_2]^+ \\ [B(C_6F_5)_4]^{-c}$	50 ^{<i>f</i>}	-15	118.19	5.25			46.60 ^g	-0.72

^{*a*} For wide lines, either exchange-broadened (with AlMe₃ and MAO) or broadened due to nonuniformity of MAO sites; ^{*b*} Chemical shift depends on Al:Ti ratio, due to fast chemical exchange (cf. entries 1 and 7). Such a pronounced dependence is not observed for Cp₂TiMe₂; thus, Cp₂TiMeCl is expected to form Cl-bridged adducts with AlMe₃ and MAO. ^{*c*} Narrow lines ($\Delta v_{1/2} \leq 15-20$ Hz). ^{*d*} Respective ¹H peaks of μ -Me protons not found (either masked by solvent or MAO signals). NF = not found. ^{*e*} Synthesized by reacting Cp₂TiCl₂ with LiMe in toluene at 0 °C. ^{*f*} Al present as AlMe₃. ^{*g*} Respective ¹H peak of μ -Me protons at -0.30.

Chart 1. Structures Proposed for Intermediates



13, due to the bridging methyl group in the Ti $-(\mu$ -Me)-Al moiety (Figure 2d).

The signals of complexes **II**₁, **II**₂, **II**₃, and **III** were also observed in the work of Tritto et al. but were not adequately interpreted;^{8,9} complexes **II**₂ and **II**₃ were assigned to $[Cp_2TiMe]^+[Cl-MAO]^-$ and $[Cp_2TiMe]^+[Me-MAO]^-$, respectively, and the signal for **III** was assigned to a nonactive species, $Cp_2TiMe-O-Al\equiv MAO$. Recent results on borate-¹⁰ and MAO-based^{5,6} systems helped us to make the correct assignment and to obtain a detailed picture on the structure of the titanium species formed upon activation of Cp_2TiMe_2 and Cp_2TiCl_2 by MAO.

We have shown that at Al:Ti ratios approaching real polymerization conditions (>100), intermediates **III** and **IV** are the major species in the reaction mixture. The Ti species **III** and **IV** are far less stable than their Zr counterparts: the latter are stable for weeks at room temperature, while the former disappear at this temperature with a half-life time of several hours. We note that the solid MAO used in our experiments contained a reduced amount of AlMe₃ (5%). However, when commercial MAO with a higher AlMe₃ content (\geq 25%) is used, species **III** is expected to dominate in practical polymerization systems, according to the equilibrium **IV** + $\frac{1}{2}$ Al₂Me₆ = **III**,⁶ and hence should be regarded as the main precursor for the catalytically active species.

The Systems [(Me₄C₅)SiMe₂N^tBu]TiCl₂/MAO and [(Me₄C₅)SiMe₂N^tBu]TiMe₂/MAO.¹¹ These systems were studied with Al:Ti ratios of 20-100 at variable temperatures (-20 to +20 °C). It was shown that the Ti species formed are stable even at room temperature for days (in accordance with ref 11); thus, there is no need for low temperature. Mixtures of ¹³C-enriched MAO with [(Me₄C₅)SiMe₂N/Bu]TiCl₂ and [(Me₄C₅)SiMe₂N/Bu]TiMe₂, respectively, in toluene at 20 °C (Al:Ti = 60-100) display the same characteristic $^{13}\mathrm{C}$ NMR peak at δ 68 $(\Delta v_{1/2} = 170 \text{ Hz}).^{12}$ This peak is inhomogeneously broadened, indicating the nonuniformity of MAO coordination sites, and on the basis of data obtained for the Cp2TiCl2/MAO system, this peak could be assigned to the terminal Ti-Me group of the "zwitterion-like" intermediate [(Me₄C₅)SiMe₂N'Bu]TiMe⁺←Me-Al⁻≡MAO. Marks et al. observed NMR resonances in a similar region for two diastereomers of the related zwitterionic

^{(10) (}a) Bochmann, M.; Lancaster, S. Angew. Chem., Int. Ed. Engl. 1994, 15, 33. (b) Bochmann, M.; Lancaster, S. J. J. Organomet. Chem. 1995, 497, 55.

⁽¹¹⁾ McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (12) The 13 C NMR peak of the corresponding $N-C(CH_3)_3$ group was detected at δ 33.8, $\Delta\nu_{1/2}=70$ Hz.

species $[(Me_4C_5)SiMe_2N'Bu]TiMe^+ - PBA^- (PBA^- = tris-$ (2,2',2''-nonafluorobiphenyl)fluoroaluminate), at δ 61.99 and 60.50 ppm.¹³ Thus, in contrast to the Cp₂TiCl₂/MAO and Cp2TiMe2/MAO systems, in the "constrainedgeometry" titanium catalysts heterobinuclear species of the type $[LTi(\mu-Me)_2AlMe_2]^+$ were not found, and only "zwitterion-like" species were detected. A similar behavior was recently reported for the titanium halfsandwich system Cp*TiCl₃/MAO, where "zwitterionlike" intermediates Cp*TiMe₂⁺←Me-Al⁻≡MAO strongly dominate in solution at Al:Ti = 300 while there was no evidence for expected adducts of the types [Cp*Ti(Me)- $(\mu$ -Me)₂AlMe₂]⁺ and [Cp*Ti{ $(\mu$ -Me)₂AlMe₂}]⁺ (Cp* = C_5Me_5).¹⁴ It is possible that in the more open halfsandwich and constrained-geometry complexes a closer approach of [Me-MAO]⁻ is favored, to give "zwitterionlike" species upon activation by MAO, while for the more restricted coordination gap aperture of metallocenes heterobinuclear ion pairs of type **III** are preferable.

Conclusions

The activation of Cp₂TiX₂ with MAO leads to the formation of several intermediates, II-IV (X = Cl, Me). At Al: Ti ratios approaching real polymerization conditions (100–300:1), complexes **III** and **IV** are the major species in solution. The heterobinuclear cationic compound $[L_2Ti(\mu-Me)_2AlMe_2]^+[MeMAO]^-$ (III) predominates in solution under the higher MAO:Ti ratios typical of polymerization conditions and is the most probable precursor of the active polymerizing species. In contrast, heterobinuclear species were found to be below the detection limit in the "constrained geometry" system [(Me₄C₅)SiMe₂N^tBu]TiX₂/MAO, most probably due to steric reasons.

Experimental Section

Methylaluminoxane (MAO) was purchased from Witco GmbH (Bergkamen, Germany) as a toluene solution (total Al content 1.8 M, Al as AlMe₃ 0.5 M). Toluene was dried over molecular sieves (4 Å) and purified by refluxing over sodium metal and distilling under dry nitrogen. Solvents were distilled over sodium or sodium-benzophenone under nitrogen and degassed in vacuo. All operations were carried out under dry nitrogen (99.999%) by standard Schlenk techniques. Solids and toluene were transferred and stored in a glovebox. Cp2TiCl2 was used as purchased; [Ph₃C][B(C₆F₅)₄]¹⁵ and [(Me₄C₅)SiMe₂-N⁺Bu]TiCl₂¹⁶ were prepared as described. ¹H and ¹³C{¹H} NMR spectra were recorded at 300.130 and 75.473 MHz, respectively, on a Bruker Avance-300 MHz NMR spectrometer. Typical operating conditions for ¹³C NMR measurements were as follows: spectral width 20 kHz; spectrum accumulation frequency 0.2-0.1 Hz; 100-10 000 transients, 45° pulse at 5

 μ s. The multiplicities and coupling constants were derived from analysis of gated decoupled spectra. Operating conditions for ¹H NMR measurements: spectral width 5 kHz; spectrum accumulation frequency 0.5-0.2 Hz; number of transients 32-64, ca. 30° pulse at 2 μ s. ¹H peaks were assigned to the respective carbon signals by double-resonance techniques. For calculations of ¹H and ¹³C chemical shifts, the resonances of the CH₃ group of the toluene solvent were taken as 2.09 and 21.40 ppm, respectively. The sample temperature measurement uncertainty and temperature reproducibility were less than ± 1 °C.

Preparation of MAO and Al₂Me₆ Samples. Solid MAO was prepared from commercial MAO (Witco) by removal of the solvent in vacuo at 20 °C. The solid product obtained (polymeric MAO with total Al content 40 wt % and Al as residual AlMe₃ ca. 5 wt %) was used for the preparation of the samples.

¹³CH₃-labeled Al₂Me₆ was prepared from 99% ¹³CH₃I (Aldrich) by sequential treatments with Al metal at 80 °C and Na metal in C12H26 at 100 °C. For this goal, a dried glass ampule was filled with argon and charged with 0.126 g (4.7 mmol) of Al metal powder, 1.0 g (7 mmol) of ¹³CH₃I (99% ¹³C), and I₂ (used as catalyst). The ampule was evacuated and sealed off at the vacuum line. The reaction mixture was kept at 80 °C for 10 h. The resulting suspension was mixed under vacuum with Na metal (0.170 g) suspended in dodecane. The mixture was stirred at 100 °C for 5 h. The product, ¹³CH₃labeled Al₂Me₆ (99% ¹³C), was distilled in vacuo from the reaction mixture.

¹³CH₃-enriched MAO was prepared by ligand exchange of 99% ¹³CH₃-labeled Al₂Me₆ (70 mol % of total Me groups) and solid MAO (30 mol % of total Me groups) in toluene solution. In a typical experiment, 0.12 g of polymeric MAO powder (total Al content 1.8 mmol) was dissolved in 5 mL of toluene, and \sim 0.3 mL (\sim 2 mmol of Al) of ¹³CH₃-labeled Al₂Me₆ was added to the solution. The reaction mixture was stirred for 24 h at 25 °C, and the liquid fraction Al_2Me_6 (70% ¹³C) was removed under vacuum to give a sample of ¹³C-enriched MAO (65-70% ¹³C) with the desired Al₂Me₆ content (polymeric MAO with total Al content of 40 wt % and Al as residual AlMe3 ca. 5 wt %). The ¹³C-enriched MAO prepared either was used for sample preparation directly or was used afterward as a ca. 1:1 mixture with nonlabeled MAO.

Preparation of Cp₂TiMe₂ and Cp₂TiMeCl + Cp₂TiMe₂ Mixture. Cp₂TiMe₂ and a mixture of Cp₂TiMeCl and Cp₂TiMe₂ (ca. 1:1) were prepared by stirring appropriate amounts of LiMe (1.6 M ether solution) with a suspension of Cp_2TiCl_2 in toluene at 0 °C for 3 h. After removal of LiCl, the resulting yellow solution was collected, volatiles were removed in vacuo, and the residue was dissolved in toluene. ¹H and ¹³C chemical shifts are presented in Table 1.

Samples of Cp_2TiCl_2 (Cp_2TiMe_2) + ¹³C-MAO (+[Ph_3C]-[B(C₆F₅)₄]). The appropriate amounts of Cp₂TiCl₂, MAO, and $[Ph_3C][B(C_6F_5)_4]$ were weighed into NMR tubes in a glovebox and the tubes closed with septum stoppers. Further addition of toluene and AlMe₃ (if necessary) was performed outside the glovebox with gastight microsyringes in the flow of nitrogen upon appropriate cooling.

Acknowledgment. This work was supported by the European Commission, INTAS grant 00-841. The authors thank Dr. D. E. Babushkin and Dr. N. V. Semikolenova for the synthesis of Al(¹³CH₃)₃ and fruitful methodology of ¹³C-enriched MAO.

OM034026L

⁽¹³⁾ Chen, Y.; Stern, C. L.; Marks, T. J. J. Am. Chem. Soc. 1997, 119, 2582.

 ⁽¹⁴⁾ Bryliakov, K. P.; Semikolenova, N. V.; Zakharov, V. A.; Talsi,
 E. P. *J. Organomet. Chem.* **2003**, *683*, 23–28.
 (15) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*,

C1.

⁽¹⁶⁾ Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S.-y. Eur. Pat. Appl. 0416815A2, 1991.