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Notes

^{1}H and ^{13}C NMR Spectroscopic Study of Titanium(IV) Species Formed by Activation of Cp$_2$TiCl$_2$ and [(Me$_4$C$_5$)SiMe$_2$N^{t}Bu]TiCl$_2$ with Methylaluminoxane (MAO)

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*Summary: Using ^{13}C and ^{1}H 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 Cp$_2$TiMeCl, Cp$_2$TiMe$_2$, [Cp$_2$TiMe(μ-Cl)Cp$_2$TiCl]$^+$[Me-MAO]$^-$ (**II$_1$**), [Cp$_2$TiMe(μ-Cl)Cp$_2$TiMe]$^+$[Me-MAO]$^-$ (**II$_2$**), [Cp$_2$TiMe(μ-Me)Cp$_2$TiMe]$^+$[Me-MAO]$^-$ (**II$_3$**), the heterobinuclear ion pair [Cp$_2$Ti(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**III**), and a "zwitterion-like" intermediate, formulated as Cp$_2$TiMe$^+$←Me-Al$^-$≡MAO (**IV**). In contrast, [(Me$_4$C$_5$)SiMe$_2$N^{t}Bu]TiCl$_2$/MAO gives only zwitterion-like, 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 Cp$_2$ZrMe$_2$/MAO, four different types of zirconium(IV) species were identified: Cp$_2$MeZr-Me→Al≡MAO (**Zr-I**), [Cp$_2$ZrMe(μ-Me)Cp$_2$ZrMe]$^+$[Me-MAO]$^-$ (**Zr-II**), [Cp$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**Zr-III**), and Cp$_2$ZrMe$^+$←Me-Al$^-$≡MAO (**Zr-IV**).[5,6] The solution structures of the cationic parts of ion pairs **Zr-II** to **Zr-IV** were unambiguously determined by ^{1}H and ^{13}C 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**, [L$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[MeMAO]$^-$, strongly dominate in the reaction mixture for most L$_2$ZrCl$_2$/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 ^{13}C NMR resonances upon activation of Cp$_2$TiMe$_2$ and Cp$_2$TiMeCl with MAO (Al:Ti = 10−40), and some of these were tentatively assigned to the ion pairs [Cp$_2$TiMe]$^+$[Cl-MAO]$^-$ and [Cp$_2$TiMe]$^+$[Me-MAO]$^-$.[8,9] However, it is natural to expect that similar ion pairs of types **II**−**IV** can be formed in the related Cp$_2$TiMe$_2$/MAO and Cp$_2$ZrMe$_2$/MAO systems. This background prompted us to reinvestigate the classical Cp$_2$TiCl$_2$/MAO system in a wider range of Al:Ti ratios. In this work, using ^{1}H and ^{13}C NMR spectroscopy and ^{13}C-enriched MAO, cationic species formed in the system Cp$_2$TiCl$_2$/MAO were characterized for the first time.

Results and Discussion

The System Cp$_2$TiCl$_2$/MAO. The ^{1}H and ^{13}C NMR spectra (Figures 1 and 2) of Cp$_2$TiCl$_2$/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 Cp$_2$TiMeCl (existing mainly as adducts with AlMe$_3$ and MAO) and Cp$_2$TiMe$_2$, the homobinuclear ion pairs [Cp$_2$TiMe(μ-Cl)-

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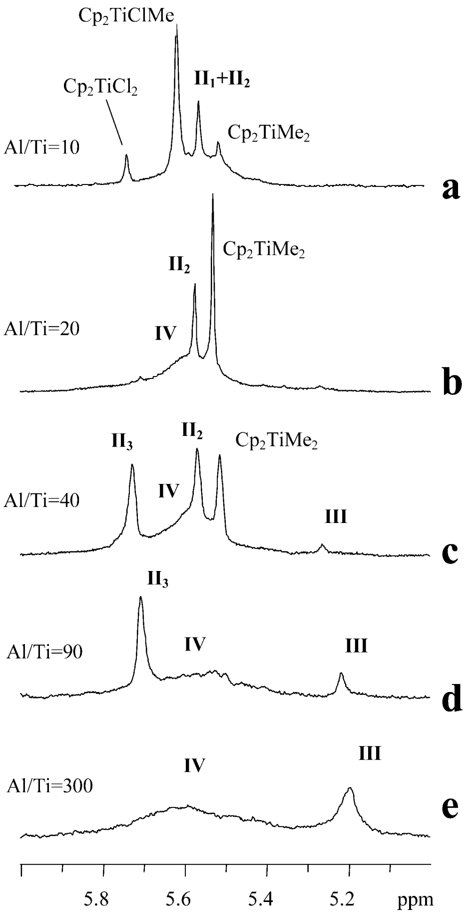


Figure 1. ^{1}H NMR spectra of Cp_2TiCl_2 + MAO in toluene at −15 °C ([Al] = 0.75 M), in the range of Cp carbon signals, with Al:Ti ratios of (a) 10, (b) 20, (c) 40, (d) 90, and (e) 300.

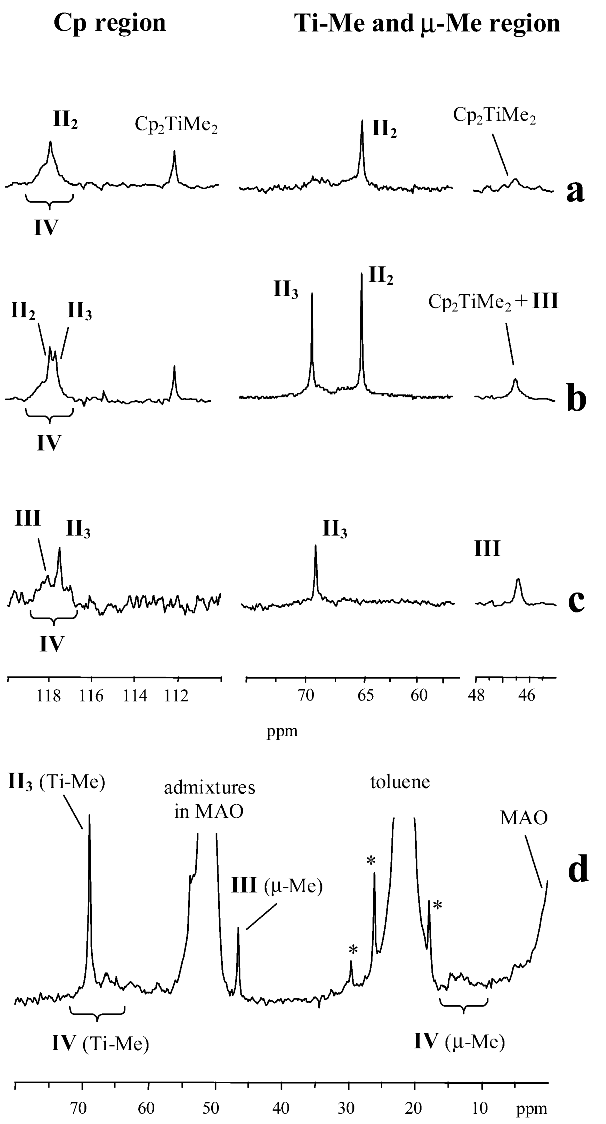


Figure 2. (a−c) ^{13}C NMR spectra of Cp_2TiCl_2 + MAO in toluene at −15 °C ([Al] = 0.75 M), in the ranges of Cp, Ti−Me, and μ-Me carbon signals (arbitrary scale), with Al:Ti ratios of (a) 20, (b) 40, and (c) 90. (d) ^{13}C NMR spectrum of Cp_2TiCl_2 + MAO in toluene at −15 °C ([Al] = 0.75 M) with Al:Ti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

$Cp_2TiCl]^+[Me\text{-}MAO]^-$ (**II$_1$**), $[Cp_2TiMe(\mu\text{-}Cl)Cp_2TiMe]^+[Me\text{-}MAO]^-$ (**II$_2$**), and $[Cp_2TiMe(\mu\text{-}Me)Cp_2TiMe]^+[Me\text{-}MAO]^-$ (**II$_3$**), the heterobinuclear ion pair $[Cp_2Ti(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$ (**III**), and the "zwitterion-like" intermediate $Cp_2TiMe^+{\leftarrow}Me\text{-}Al^-{\equiv}MAO$ (**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 Cp_2ZrMe_2/MAO system,[6] with Cp_2TiCl_2/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 **II$_1$** could be detected only at very low Al:Ti ratios (e.g. at Al:Ti = 10, [**II$_1$**]:[**II$_2$**] ≈ 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 ^{13}C NMR Ti−CH_3 signals, shifted downfield with respect to Cp_2TiMe_2 and $Cp_2TiMeCl$ due to their cationic nature. The chemical shift of **II$_2$** is only slightly affected by the outer-sphere anion, as shown by comparison with the ion pair $[Cp_2TiMe(\mu\text{-}Cl)Cp_2TiMe]^+[B(C_6F_5)_4]^-$ synthesized by reacting a mixture of $Cp_2TiMeCl$ and Cp_2TiMe_2 (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, Cp_2TiMe_2 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 Cp_2ZrMe_2/MAO system. To support our assignment of the NMR peaks of **III**, the related complex $[Cp_2Ti(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ was prepared in situ by mixing of Cp_2TiMe_2, $AlMe_3$, and $[CPh_3][B(C_6F_5)_4]$ in a 1:50:1 ratio (toluene, −15 °C). The chemical shifts of the corresponding peaks of $[Cp_2Ti(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ and **III** were very similar (Table 1).

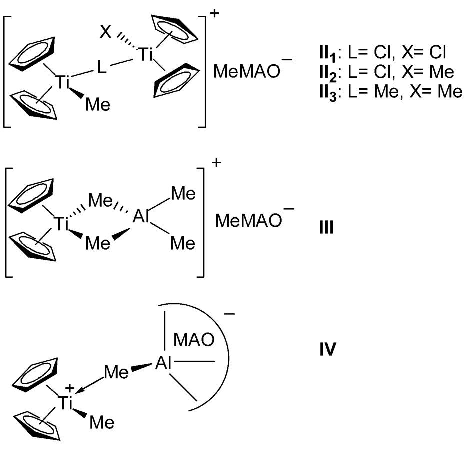
The assignment of the NMR signals of the tight ion pair **IV** was simplified by their characteristic broadening (Figures 1 and 2, Table 1). Like the related Zr system,[6] the proposed structure of compound **IV** is supported by the detection of a ^{13}C NMR signal near δ

Table 1. ^{13}C and ^{1}H NMR Chemical Shifts (ppm), Line Widths $\Delta\nu_{1/2}$[a] (Hz), and J^1_{CH} Coupling Constants (Hz) for Complexes II−IV and Reference Complexes in Toluene

no.	species	Al:Ti	T, °C	^{13}C (Cp)	^{1}H (Cp)	^{13}C (Ti−Me)	^{1}H (Ti−Me)	^{13}C (μ-Me)	^{1}H (Al−Me)
1	$Cp_2TiClMe$	5	−20	116.03[b]	5.62[b]	53.06[b] ($\Delta\nu_{1/2} = 30$)	0.83[b]		
	$Cp_2TiClMe$	10	−15	117.06[b]	5.60[b]	59.56[b] ($\Delta\nu_{1/2} = 80$)	0.85[b]		
2	Cp_2TiMe_2	20	−15	112.07	5.50	46.25 ($\Delta\nu_{1/2} = 80$) ($J^1_{CH} = 123$)	−0.21		
3	$[Cp_2TiMe(\mu\text{-}Cl)Cp_2TiCl]^+$ $MeMAO^-$ (**II$_1$**)[c]	10	−15	117.9	5.55	64.38 ($J^1_{CH} = 128$)	0.79		
	$[Cp_2TiMe(\mu\text{-}Cl)Cp_2TiMe]^+$ $MeMAO^-$ (**II$_2$**)[c]	20−40	−15	117.9	5.55	64.67 ($J^1_{CH} = 128$)	0.79		
	$[Cp_2TiMe(\mu\text{-}Me)Cp_2TiMe]^+$ MeMAO (**II$_3$**)[c]	90	−15	117.62	5.71	68.81 ($J^1_{CH} = 128$)	0.34	NF[d]	
4	$[Cp_2Ti(\mu\text{-}Me)_2AlMe_2]^+$ $MeMAO^-$ (**III**)[c]	90	−15	118.20	5.20			46.48[d] ($J^1_{CH} = 119$)	−0.74
5	$Cp_2TiMe^+\leftarrow Me\text{-}Al\equiv MAO^-$ (**IV**)[c]	40−300	−15	117.9 ($\Delta\nu_{1/2} = 100$)	5.6 ($\Delta\nu_{1/2} = 75$)	66 ($\Delta\nu_{1/2} = 150$)	NF[d]	13[d] ($\Delta\nu_{1/2} = 150$)	
6	Cp_2TiCl_2[c]		25	119.50	5.86				
7	$Cp_2TiClMe$[c,e]		−20	115.45	5.66	49.31 ($J^1_{CH} = 129$)	0.78		
8	Cp_2TiMe_2[c,e]		−20	113.10	5.60	46.20 ($J^1_{CH} = 124$)	0.01		
9	$[Cp_2TiMe(\mu\text{-}Cl)Cp_2TiMe]^+$ $[B(C_6F_5)_4]^-$ [c]		−15	117.7	5.50	63.6	0.69		
10	$[Cp_2Ti(\mu\text{-}Me)_2AlMe_2]^+$ $[B(C_6F_5)_4]^-$ [c]	50[f]	−15	118.19	5.25			46.60[g]	−0.72

[a] For wide lines, either exchange-broadened (with $AlMe_3$ 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 Cp_2TiMe_2; thus, $Cp_2TiMeCl$ is expected to form Cl-bridged adducts with $AlMe_3$ and MAO. [c] Narrow lines ($\Delta\nu_{1/2} \leq 15−20$ Hz). [d] Respective ^{1}H peaks of μ-Me protons not found (either masked by solvent or MAO signals). NF = not found. [e] Synthesized by reacting Cp_2TiCl_2 with LiMe in toluene at 0 °C. [f] Al present as $AlMe_3$. [g] Respective ^{1}H peak of μ-Me protons at −0.30.

Chart 1. Structures Proposed for Intermediates II−IV



13, due to the bridging methyl group in the Ti←(μ-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 $[Cp_2TiMe]^+[Cl\text{-}MAO]^-$ and $[Cp_2TiMe]^+[Me\text{-}MAO]^-$, 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 $AlMe_3$ (5%). However, when commercial MAO with a higher $AlMe_3$ content (≥25%) is used, species **III** is expected to dominate in practical polymerization systems, according to the equilibrium **IV** + $^1/_2Al_2Me_6$ = **III**,[6] and hence should be regarded as the main precursor for the catalytically active species.

The Systems $[(Me_4C_5)SiMe_2N^tBu]TiCl_2$/MAO and $[(Me_4C_5)SiMe_2N^tBu]TiMe_2$/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 ^{13}C-enriched MAO with $[(Me_4C_5)SiMe_2N^tBu]TiCl_2$ and $[(Me_4C_5)SiMe_2N^tBu]TiMe_2$, respectively, in toluene at 20 °C (Al:Ti = 60−100) display the same characteristic ^{13}C NMR peak at δ 68 ($\Delta\nu_{1/2}$ = 170 Hz).[12] This peak is inhomogeneously broadened, indicating the nonuniformity of MAO coordination sites, and on the basis of data obtained for the Cp_2TiCl_2/MAO system, this peak could be assigned to the terminal Ti−Me group of the “zwitterion-like” intermediate $[(Me_4C_5)SiMe_2N^tBu]TiMe^+\leftarrow Me\text{-}Al^-{\equiv}MAO$. Marks et al. observed NMR resonances in a similar region for two diastereomers of the related zwitterionic

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(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 $[(Me_4C_5)SiMe_2N^tBu]TiMe^+ \leftarrow PBA^-$ ($PBA^- =$ tris(2,2′,2″-nonafluorobiphenyl)fluoroaluminate), at δ 61.99 and 60.50 ppm.[13] Thus, in contrast to the Cp_2TiCl_2/MAO and Cp_2TiMe_2/MAO systems, in the “constrained-geometry” titanium catalysts heterobinuclear species of the type $[LTi(\mu\text{-}Me)_2AlMe_2]^+$ were not found, and only “zwitterion-like” species were detected. A similar behavior was recently reported for the titanium half-sandwich system Cp^*TiCl_3/MAO, where “zwitterion-like” intermediates $Cp^*TiMe_2{}^+ \leftarrow Me\text{-}Al^- \equiv MAO$ strongly dominate in solution at Al:Ti = 300 while there was no evidence for expected adducts of the types $[Cp^*Ti(Me)(\mu\text{-}Me)_2AlMe_2]^+$ and $[Cp^*Ti\{(\mu\text{-}Me)_2AlMe_2\}_2]^+$ ($Cp^* = C_5Me_5$).[14] It is possible that in the more open half-sandwich and constrained-geometry complexes a closer approach of $[Me\text{-}MAO]^-$ is favored, to give “zwitterion-like” 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 Cp_2TiX_2 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 $[L_2Ti(\mu\text{-}Me)_2AlMe_2]^+[MeMAO]^-$ (**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 $[(Me_4C_5)SiMe_2N^tBu]TiX_2$/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 $AlMe_3$ 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. Cp_2TiCl_2 was used as purchased; $[Ph_3C][B(C_6F_5)_4]$[15] and $[(Me_4C_5)SiMe_2N^+Bu]TiCl_2$[16] were prepared as described. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.130 and 75.473 MHz, respectively, on a Bruker Avance-300 MHz NMR spectrometer. Typical operating conditions for ^{13}C 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 μs. 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 μs. ^1H peaks were assigned to the respective carbon signals by double-resonance techniques. For calculations of ^1H and ^{13}C chemical shifts, the resonances of the CH_3 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 Al_2Me_6 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 $AlMe_3$ ca. 5 wt %) was used for the preparation of the samples.

$^{13}CH_3$-labeled Al_2Me_6 was prepared from 99% $^{13}CH_3I$ (Aldrich) by sequential treatments with Al metal at 80 °C and Na metal in $C_{12}H_{26}$ 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 $^{13}CH_3I$ (99% ^{13}C), and I_2 (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, $^{13}CH_3$-labeled Al_2Me_6 (99% ^{13}C), was distilled in vacuo from the reaction mixture.

$^{13}CH_3$-enriched MAO was prepared by ligand exchange of 99% $^{13}CH_3$-labeled Al_2Me_6 (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 ∼0.3 mL (∼ 2 mmol of Al) of $^{13}CH_3$-labeled Al_2Me_6 was added to the solution. The reaction mixture was stirred for 24 h at 25 °C, and the liquid fraction Al_2Me_6 (70% ^{13}C) was removed under vacuum to give a sample of ^{13}C-enriched MAO (65−70% ^{13}C) with the desired Al_2Me_6 content (polymeric MAO with total Al content of 40 wt % and Al as residual $AlMe_3$ ca. 5 wt %). The ^{13}C-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 Cp_2TiMe_2 and $Cp_2TiMeCl$ + Cp_2TiMe_2 Mixture. Cp_2TiMe_2 and a mixture of $Cp_2TiMeCl$ and Cp_2TiMe_2 (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 ^{13}C chemical shifts are presented in Table 1.

Samples of Cp_2TiCl_2 (Cp_2TiMe_2) + ^{13}*C*-MAO (+$[Ph_3C][B(C_6F_5)_4]$). The appropriate amounts of Cp_2TiCl_2, 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 $AlMe_3$ (if necessary) was performed outside the glovebox with gastight microsyringes in the flow of nitrogen upon appropriate cooling.

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