Activation of Bis(pyrrolylaldiminato) and (Salicylaldiminato)(pyrrolylaldiminato) Titanium Polymerization Catalysts with Methylalumoxane

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Cationic intermediates formed upon activation of an olefin polymerization catalyst based on bis[*N*-phenylpyrrolylaldiminato]titanium(IV) dichloride (L_2TiCl_2, **I**) and [*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato-*N′*-phenylpyrrolylaldiminato]titanium(IV) dichloride ($L'LTiCl_2$, **II**) with methylalumoxane (MAO) have been identified. Outer-sphere ion pairs of the type $[L_2TiMe(S)]^+[MeMAO]^-$ and $[L'LTiMe(S)]^+[MeMAO]^-$ capable of ethene polymerization have been characterized by ^1H and ^{13}C NMR spectroscopy. Unlike methyl metallocenium cations, the barrier of the first ethene insertion into the Ti−Me bonds of these species is not significantly higher than that of subsequent insertions. Surprisingly, whereas homoligated catalyst precursors L_2TiCl_2 in the presence of MAO are prone to ligand transfer to aluminum, under the same conditions the heteroligated system $L'LTiCl_2$/MAO proved resistant to ligand scrambling.

Introduction

Complexes of group IV metals with pyrrolylaldiminato ligands[1−4] have attracted particular attention as single-site catalysts of olefin polymerization.[5−11] Titanium complexes were the first to show high catalytic activities and are therefore more developed to date; however, zirconium and hafnium counterparts are currently being investigated as well.[4,12,13] Bis(pyrrolylaldiminato) titanium complexes ("PI catalysts") show attractive catalytic properties: when activated with methylalumoxane (MAO), they demonstrate high ethene polymerization activities (comparable to those of metallocenes), whereas activation with $Al(iBu)_3/[CPh_3]^+[B(C_6F_5)_4]^-$ allows the preparation of high molecular weight polyethene (M_w up to 5×10^6).[2] Moreover, bis(pyrrolylaldiminato) titanium catalysts promote the living ethene−norbornene copolymerization with high comonomer incorporation (up to 46.5%) to yield copolymers consisting of essentially alternating ethene and norbornene units, even though ethene homopolymerization is not living and norbornene is not polymerized at all.[9] Very recently, heteroligated (salicylaldiminato)(pyrrolylaldiminato) titanium complexes have been reported that combine the high ethene polymerization activity of salicylaldiminato systems with the more open structure required for comonomer incorporation and display significantly improved activity and high comonomer incorporation compared to homoligated couterparts.[14−17]

On the other hand, the activation processes of pyrrolylaldiminato and (salicylaldiminato)(pyrrolylaldiminato) titanium complexes with commonly used cocatalysts have so far not been investigated in detail. Recently, we and others published a spectroscopic study of the cationic intermediates formed upon activation of a bis(salicylaldiminato) titanium catalyst capable of promoting living ethene polymerization.[18−20] Here we report the results of a detailed study of the interaction of the catalyst precursors **I** and **II** with MAO by ^1H and ^{13}C NMR spectros-

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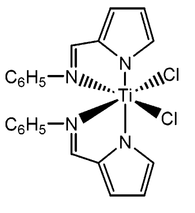
Table 1. Selected ^{13}C and ^{1}H NMR Chemical Shifts (ppm), Line Widths $\Delta\vartheta_{1/2}$ (Hz), Multiplicities, and J^{1}_{CH} Coupling Constants (Hz) for Complexes I and I_2−I_4 in Toluene-d_8/1,2-Difluorobenzene

species	Al:Ti	*T*, °C	^{1}H (Ti−Me)	^{1}H (N=CH)	^{1}H (L)	^{13}C (Ti−Me)
L_2TiCl_2 (**I**)		20		7.82	5.89 (dd, *J* = 2.3, 3.5), 6.05 (d, *J* = 3.5)	
$L_2TiClMe$ (**I$_2$**)	15	−10	2.37 ($\Delta\vartheta_{1/2}$ = 3)	8.04 ($\Delta\vartheta_{1/2}$ = 30) 7.33[a]	6.22	92.1 (J^{1}_{CH} = 127), ($\Delta\nu_{1/2}$ = 9)
$L_2TiClMe$ (**I$_2$**)	15	−60	2.37 ($\Delta\vartheta_{1/2}$ = 10)	8.20 ($\Delta\vartheta_{1/2}$ = 9) 7.25[a]		*b*
$[L_2TiMe(S)]^+$ $[MeMAO]^-$ (**I$_3$**)	50	−20	1.85 ($\Delta\vartheta_{1/2}$ = 8)	9.0 ($\Delta\vartheta_{1/2}$ = 100)	6.0	82.0 (J^{1}_{CH} = 125)
I$_4$	50	−20	1.65	7.5−8.0		83.4 (J^{1}_{CH} = 125)
$[L_2TiP(S)]^+$ $[MeMAO]^-$ (**I$_3$′**)	50	−30		n.r.d.[f]	n.r.d.	*c*
$LAlMe_2$	50	−10		7.3[d,e]	6.26[d]	

[a] Overlapping with toluene. [b] Not measured. [c] ^{13}C: 106.5 ($-H_2{}^{13}C-Ti$). [d] Peak position is dependent on temperature and Al/Ti ratio. [e] Al−CH_3 peak at δ −0.24; peak position is dependent on temperature and Al/Ti ratio. [f] n.r.d. = not reliably detected.

copy, which provide experimental evidence for structures and reaction pathways of relevant intermediates in these catalyst systems.



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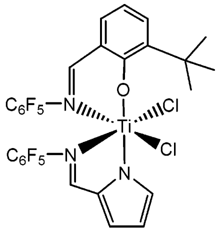

II

Results and Discussion

The I/MAO System. The ^{1}H NMR spectrum of the initial complex **I** in toluene-d_8/1,2-difluorobenzene (5:1) at 20 °C displays sharp and well-resolved peaks (Table 1). After addition of MAO (Al:Ti = 10−15), the major part of **I** is converted to another complex identified as $L_2TiMeCl$ (**I$_2$**) (Figure 1a, Table 1). At 20 °C, the imine resonance of **I$_2$** is broadened and thus unobservable; however, lowering the temperature below −10 °C results in clear signal decoalescence into two peaks, in agreement with the expected nonequivalence of two pyrrole−imine protons in $L_2TiMeCl$. The apparent exchange value $\Delta G^{\ddagger}_{ex}$ was estimated to be 13.6 kcal mol^{-1} at the coalescence temperature of 15 °C (cf. ref 16). The ^{1}H NMR peak of the Ti−CH_3 group of **I$_2$** was observed at δ 2.37, and an experiment with ^{13}C-enriched MAO revealed the corresponding Ti−^{13}CH$_3$ resonance at δ 92.1 (q, J^{1}_{CH} = 127 Hz, $\Delta\nu_{1/2}$ = 9 Hz, 10 °C, Table 1). We note that the active species in bis(pyrrolylaldiminato) titanium systems are thermally less stable than those in bis(salicylaldiminato) titanium systems;[18] therefore the spectroscopic measurements of the samples with higher Al/Ti ratios should be conducted at temperatures below −10 °C.

In all cases the formation of varying amounts of the aluminum complex $LAlMe_2$ (where L = *N*-phenylpyrrolylaldiminate) was observed, formed via ligand transfer to $AlMe_3$. The compound $LAlMe_2$ was also generated independently by interaction of **I** with $AlMe_3$ at Al/Ti = 20 and was identified by its C*H*=N and Al−CH_3 resonances that fall in the region typical for L′ lMe$_2$ complexes with L′ = salicylaldiminato ligands.[18,21]

At higher Al:Ti ratios of 20−30, formation of a new complex **I$_3$** could be observed in the **I**/MAO system, along with complex **I$_2$**. In contrast to **I$_2$**, compound **I$_3$** is characterized by an ^{1}H NMR resonance for the Ti−CH_3 group at δ 1.86 (−20 °C), which corresponds to the ^{13}C NMR signal for Ti−^{13}CH$_3$ at δ 82.0 ($^{1}J_{CH}$ = 125 Hz; Table 1). **I$_3$** becomes the predominant species at Al:Ti = 50 (Figure 1b). Further increases of the Al:Ti ratio to 100−200 do not give rise to any new complexes. By analogy with the bis(salicylaldiminato) titanium system,[18] **I$_3$** is likely to be the cationic outer-sphere intermediate $[L_2TiMe]^+[MeMAO]^-$. Although one should expect two non-equivalent imine peaks for **I$_3$**, a single broadened signal is

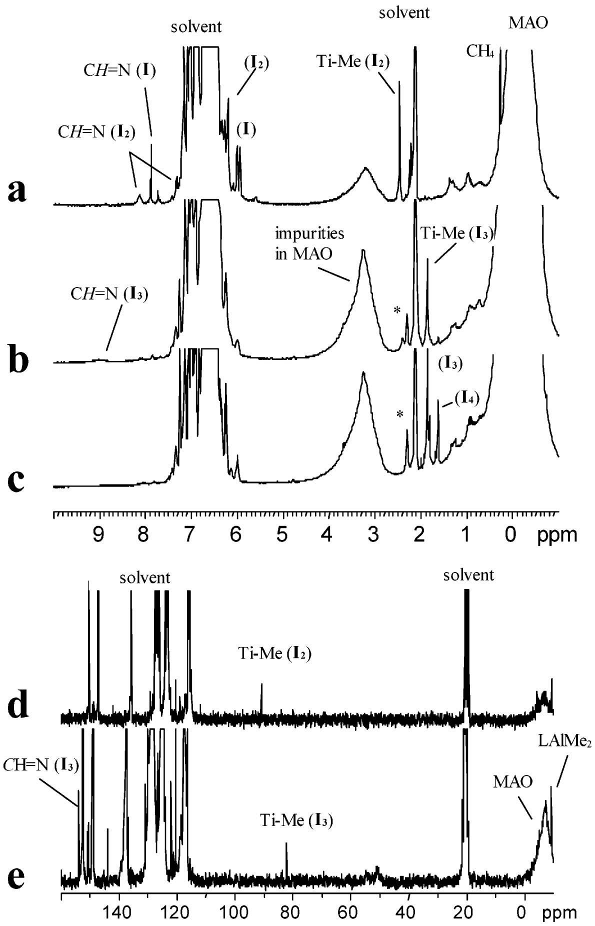

Figure 1. ^{1}H NMR spectra (−20 °C) of **I**/MAO samples: (a) Al:Ti = 10; (b) Al:Ti = 50; (c) Al:Ti = 50 after storing at −20 °C overnight. Asterisks mark peaks assignable to the elusive L_2TiMe_2 complex. ^{13}C NMR spectra of **I**/MAO-^{13}C samples: (d) Al:Ti = 10, −10 °C; (e) Al:Ti = 50, −20 °C.

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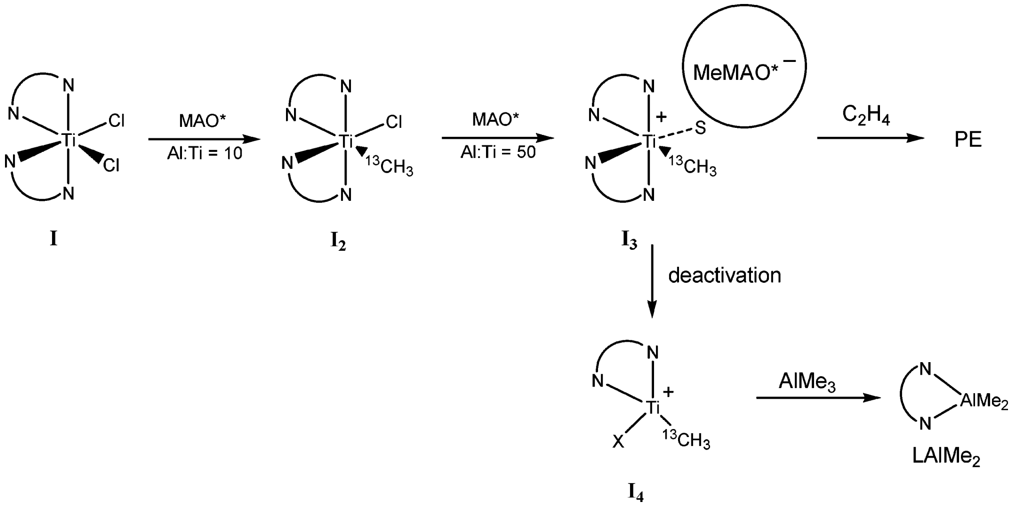
Scheme 1. Formation and Deactivation of the Active Sites in the System I/MAO* (MAO* = MAO-^{13}C, N$\frown$N = pyrrolylaldiminato ligand, X = unidentified monoanionic ligand)



observed at temperatures from −60 to −10 °C (δ 9.0, $\Delta\vartheta_{1/2} =$ 100 Hz at −20 °C). The width of the Ti−CH_3 resonance is highly temperature dependent ($\Delta\vartheta_{1/2} =$ 8 Hz at −20 °C, 15 Hz at −30 °C, and 30 Hz at −40 °C), indicative of slow exchange of the Ti−Me group between the two coordination sites of [L$_2$-TiMe]$^+$. The remaining site of **I$_3$** is probably occupied by a weakly coordinated solvent molecule (S), and we therefore formulate **I$_3$** as [L$_2$TiMe(S)]$^+$[Me−MAO]$^-$ (Scheme 1). The relatively sharp ^{1}H and ^{13}C NMR peaks of **I$_3$** indicate that the [Me−MAO]$^-$ counterion is placed in the outer coordination sphere of titanium.[22] The reactive nature of **I$_3$** will be further illustrated by the reaction with ^{13}C$_2$H$_4$.

We note that, just as was the case of the bis(salicylaldiminato) titanium system,[18] the dimethyl product L$_2$TiMe$_2$ could not be reliably detected in the **I**/MAO system. We did observe a small sharp ^{1}H peak at δ 2.30 (−10 °C) that might be ascribed to L$_2$Ti(CH_3)$_2$ protons in samples of **I**/MAO at Al:Ti = 20−50 in the course of conversion of **I$_2$** to **I$_3$** (Figure 1b); however, its concentration was too low for a reliable identification.

As distinct from the bis(salicylaldiminato)TiCl$_2$/MAO system, with time the ion pair **I$_3$** irreversibly converts into another (presumably cationic) titanium(IV) species **I$_4$**, which is characterized by ^{1}H and ^{13}C NMR peaks close to those of **I$_3$** (Figure 1c, Table 1). **I$_4$** is far more stable than **I$_3$**: traces of **I$_4$** can be observed even at +20 °C. Taking into account the fact that formation of **I$_4$** is always accompanied by the appearance of LAlMe$_2$ and that decomposition of **I$_4$** at room temperature results in further increase in the LAlMe$_2$ concentration, one can conclude that the pyrrolylaldiminato ligand in **I$_4$** remains unaffected (i.e., no reduction of the imine functionality is apparent).[30] It is likely therefore that **I$_4$** is a cationic titanium(IV) complex derived from ligand transfer to Al and also contains an as yet unidentified negatively charged ligand X (methyl?). Species **I$_4$** is far less reactive toward ethene than **I$_3$** (see below).

To corroborate the role of **I$_3$** as the ethene polymerizing species, we injected ^{13}C-labeled ethene into the NMR tubes containing **I$_3$** and **I$_4$** (at ca. 1:2 ratio) at low temperatures. Addition of ^{13}C$_2$H$_4$ (ethene:Ti = 8) into this sample at −30 °C resulted in the immediate disappearance of the Ti−CH_3 and Ti−^{13}CH$_3$ peaks of **I$_3$**, whereas those of **I$_4$** remained unaffected (see Supporting Information). At the same time a very small ^{13}C NMR peak was observed at δ 106.5 that, in analogy with the Ti−^{13}CH$_2$ signal in the bis(salicylaldiminato) system,[18] might be assigned to the Ti−^{13}CH$_2$− carbon of the titanium polymeryl species.[31] After warming the sample to room temperature, the ^{13}C NMR signal of polyethene was observed (δ 30.1), and all ethene was found to be consumed. In contrast, when ethene was injected into a separate sample containing only **I$_4$**, even after 5 min at −10 °C only partial consumption of ethene was detected by ^{1}H NMR spectroscopy.

Thus, the active intermediate in the system **I**/MAO is an outer-sphere ion pair, [L$_2$TiMe(S)]$^+$[Me-MAO]$^-$ (**I$_3$**). In the absence of ethene, it converts to another titanium species, **I$_4$**, which is far less reactive toward ethene, and even less so to LAlMe$_2$. This is likely to be the major route of catalyst deactivation of system **I**.

Apart from the formation of **I$_4$**, a major catalyst deactivation pathway is the reduction of Ti(IV) to Ti(III). EPR spectra (toluene-d_8/1,2-difluorobenzene, 20 °C) of the samples of **I**/MAO, recorded after the decay of the Ti(IV) species was confirmed by NMR spectroscopy, are a superposition of two types of signals: a sharp isotropic signal at g 1.967 and an axially anisotropic one ($g_x = 1.992$, $g_y = 1.966$, $g_z = 1.966$).

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(22) For zwitterion-like inner-sphere ion pairs formed by MAO and metallocenes,[23−25,27] half-titanocenes,[26] and constrained-geometry complexes,[27] broad non-uniform NMR peaks are observed.

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(28) Although one might expect that **I$_4$** may be formed by a reaction of MAO with the CH=N functional group of **I$_3$** (in analogy with the imine to amine reduction by Al(iBu)$_3$ as previously described by Fujita and co-workers for bis(salicylaldimine) titanium complexes[29,30]), the CH=N group seems to be unaffected under our experimental conditions.

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(31) In distinction to the "living" bis(salicylaldimine) titanium system (where titanium polymeryl species are stable at −20 °C),[18] in the **I**/MAO system the Ti−^{13}CH$_2$− peak is expected to be elusive because of β-hydrogen elimination/chain transfer processes.

Scheme 2. Formation and Deactivation of the Active Sites in the System II/MAO* (MAO* = MAO-^{13}C

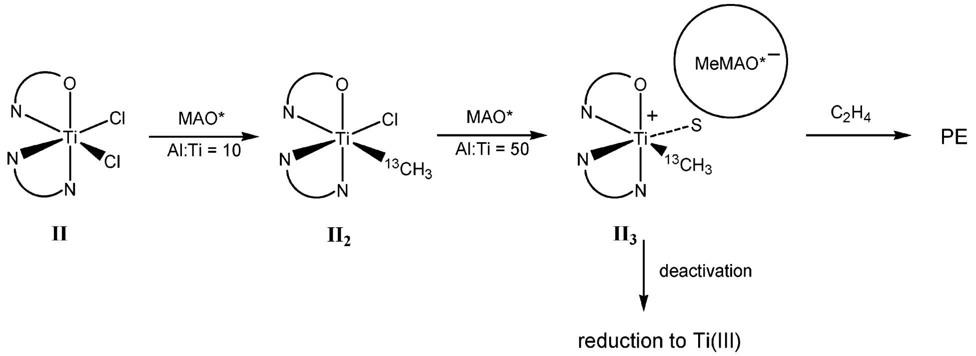

Table 2. Selected ^{13}C and ^{1}H NMR Chemical Shifts (ppm), Line Widths $\Delta\vartheta_{1/2}$ (Hz), Multiplicities, and J^1_{CH} Coupling Constants (Hz) for Complexes II, II$_2$, and II$_3$ in Toluene-d_8/1,2-Difluorobenzene

species	Al:Ti	*T*, °C	^{1}H (N=CH)	^{1}H (Ti−Me)	^{1}H (L′, L)	^{1}H (*t*Bu)	^{13}C (Ti−Me)	^{13}C (*t*Bu)
L'LTiCl$_2$ (**II**)		−20	7.86, 7.78		5.86, 6.22	1.36		*a*
L'LTiClMe (**II$_2$**)	12	−20	8.29 ($\Delta\vartheta_{1/2} = 11$) 7.60 ($\Delta\vartheta_{1/2} = 8$)	1.97 ($\Delta\vartheta_{1/2} = 8$)	n.r.d.^{b}	1.46 ($\Delta\vartheta_{1/2} = 8$)	82.1 ($J^1_{CH} = 127$, $\Delta\nu_{1/2} = 13$)	29.4
L'LTiClMe (**II$_2$**)	12	0	8.21 ($\Delta\vartheta_{1/2}= 27$) 7.66 ($\Delta\vartheta_{1/2} = 21$)	1.97 ($\Delta\vartheta_{1/2} = 25$)	6.16, 6.27	1.48 ($\Delta\vartheta_{1/2} = 25$)	*a*	*a*
[L′LTiMe(S)]$^+$ [MeMAO]$^-$ (**II$_3$**)	50	−20	8.08 ($\Delta\vartheta_{1/2} = 35$) 7.72 ($\Delta\vartheta_{1/2} = 30$)	2.24 ($\Delta\vartheta_{1/2} = 30$)	n.r.d.	1.57 ($\Delta\vartheta_{1/2} = 30$)	102.9	29.9
[L′LTiMe(S)]$^+$ [MeMAO]$^-$ (**II$_3$**)	50	−10	8.08 ($\Delta\vartheta_{1/2} = 20$) 7.72 ($\Delta\vartheta_{1/2} = 20$)	2.27 ($\Delta\vartheta_{1/2} = 18$)	n.r.d.	1.55	102.6 ($\Delta\nu_{1/2} = 27$)	30.0

^{a} Not measured. ^{b} n.r.d. = not reliably detected.

The fraction of the latter increases with increasing Al/Ti ratio. The former peak probably belongs to a free titanium(III) species in solution. The latter signal may be associated with a titanium(III) complex coordinated to bulky MAO molecules, which leads to restricted tumbling of the Ti(III) species. The g_{iso} values of 1.975 are close to those measured for Ti(III) species observed in *ansa*-titanocene/MAO systems.[32]

The II/MAO System. The activation of complex **II** with MAO (Scheme 2) proceeds quite similarly to the system **I**/MAO. At low Al:Ti ratios of 5−15, the monomethylated complex **II$_2$** (L′LTiClMe) is observed (Table 2 and Figure 2a). Since the ligands L′ and L are different in **II**, two separate imine protons are observed for **II$_2$** at temperatures from −60 to +20 °C. Slow exchange (on the NMR time scale) between Ti−Cl and Ti−Me ligands is apparent at −20 °C, since at higher temperatures (e.g., 0 °C, Table 2) rather broader ^{1}H NMR peaks are observed for **II$_2$**.

At higher Al:Ti ratios (≥50), the cationic intermediate [L′LTiMe(S)]$^+$[Me-MAO]$^-$ (**II$_3$**) was detected as the main species (Table 2 and Figure 2b). It is characterized by two separate ^{1}H peaks of imine protons from the salicylaldiminato and pyrrolylaldiminato ligands (δ 8.08 and 7.72 at −20 °C) and the Ti−C*H*$_3$ peak at δ 2.24 (which corresponds to a Ti−^{13}*C*H$_3$ peak at δ 102.9). The widths of NMR lines of **II$_3$** are also temperature sensitive: lowering the temperature to −40 °C results in the disappearance of the imine and Ti−Me ^{1}H signals, whereas at −10 °C **II$_3$** has sharper ^{1}H resonances; thus, at −20 to −10 °C the case of fast exchange (on the NMR time scale) is realized. Again we note that in the **II**/MAO system we could not reliably detect the dimethyl species L′LTiMe$_2$; apparently, once formed, the latter rapidly converts into **II$_3$**.

Like **I$_3$**, intermediate **II$_3$** is thermally unstable and decomposes within 3 h at −10 °C, or within several minutes at +10 °C. However, in the system **II**/MAO we did *not* detect the formation of ligand-to-aluminum transfer products of the type LAlMe$_2$ (vide supra) or L′AlMe$_2$[18] in the course of **II$_3$** decomposition. The main catalyst deactivation pathway in this system therefore appears to be the reduction of Ti(IV) to Ti(III).

The formation of a second cationic titanium−methyl species analogous to **I$_4$** has also not been observed in this system, and we can thus conclude that the heteroligated (salicylaldiminato)(pyrrolylaldiminato) titanium system is much less prone to ligand scrambling than the bis(salicylaldiminato) and bis(pyrrolylaldiminato) catalysts.

The reactivity of **II$_3$** toward ethene was probed by addition of ethene-^{13}C. In agreement with the high reactivity of the **II**/MAO catalyst,[14] even immediately after the injection at −20 °C of 8 equiv of ethene to the sample containing predominantly **II$_3$** (Al:Ti = 50), there were no traces of ethene-^{13}C observed in the ^{1}H NMR spectrum and the Ti−Me peak of **II$_3$** was not apparent any more either. At the same time ^{13}C NMR spectroscopy showed the formation of free ethene oligomers (inner methylene groups at δ 30.6, β and γ carbons of the polymer chain at δ 23.5 and 32.7)[33,34] (see Supporting Information).

In contrast to the bis(salicylaldiminato) system,[18] in the bis(pyrrolylaldiminato) catalyst the Ti−^{13}*C*H$_2$− peak of the titanium−polymeryl moiety was not detected in the ^{13}C NMR spectrum, in part due to fast β-hydrogen elimination and chain transfer processes and, probably, significant line broadening at low temperatures. Spectra of **II**/MAO samples (Al:Ti = 50) recorded at −20 °C after the addition of 8 equiv of ^{13}C$_2$H$_4$ show only a vinyl-terminated ethene oligomer chain (see Supporting Information, Figure S4). The same sample warmed to room temperature and recooled to −20 °C shows the formation of at least one other type of vinyl end groups. A possible explanation

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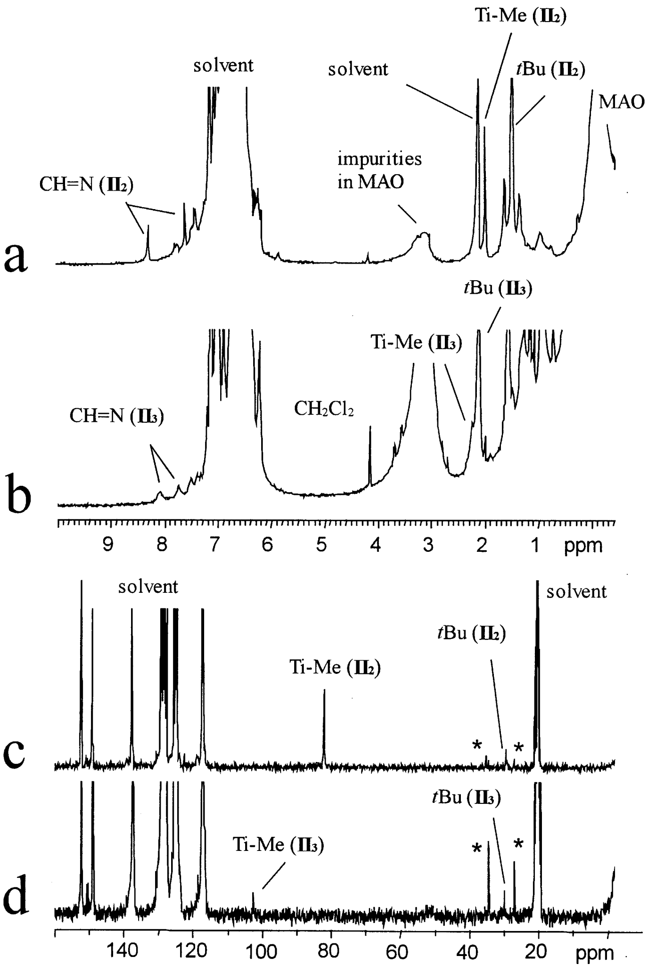

Figure 2. ^1H NMR spectra (−20 °C) of **II**/MAO samples: (a) Al:Ti = 10; (b) Al:Ti = 50. ^{13}C NMR spectra of **I**/MAO-^{13}C samples: (c) Al:Ti = 10, −20 °C; (d) Al:Ti = 50, −10 °C. Asterisks mark impurities in MAO.

for these observations is that at −20 °C some of the oligomeryl chains were released via chain transfer to monomer, which consumes any remaining ethene, while on warming further chain release via β-H elimination takes place.

Conclusions

The formation of cationic species formed in two nonmetallocene catalytic systems based on bis[*N*-phenylpyrrolylaldiminato]titanium(IV) dichloride (L_2TiCl_2, **I**) and [*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato-*N*′-phenylpyrrolylaldiminato]titanium(IV) dichloride (L′LTiCl$_2$, **II**) has been studied. It was found that the first step of the activation of the above catalysts with methylalumoxane (MAO) is the monomethylation to give $L_2TiMeCl$ (**I$_2$**) and L′LTiMeCl (**II$_2$**), respectively, whereas there was little evidence for the formation of titanium dimethyl products. At Al:Ti ratios > 50 these species quantitatively convert to outer-sphere ion pairs of the type $[L_2TiMe(S)]^+[MeMAO]^-$ (**I$_3$**) and $[L'LTiMe(S)]^+[MeMAO]^-$ (**II$_3$**) (where S is a weakly coordinated solvent molecule). These ion pairs have been shown to be active for ethene polymerization.

The two systems follow different deactivation pathways. Species **I$_3$** deactivates predominantly via transfer of a pyrrolylaldiminato ligand to $AlMe_3$, whereas in the mixed-ligand system **II**/MAO such ligand transfer is not evident, and the main deactivation pathway appears to be reduction of Ti(IV) to Ti(III). This absence of ligand scrambling may contribute to the high ethene polymerization activity of catalysts based on **II**.

Experimental Section

All operations were carried out under dry argon by standard Schlenk techniques. Methylalumoxane (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). Ethene-$^{13}C_2$ (99% ^{13}C) was purchased from Aldrich. Toluene-d_8 and 1,2-difluorobenzene were dried over molecular sieves (4 Å), degassed in vacuo, and stored under dry argon. Toluene was distilled over sodium or sodium benzophenone under nitrogen and degassed in vacuo. Solids and toluene-d_8 were transferred and stored in a glovebox. Bis(*N*-phenylpyrrolylaldiminato)titanium(IV) dichloride[2] (L_2TiCl_2, **I**) and [*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato-*N*′-phenylpyrrolylaldiminato]titanium(IV) dichloride[14] (L′LTiCl$_2$, **II**) were prepared as described (one can find its ^1H NMR spectrum in the Supporting information, Figure S1). ^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; 100−2000 transients, 90° pulse at 7 μs. Multiplicities and coupling constants were derived from analysis of gated decoupled spectra. For the acquisition of Ti−$^{13}CH_3$ groups of species **I$_2$**, **II$_2$**, **I$_3$**, **II$_3$**, and **I$_4$**, ^{13}C-enriched MAO was used as activator. 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. $^{13}C,^1H$-correlations were established using double-resonance techniques. For calculations of ^1H and ^{13}C chemical shifts, the resonances of the methyl group of the toluene-d_8 solvent were taken as δ 2.11 and 20.40, respectively. The sample temperature measurement uncertainty and temperature reproducibility were less than ±1 °C. EPR spectra were recorded on a Bruker ER-200D EPR spectrometer at 9.678 GHz in 3 mm outer diameter quartz tubes at room temperature.

Preparation of MAO and Al_2Me_6 Samples. Solid MAO was prepared from commercial MAO (Witko) by removal of the solvent in vacuo at 20 °C for 1 day. 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. $^{13}CH_3$-enriched MAO was prepared by methyl exchange of 99% $^{13}CH_3$-enriched Al_2Me_6 (30 mol % of total Me groups) and solid MAO (70 mol % of total Me groups) in toluene solution followed by subsequent removal of volatiles under vacuum at room temperature to give a sample of ^{13}C-enriched MAO (ca. 30% ^{13}C) with desired Al_2Me_6 content (polymeric MAO with total Al content of 40% and Al as residual Al_2Me_6 ca. 5 wt %). A more detailed description is presented in ref 27.

Preparation of I/MAO and II/MAO (+ethene) Samples. Taking into account that the species of interest (ion pairs **I$_3$**, **I$_4$**, **II$_3$**) have limited solubility in relatively nonpolar toluene and tend to form oily precipitates in the NMR tubes, we increased the solvent polarity by adding 15 vol % of 1,2-difluorobenzene to the solvent.[18,27]

The appropriate amounts of **I** (**II**) and MAO (generally 10^{-5} mol of Ti) were weighed in an NMR tube in a glovebox, and the tube was closed with a septum stopper. Further addition of toluene-d_8 and 1,2-difluorobenzene was performed outside the glovebox with gastight microsyringes in a flow of argon upon appropriate cooling.

^1H NMR (**I$_2$**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 8.04 (1H, $\Delta\vartheta_{1/2} = 30$, C*H*=N), 7.33 (1H, C*H*=N), 6.22 (1H, pyrrol ligand), 2.37 (s, 3H, $\Delta\vartheta_{1/2} = 3$ Hz, Ti−C*H*$_3$). ^{13}C NMR: δ 92.1 (1C, $J^1_{CH} = 125$, $\Delta\nu_{1/2} = 9$ Hz).

^1H NMR (**II$_2$**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 8.29 (1H, $\Delta\vartheta_{1/2} = 11$, C*H*=N), 7.60 (1H, $\Delta\vartheta_{1/2} = 8$, C*H*=N), 1.97 (s, 3H, $\Delta\vartheta_{1/2} = 8$ Hz, Ti−C*H*$_3$), 1.46 (s, 9H, $\Delta\vartheta_{1/2} = 8$ Hz, C(C*H*$_3$)$_3$).

^{13}C NMR: δ 82.1 (1C, $J^1_{\mathrm{CH}} = 127$, $\Delta\nu_{1/2} = 13$, $\mathrm{Ti{-}}C\mathrm{H_3}$), 29.4 (3C, $\mathrm{C(}C\mathrm{H_3)_3}$).

^{1}H NMR (**I$_3$**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 9.0 (2H, $\Delta\vartheta_{1/2} = 100$ Hz, $\mathrm{C}H\mathrm{{=}N}$), 6.0 (2H, $J_{\mathrm{HH}} = 7.5$ Hz, pyrrol ligand), 1.85 (s, 3H, $\Delta\vartheta_{1/2} = 100$ Hz, $\mathrm{Ti{-}C}H_3$). ^{13}C NMR: δ 153.8 (2C, $J^1_{\mathrm{CH}} = 170$ Hz, $C\mathrm{H{=}N}$), 82.0 (1C, $J^1_{\mathrm{CH}} = 125$, $\mathrm{Ti{-}}C\mathrm{H_3}$).

^{1}H NMR (**II$_3$**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 8.08 (1H, $\Delta\vartheta_{1/2} = 35$ Hz, pyrrole-imine $\mathrm{C}H\mathrm{{=}N}$), 7.72 (1H, $\Delta\vartheta_{1/2} = 30$ Hz, phenoxy-imine $\mathrm{C}H\mathrm{{=}N}$), 2.24 (s, 3H, $\Delta\vartheta_{1/2} = 8$ Hz, $\mathrm{Ti{-}C}H_3$), 1.57 (s, 9H, $\mathrm{C(C}H_3\mathrm{)_3}$). ^{13}C NMR: δ 102.9 (1C, $\mathrm{Ti{-}}C\mathrm{H_3}$), 29.9 (3C, $\mathrm{C(}C\mathrm{H_3)_3}$).

Addition of ethene or $^{13}\mathrm{C}_2$-ethene (ethene:Ti = 6 or 8) to the above samples was performed with a gastight syringe by bubbling the gas through the cooled solutions of **I$_3$** and **II$_3$**. The sample was placed in the NMR probe thermostated at −20 °C, and the NMR spectra were run at this temperature and then at higher temperatures, if appropriate.

Upon polymerization of $^{13}\mathrm{C_2H_4}$ by **II$_3$** at −20 °C, warming the sample to room temperature, and recooling to −20 °C, two sets of $^{13}C\mathrm{H_2{=}}$NMR signals corresponding to two types of vinyl end groups ($\mathrm{V_1}$ and $\mathrm{V_2}$) were observed.

^{13}C NMR ($\mathrm{V_1}$, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 146.1 (partly overlapped with toluene, dd, $J^1_{\mathrm{CC}} = 72$ Hz, 42 Hz, $\mathrm{H_2{}^{13}C{=}{}^{13}}C\mathrm{H{-}}$), 110.1 (d, $J^1_{\mathrm{CC}} = 72$ Hz, $\mathrm{H_2{}^{13}}C\mathrm{{=}{}^{13}CH{-}}$), 38.2 (dd, $J^1_{\mathrm{CC}} = 42$ Hz, 33 Hz, $\mathrm{H_2{}^{13}C{=}{}^{13}CH{-}{}^{13}}C\mathrm{H_2{-}}$), 32.7 (unresolved, $-{}^{13}C\mathrm{H_2{-}{}^{13}CH_2{-}{}^{12}CH_3}$), 30.6 (PE×bc $\{-{}^{13}C\mathrm{H_2}-\}_n$), 23.5 (d, $J^1_{\mathrm{CC}} = 34$ Hz, $-\mathrm{{}^{13}CH_2{-}{}^{13}}C\mathrm{H_2{-}{}^{12}CH_3}$).

^{13}C NMR ($\mathrm{V_2}$, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 108.9 (d, $J^1_{\mathrm{CC}} = 72$ Hz, $\mathrm{H_2{}^{13}}C\mathrm{{=}{}^{13}CH{-}}$), 36.7 (broad triplet, $\mathrm{H_2{}^{13}C{=}{}^{13}CH{-}{}^{13}}C\mathrm{H_2{-}}$), 32.7 (unresolved, $-{}^{13}C\mathrm{H_2{-}{}^{13}CH_2{-}{}^{12}CH_3}$), 30.6 (PE×bc $\{-{}^{13}C\mathrm{H_2}-\}_n$), 23.5 (d, $J^1_{\mathrm{CC}} = 34$ Hz, $-\mathrm{{}^{13}CH_2{-}{}^{13}}C\mathrm{H_2{-}{}^{12}CH_3}$).

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Supporting Information Available: ^{1}H NMR spectrum of species LA1Me$_2$, ^{13}C NMR spectra of species **I$_3$**, **I$_4$**; ^{1}H and ^{13}C NMR spectra of species **II$_3$** before and after addition of ethene-^{13}C; and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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