Selective ethylene trimerization by titanium complexes bearing phenoxy-imine ligands with a pendant arm: NMR– and EPR–spectroscopic studies of the reaction intermediates

Jing Ma,[a] Ke-Qing Zhao,[a] Igor E. Soshnikov,[b,c] Nina V. Semikolenova,[b] Vladimir A. Zakharov,[b] Konstantin P. Bryliakov,[b,c] Carl Redshaw[a,d] and Evgenii P. Talsi[*b,c]

[a] College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610066, China.

[b] Boreskov Institute of Catalysis, Pr. Lavrentieva 5, Novosibirsk 630090, Russian Federation

[c] Novosibirsk State University, Pirogova 2, Novosibirsk 630090, Russian Federation

[d] Department of Chemistry, The University of Hull, Cottingham Rd, Hull, HU6 7RX, U.K.

* To whom correspondence should be addressed. Fax: 7 383 3308056. E-mail: talsi@catalysis.ru.

Abstract

The catalyst systems $LTiCl_3$/MAO (L = phenoxyimine ligand with a pendant aryl-O–CH_3 donor arm) display exceptionally high activity in selective ethylene trimerization. By means of NMR and EPR spectroscopy, the nature of the Ti species formed in the catalyst systems $LTiCl_3$/MAO, $LTiCl_3$/MMAO and $LTiCl_3$/AlR_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ (R = Me, Et, ^iBu) has been studied. It was shown that outer-sphere ion pairs of the type $[LTi^{IV}Me_2]^+[A]^-$ ($[A]^- = [MeMAO]^-$, $[MeMMAO]^-$, or $[B(C_6F_5)_4]^-$) are formed at the initial stage of the interaction of the catalyst $LTiCl_3$ with MAO, MMAO and $AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$. These ion pairs further partially convert into Ti^{III} and Ti^{II} species. In the systems $LTiCl_3$/MAO and $LTiCl_3$/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$, complexes with proposed structures $LTi^{III}Me_2$, $LTi^{II}Cl$ and $[LTi^{II}(S)]^+[A]^-$ ($[A]^- = [MeMAO]^-$ or $[B(C_6F_5)_4)]^-$, S = solvent or vacancy) were observed (concentration of Ti^{III} species was lower than that of Ti^{II} congeners). In contrast, in the system $LTiCl_3$/MMAO, concentration of Ti^{III} species (ion pairs of the

type $[LTi^{III}(\mu\text{-H})(\mu\text{-Cl})Al^{i}Bu_2]^{+}[MeMMAO]^{-})$ was higher than that of the Ti^{II} counterparts (ion pairs $[LTi^{II}(S)]^{+}[MeMMAO]^{-}$). The system $LTiCl_3/MMAO$ displays lower selectivity in ethylene trimerization, compared to $LTiCl_3/MAO$, due to undesirable PE formation. Probably, the ion pairs of Ti^{II} participate in ethylene trimerization.

Introduction

Linear α-olefins 1-hexene and 1-octene are important comonomers utilized in the copolymerization with ethylene to generate linear low-density polyethylene. They are produced predominantly via nonselective oligomerization of ethylene. This oligomerization generally yields a broad range of olefins that obey a Schulz–Flory distribution (SHOP process or the Sablin process)[1]. Therefore, catalyst systems that are selective for particular target alkenes would be of great industrial and academic interest. The first process for the selective production of 1-hexene was commercialized in 2003 by Chevron-Phillips[2]. A typical Phillips trimerization catalyst is prepared by combining chromium(III) 2-ethylhexanoate $(Cr(EH)_3)$, 2.5-dimethylpyrrole, triethylaluminum $(AlEt_3)$, and diethylaluminum chloride $(AlEt_2Cl)$.[2,3] In spite of the progress on novel chromium-based catalyst systems capable of the ethylene selective trimerization and tetramerization,[4-7] the Phillips trimerization process remains the only example of the commercial selective trimerization of ethylene.
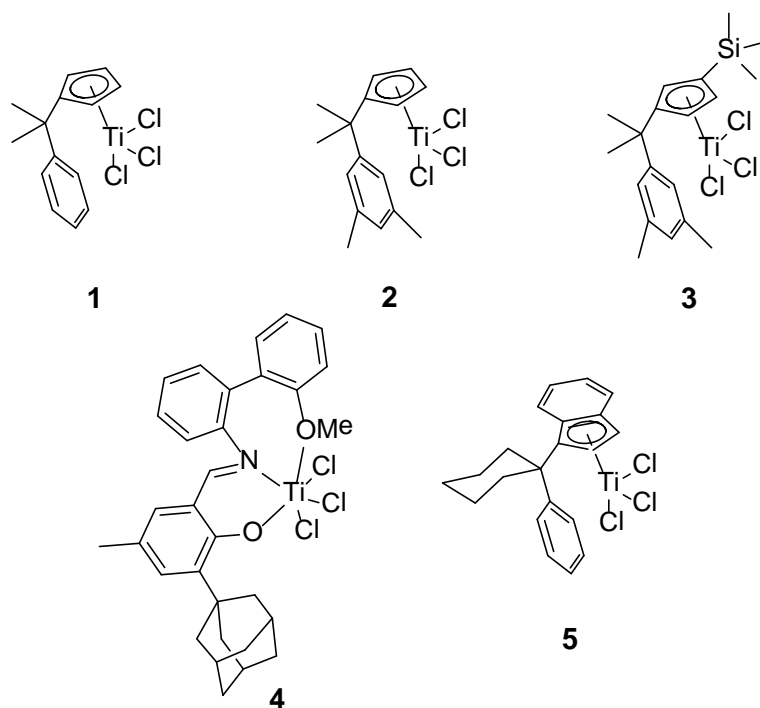
Chart 1. Structures of complexes **1**-**5**.

Hessen and coworkers discovered a new family of titanium based, highly active and highly selective catalyst systems for ethylene trimerization.[8-12] The catalyst system $[(\eta^5\text{-}C_5H_4CMe_2Ph)TiCl_3]$(**1**)/MAO was utilized in toluene (MAO = methylaluminoxane),[8] and the catalysts **2** and **3** bearing substituents at C_5 and C_6 rings (Chart 1) displayed trimerization productivity comparable with that of the parent catalyst **1**.[9] More recently, Fujita, Kawamura and coworkers prepared a titanium(IV) complex **4** bearing a phenoxy-imine ligand with a pendant aryl-OCH_3 donor for selective ethylene trimerization (Chart 1). This complex when activated by MAO produced 1-hexene with exceptionally high activity (up to 132 kg 1-hexene (g Ti)$^{-1}$ h^{-1} bar^{-1}).[13] Very recently, a series of half-sandwich indenyl titanium(IV) complexes bearing a pendant aryl group at the indenyl moiety have been synthesized. Upon activation with MAO, some of these complexes have demonstrated ethylene trimerization activity close to that of **1** (complex **5**, Chart 1).[14]

The disadvantage of chromium and titanium trimerization catalysts is the formation of 2-5 wt. % of high molecular weight polyethylene (PE), which can result in reactor fouling. This is especially true for less temperature stable titanium-based catalyst systems (typical reaction temperatures are 30-80 °C for titanium, and 110-125 °C for chromium catalysts).[10] The nature of activator has a dramatic

effect on the 1-hexene/PE ratio. It was found that for the catalyst system **3**/MAO/C_2H_4, the C_6/PE ratio is 44, whereas for the catalyst system **3**/MAO/Al^{i}Bu$_3$/C_2H_4 this ratio is 17.[10] Thus, additives such as Al^{i}Bu$_3$ tend to promote undesirable PE formation. For the rational improvement of existing trimerization titanium catalysts, a clear understanding of the mechanisms of ethylene trimerization and polymerization is required.

The hypothetical mechanism of ethylene trimerization by the catalysts **1-3** is depicted in Scheme 1.[10] This metallacyclic mechanism is analogous to that proposed for chromium catalysts.[3, 4] It is assumed that ethylene trimerization involving catalyst **4** proceeds via the same mechanism.[13] Unfortunately, attempts to isolate or spectroscopically observe Ti(IV) or Ti(II) species, responsible for ethylene trimerization, have not thus far been successful. The nature of the titanium species, responsible for the undesirable PE formation, is also unclear.

This paper aims at using NMR and EPR spectroscopic monitoring of the Ti(IV), Ti(III) and Ti(II) species formed upon the activation of titanium(IV) phenoxy-imine pre-catalyst **4** with various activators (MAO, MMAO, AlR$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^−$, R = Me, Et, ^{i}Bu), to elucidate possible roles of the observed titanium species during ethylene trimerization and polymerization reactions.
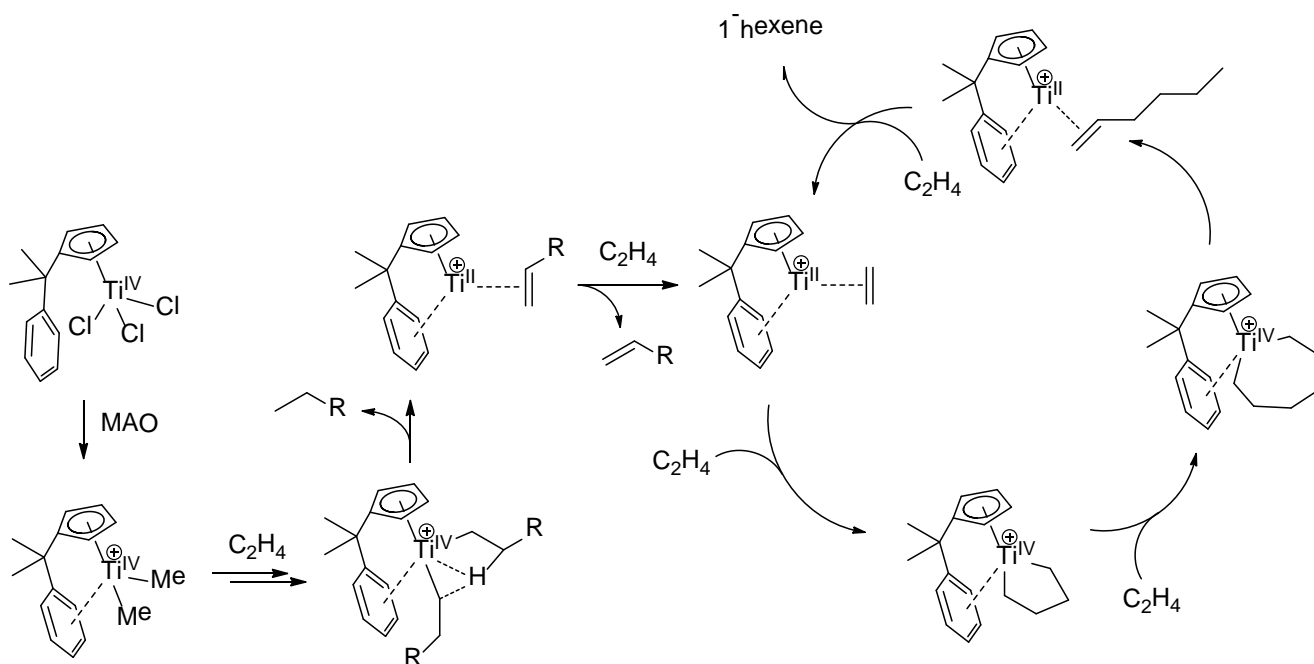
Scheme 1. Proposed metallocyclic mechanism of the selective ethylene trimerization.[10]

Results and discussion

Formation of outer-sphere ion pairs [LTi^{IV}Me₂]⁺[MeMAO]⁻ and [LTi^{IV}Me₂]⁺[B(C₆F₅)₄]⁻ **upon interaction of the pre-catalyst 4 with MAO and AlMe₃/[CPh₃]⁺[B(C₆F₅)₄]⁻.** Generation and NMR spectroscopic characterization of the cation $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ph)TiMe_2]^+$ was first reported by Bochmann and coworkers.[15] Hessen and coworkers have shown that reaction of the neutral complex $(\eta^5\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)TiMe_3$ with the Lewis acid $B(C_6F_5)_3$ affords the ion pair $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)TiMe_2]^+[MeB(C_6F_5)_3]^-$.[11] Later, the ion pair $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)TiMe_2]^+[B(C_6F_5)_4]^-$ was characterized by X-ray crystallography.[12] Crystallographic data confirmed the η^6-coordination of the arene moiety to the titanium centre (Scheme 2). Hagen and coworkers have shown that neutral mono- and dialkylated Ti(IV) complexes $[(\eta^5,\eta^6\text{-}C_5H_4C(Ph)C_5H_{10})TiCl_2Me]$ and $[(\eta^5,\eta^6\text{-}C_5H_4C(Ph)C_5H_{10})TiClMe_2]$ are formed in the course of the interaction of $[(\eta^5,\eta^6\text{-}C_5H_4C(Ph)C_5H_{10})TiCl_3]$ with MAO and AlMe₃.[10] Very recently, Sattler, Labinger and Bercaw have shown that the reaction of **4-Me** (Chart 1) with 1 equiv of $B(C_6F_5)_3$ gives the outer sphere (solvent separated) ion pair [LTi^{IV}Me₂]⁺[MeB(C₆F₅)₃]⁻ (L = phenoxy-imine), which is an effective pre-catalyst for the selective trimerization of ethylene.[16] However, no spectroscopic data on the structure of the intermediates formed upon activation of titanium ethylene trimerization pre-catalysts with MAO were reported.
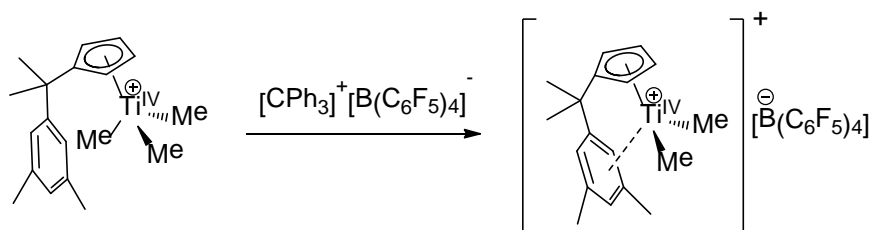
Scheme 2. Preparation of $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)TiMe_2]^+[B(C_6F_5)_4]^-$.

Previously, it was shown that the activation of L_2TiCl_2 with a large excess of MAO (Al/Ti= 25-500, L_2 is a pair of metallocene or post-metallocene ligands) leads to the formation of ion pairs of the type $[L_2TiMe^+\cdots MeMAO^-]$ (**A**), $[L_2TiMe(S)]^+[MeMAO]^-$ (**B**) (S= solvent or vacancy), and $[L_2Ti(\mu\text{-}Me)_2AlMe_2]^+[MeMAO]^-$ (**C**), depending on the structure of L_2.[17,18 and references therein] In the inner-sphere pairs of the type **A**, the non-uniform $MeMAO^-$ counter anions are directly bound to the metal center, whereas in **B** and **C**, $MeMAO^-$ remains in the outer coordination sphere. In effect, the inner-sphere ion pairs **A** are characterized by extremely broad and poorly resolved NMR resonances, while the cationic parts of the outer-sphere ion-pairs **B** and **C** display very sharp and characteristic NMR peaks.[17, 18]

Data on the structure of the ion pairs formed in the $LTiCl_3/MAO$ systems (L = metallocene or post-metallocene ligand) is very restricted. Activation of $Cp*TiMe_3$ or $Cp*TiCl_3$ with a large excess of MAO (Al/Ti > 200) was shown to result in the formation of an inner sphere ion pair of the type **A** $[Cp*TiMe_2^+\cdots MeMAO^-]$ ($Cp* = C_5(CH_3)_5$);[19] ^1H and ^{13}C NMR resonances of this ion pair are very broad and poorly resolved.

In the present work we have found that activation of **4** with MAO results in the formation of an outer-sphere ion pair of type **B** $[LTiMe_2]^+[MeMAO]^-$. The ^1H and ^{13}C NMR characterization of the cationic parts of these species is reported below.

The starting complex **4** displays sharp ^1H and ^{13}C NMR resonances typical for diamagnetic titanium(IV) species (Figure 1a; Table 1, 2). The ^1H resonances for the HC=N and OCH_3 protons of **4** are well separated from other signals and can be used for monitoring the transformations of **4** upon activation. It was found that interaction of **4** with MAO (toluene-d_8, 25 °C, [Al]/[Ti] = 40-300) leads to immediate and quantitative conversion of **4** into the outer-sphere ion pair $[LTi^{IV}Me_2]^+[MeMAO]^-$ (**4a**) (Figure 1b; Table 1, 2, Chart 2). A similar ion pair $[LTi^{IV}Me_2]^+[B(C_6F_5)_4]^-$ (**4a′**) was observed upon the interaction of **4** with $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ (Figure 1c; Table 1, 2, Chart 2). **4a** and **4a′** exhibit the ^1H and ^{13}C NMR resonances of two nonequivalent Ti-CH_3 groups (Figure 1b, 1c; Table 1, 2).

4a   [A]⁻ = [MeMAO]⁻
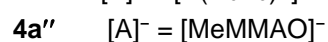**4a′**   [A]⁻ = [B(C₆F₅)₄]⁻
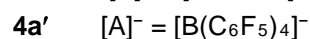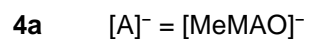**4a″**   [A]⁻ = [MeMMAO]⁻
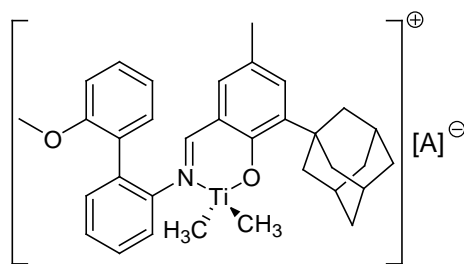
Chart 2. Proposed structures of the cationic Ti(IV) species formed upon the activation of **4** with MAO, AlMe₃/[Ph₃C]⁺[B(C₆F₅)₄]⁻ and MMAO.

When MMAO (MAO modified by Al^{i}Bu₃ additive) was used as an activator, a diamagnetic Ti(IV) species **4a″** was observed only at low temperatures (−30 °C). At higher temperatures, rapid reduction of the Ti(IV) to a low-valence state was observed. The ^{1}H chemical shifts of the HC=N- and O-CH_3-protons of **4a″** (δ 7.41 and 3.74, respectively) are very close to those of **4a** and **4a′** (Table 1). The Ti-CH_3 peaks of **4a″** in the sample **4**/MMAO at −30 °C are masked by the resonances of MMAO; nevertheless, **4a″** can be reasonably assigned to the ion pair [LTi^{IV}Me₂]⁺[MeMMAO]⁻ (Chart 2).

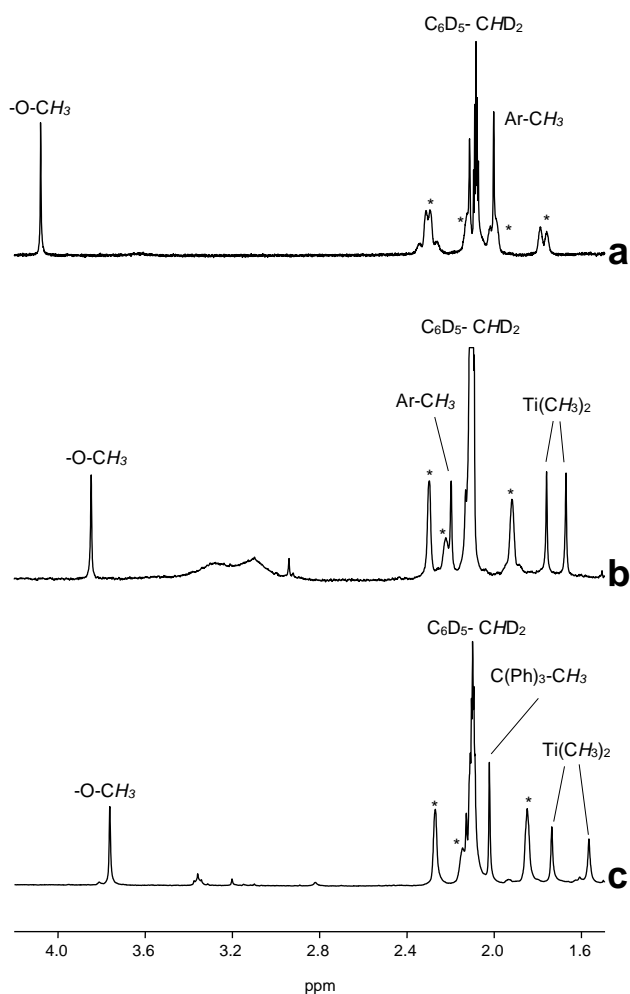**Figure 1.** ^{1}H NMR spectrum (25 °C, toluene-d_8) of **4** (a). ^{1}H NMR spectra (25 °C, toluene-d_8) of the samples **4**/MAO ([Al]/[Ti] = 40, [Ti] = 5×10^{-3} M) (b) and **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ([Al]:[Ti]:[B] = 10:1:1.2, [Ti] = 5×10^{-3} M) (c). The aromatic region is omitted for clarity. Asterisks mark Ada-H signals. The region 2.8÷3.5 ppm in (b) and (c) contains the signals of MAO and AlMe$_3$ oxidation products.

Table 1. ^{1}H NMR parameters for the Ti(IV) complexes formed at the initial stage of the interaction of 4 with MAO, AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and MMAO.[a]

No	species	HC=N	Ar−H	O−CH$_3$	Ada-H (15H)	Ar−CH$_3$	Ti(CH$_3$)$_2$
1	LTiCl$_3$ (**4**)[b]	s, 8.20	m, 10H, 7.63-7.17	s, 4.42	m, 2.33-1.83	s, 2.41	-
2	LTiCl$_3$ (**4**)	s, 7.44	m, 8H, 7.2-6.7	s, 4.08	m, 2.31-1.78	s, 2.01	-
3	[LTiMe$_2$]$^+$[MeMAO]$^-$ (**4a**)	s, 7.46	d, 1H, 6.00 (J^1_{HH}=7.5 Hz) m, 7H, 7.4-6.9	s, 3.84	m, 2.28-1.91	s, 2.19	s, 1.78 s, 1.66
4	[LTiMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**4a′**)	s, 7.58	d, 1H, 6.00 (J^1_{HH}=7.5 Hz) m, 7H, 7.3-6.7	s, 3.75	m, 2.26-1.84	N/A	s, 1.73 s, 1.56
5	[LTiMe$_2$]$^+$[MeMAO]$^-$ (**4a**)[c]	s, 7.38	N/A	s, 3.59	m, 2.32-1.85	s, 2.21	s, 1.74 s, 1.59

| 6 | [LTiMe$_2$]$^+$[MeMMAO]$^-$ (**4a''**)[c] | s, 7.41 | N/A | s, 3.74 | N/A | N/A | N/A |

[a] toluene-d_8, 25 °C, unless otherwise stated. [b] in CH$_2$Cl$_2$. [c] recorded at −30 °C. N/A – not assigned

Table 2. ^{13}C NMR parameters for the Ti(IV) complexes formed at the initial stage of the interaction of 4 with MAO and AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ in toluene.

No	species	HC=N	Ar-C	O−CH$_3$	Ada-C	Ar−CH	Ti(CH$_3$)$_2$
1	LTiCl$_3$ (**4**)[b]	168.87	160-120 (18C)	72.12	29.11 (3C) 36.72 (1C) 36.75 (3C) 40.67 (3C)	20.67	-
2	[LTiMe$_2$]$^+$[MeMAO]$^-$ (**4a**)	174.26	160-120 (18C)	71.03	29.42 (3C) 37.20 (3C) 37.84 (1C) 41.56 (3C)	N/A	85.31 (J^1_{CH}=126 Hz)[c] 82.02 (J^1_{CH}=125 Hz)[c]
3	[LTiMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**4a'**)	174.30	N/A	71.65	29.44 (3C) 37.19 (3C) 37.78 (1C) 41.44 (3C)	N/A	84.35 80.44

[a] toluene-d_8, 25 °C, unless otherwise stated. [b] solution in CH$_2$Cl$_2$. [c] determined using ^{13}C NMR gated decoupling experiment. N/A – not assigned.

The ion pairs [LTi^{IV}Me$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**4a'**) and [LTi^{IV}Me$_2$]$^+$[MeMAO]$^-$(**4a**) prevail in the systems **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and **4**/MAO only at the initial stage of the interaction of **4** with activators and then convert into other titanium species. To elucidate the structure of the latter, we undertook an EPR and NMR spectroscopic study of the interaction of **4** with AlR$_3$ and AlR$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (R = Me, Et, ^{i}Bu).

Ti^{III} species formed upon the interaction of 4 with AlR$_3$ (R = Me, Et, ^{i}Bu). EPR spectra (25 °C, toluene) of the samples **4**/AlR$_3$ (R = Me, Et) at high [Al]/[Ti] ratios (10-100) displayed an intense resonance at g_0= 1.954, $\Delta\nu_{1/2}$= 10 G, typical for Ti(III) species (Figure 2a, b). In the EPR spectrum of the sample **4**/Al^{i}Bu$_3$ ([Al]/[Ti]= 10), a similar resonance at g_0= 1.953 was observed (Figure 2c).
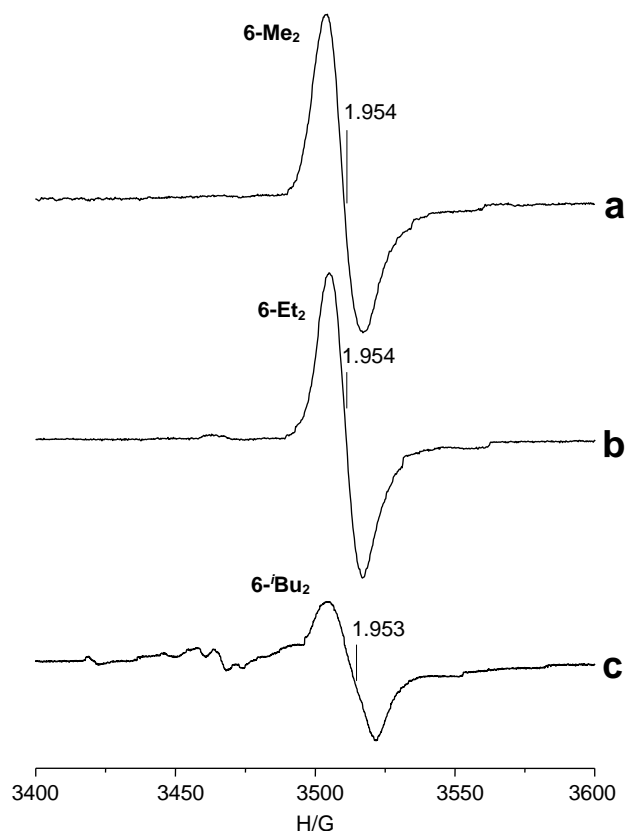
Figure 2. EPR spectra (25 °C, X-band, toluene) of various systems: **4**/AlMe$_3$ ([Al]:[Ti] = 10, [Ti] = 5×10^{-3} M) (a); **4**/AlEt$_3$ ([Al]:[Ti] = 10, [Ti] = 5×10^{-3} M) (b); **4**/Al^{i}Bu$_3$ ([Al]/[Ti] = 10, [Ti] = 5×10^{-3} M) (c).

The maximum concentration of the Ti^{III} species observed in the systems **4**/AlR$_3$ (R = Me, Et) was about 20 % of the titanium content, whereas in the system **4**/Al^{i}Bu$_3$ this concentration reached 70 % of the titanium content. We assume that the Ti^{III} species observed in the catalyst systems **4**/AlR$_3$ at high [Al]/[Ti] ratios are dialkylated complexes of the form LTi^{III}R$_2$ (**6-R$_2$**) (Chart 3).
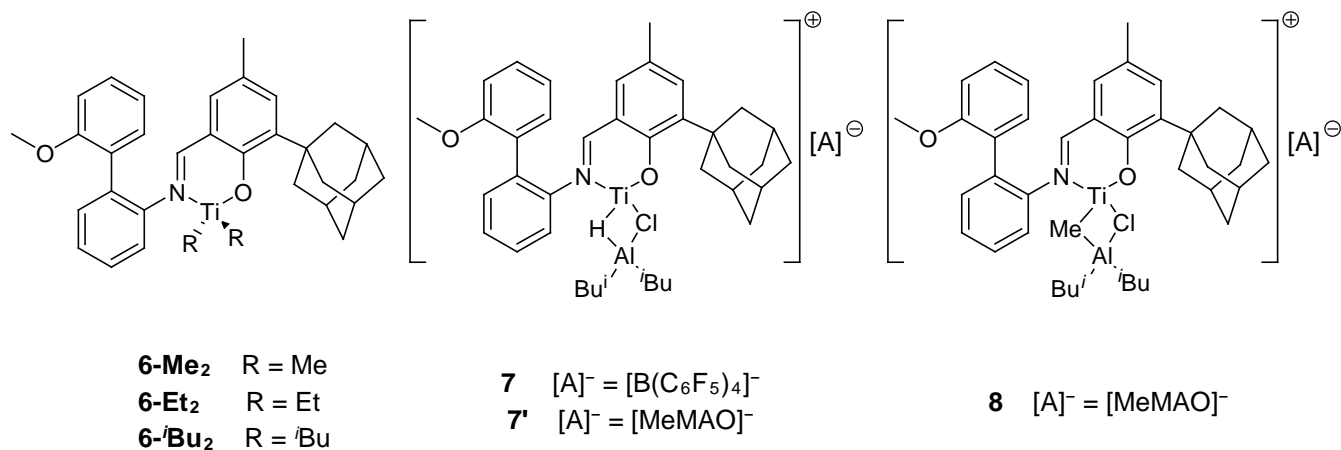

Chart 3. Proposed structures of the Ti(III) species observed in the present work.

Ti^{III} species formed upon interaction of 4 with AlR$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and AlR$_3$/MAO (R = Me, Et, ^{i}Bu). The addition of MAO to the systems **4**/AlMe$_3$ and **4**/AlEt$_3$ ([Al]/[Ti] = 10) did not considerably change the observed signal of **6-R$_2$** (R = Me, Et).

The EPR spectra of the systems **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and **4**/AlEt$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ([Al]:[Ti]:[B] = 10:1:1.2, [Ti] = 5×10^{-3} M) displayed an intense multi-line signal of the free radical Ph$_3$C$^\bullet$ at g_0= 2.003, and a weak signal of **6-R$_2$** at g_0 = 1.954 just after mixing the reagents at 25 °C. No other Ti(III) species were observed. The concentration of Ti^{III} species (**6-R$_2$**) in the systems **4**/AlR$_3$/MAO and **4**/AlR$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (R = Me, Et) did not exceed 10 % of the titanium content.

In contrast, the addition of [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ to the sample **4**/Al^{i}Bu$_3$ ([Al]/[Ti] = 10) led to a decrease of the EPR resonance of **6-^{i}Bu$_2$** (g_0= 1.953) and formation of two new signals, namely a weak multi-line signal for the triphenylmetyl radical Ph$_3$C$^\bullet$, and an intense signal at g_0= 1.975 from a new complex **7** (Figure 3a). The EPR signal of **7** exhibits a hyperfine splitting (a_H= 5 G) from one proton (Figure 3a, insert), and can be assigned to a cationic hydride complex of Ti(III).

We propose the alkylaluminum-complexed structure [LTi^{III}(μ-H)(μ-Cl)Al^{i}Bu$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ for the titanium hydride cationic species **7** (Chart 3), similar structures have been previously reported for neutral and cationic Zr^{IV} and Zr^{III} hydride species.[20-22] The evaluated concentration of **7** is more than 50 % of the initial concentration of **4**.

The addition of MAO to the sample **4**/Al^{i}Bu$_3$ resulted in the appearance of two intense resonances at g_0 = 1.975 and 1.986 (Figure 3b). The resonance at g_0 = 1.975 coincided with that of **7** and can be assigned to the ion pair [LTi^{III}(μ-H)(μ-Cl)Al^{i}Bu$_2$]$^+$[MeMAO]$^-$ (**7′**). The resonance at g_0 = 1.986 belongs to a new complex **8**. In contrast to **7** and **7′**, complex **8** displayed no hyperfine splitting from hydrogen and can be assigned to the ion pair [LTi^{III}(μ-Me)(μ-Cl)Al^{i}Bu$_2$]$^+$[MeMAO]$^-$ (Chart 3). The EPR spectrum of the system **4**/MMAO is similar to that for the system **4**/Al^{i}Bu$_3$/MAO, and exhibits resonances analogous to **7′** and **8**. The concentration of the Ti^{III} species in the systems

4/Al^{i}Bu$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, 4/Al^{i}Bu$_3$/MAO, and 4/MMAO exceeded 50 % of the total titanium content.
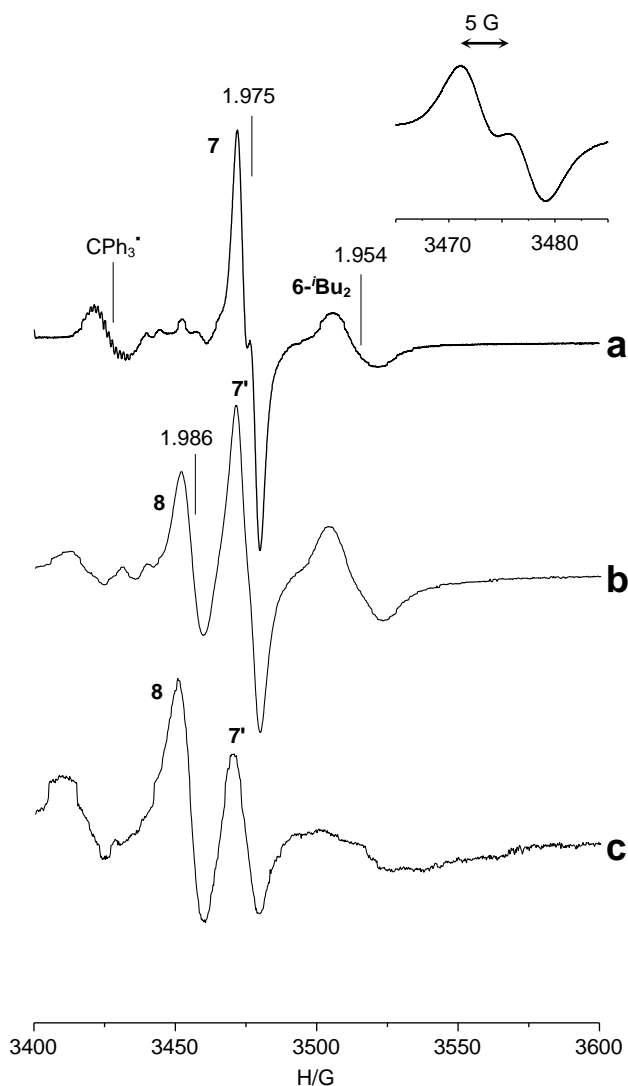
Figure 3. EPR spectra (25 °C, X-band, toluene) of the samples 4/Al^{i}Bu$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)]$_4^-$ ([Ti]:[Al]:[B] = 1:10:1.2, [Ti] = 5×10^{-3} M) (a); 4/Al^{i}Bu$_3$/MAO ([4]:[Al^{i}Bu$_3$]:[MAO] = 1:10:40, [Ti] = 5×10^{-3} M) (b); 4/MMAO ([Al]/[Ti] = 10, [Ti] = 5×10^{-3} M) (c) . Insert shows the expanded resonance of 7.

From the above studies, it is clear that the systems 4/Al^{i}Bu$_3$/MAO, 4/Al^{i}Bu$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and 4/AlMe$_3$/MAO, 4/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ sharply differ in the nature and concentration of the Ti^{III} species present in the reaction solution. In the first two systems, the total concentration of Ti^{III} species (ion pairs 7, $7'$ and 8) is more than 50 % of the total titanium content, while in the second two systems, only a minor part of the titanium (less than 10 %) exists in the reaction solution in the form of Ti^{III} species (neutral complex 6-Me$_2$).

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Ti^{II} species formed upon interaction of 4 with AlR$_3$ (R = Me, Et). The ^{1}H NMR spectrum (toluene-d_8, 25 °C) of the sample **4**/AlMe$_3$ ([Al]:[Ti] = 5:1) recorded 10 min after mixing the reagents at 25 °C displayed broadened and paramagnetically shifted resonances falling within the range -20 to +20 ppm, which can be ascribed to high-spin Ti^{II} complexes[23] (complexes **9** and **10**, Figure 4a). Complex **9** prevails in the sample at a low [Al]:[Ti] ratio (≤ 5). Some of the resonances of complex **9** in the range δ -5…+10 overlapped with the resonances of diamagnetic species present in the reaction mixture. Using the inversion-recovery experiments with 25 ms delay between 180° and 90° pulses, we have assigned the broad resonance at δ 2 (15H) to adamantyl protons of **9**. On the basis of integration, the resonances of **9** at δ 14.5 (3H), -6.81 (3H), -10.1 (1H) and -13.1 (1H) were assigned to O-CH_3, Ar-CH_3 and aromatic protons (Ar-H) of the phenolic moiety of the phenoxyimine ligand (Figure 4a), <mark>respectively.</mark>
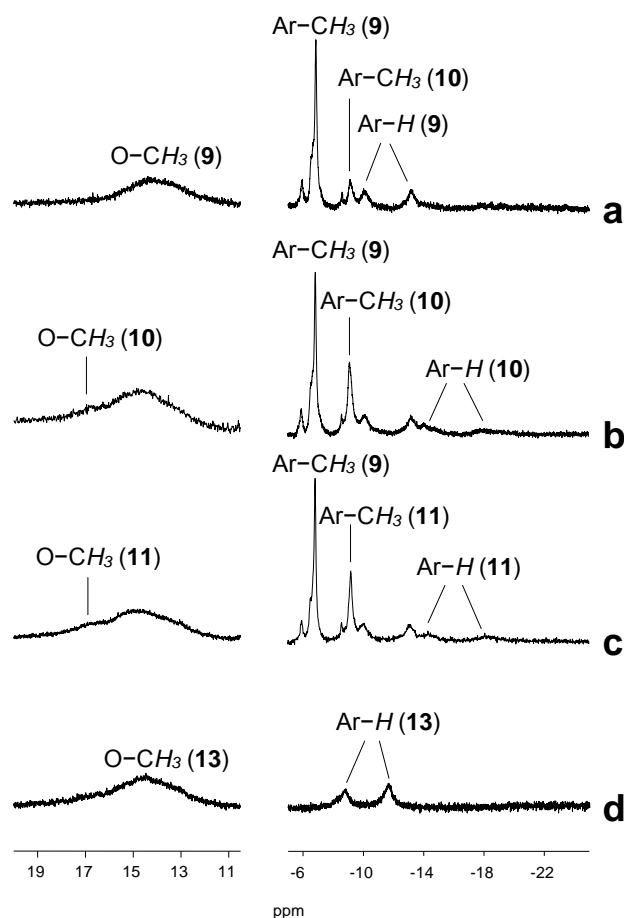
Figure 4. ^{1}H NMR spectra (25 °C, toluene-d^8) of the samples **4**/AlMe$_3$ ([Al]/[Ti] = 5, [Ti] = 5×10^{-3} M) (a); **4**/AlMe$_3$ ([Al]/[Ti] = 15, [Ti] = 5×10^{-3} M) (b); **4**/AlEt$_3$ ([Al]/[Ti] = 5, [Ti] = 5×10^{-3} M) (c); **12**/AlMe$_3$ ([Al]/[Ti] = 5, [Ti] = 5×10^{-3} M) (d).

Upon increasing the [Al]:[Ti] ratio up to 15:1, resonances of a new complex **10** grew at the expense of those of **9** (Figure 4b). As in the case of **9**, the resonances at δ 17.0, -9.1, -14.3 and -18 can be assigned to O-C*H$_3$*, Ar-C*H$_3$* and Ar-*H* protons of **10**, respectively. Most probably, **9** and **10** are the complexes LTi^{II}Cl and LTi^{II}Me (Chart 4).

It can be expected, that the system **4**/AlEt$_3$, similar to the system **4**/AlMe$_3$, will display resonances of complexes LTi^{II}Cl and LTi^{II}Et (**11**). In agreement with this assumption, the ^{1}H NMR spectrum of the sample **4**/AlEt$_3$ ([Al]/[Ti] = 5) exhibited resonances of **9**, and those almost identical to the resonances of **10**, which can be ascribed to complex **11** (Figure 4c, Chart 4). Not surprisingly, the replacement of Ti-Me by Ti-Et (when passing from **10** to **11**) did not essentially change the chemical shifts of the protons which are rather far from the Ti-R moiety.
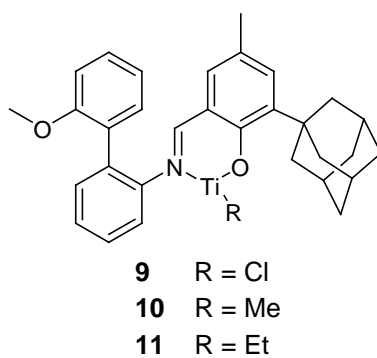

9	R = Cl
10	R = Me
11	R = Et

Chart 4. Proposed structures of the Ti(II) species **9**-**11** observed in the present work.

To support the assignment of the resonance at δ -6.81 to Ar-C*H$_3$* protons of **9**, we have synthesized the titanium(IV) complex L$_1$Ti^{IV}Cl$_3$ (**12**) analogous to **4**, but without the Ar-CH$_3$ substituents present in the phenolic moiety (Chart 5). The ^{1}H NMR spectrum of the sample **12**/AlMe$_3$ ([Al]/[Ti] = 5) in the range -15…0 ppm displayed only resonances at δ -8.75 (1H) and -11.8 (1H), which can be assigned to aromatic protons of the phenolic moiety of L$_1$Ti^{II}Cl (**13**) (Chart 5; Figure 4d).
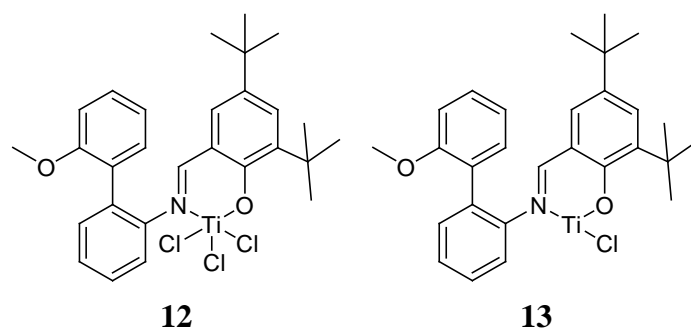
Chart 5. Proposed structures of the complexes **12** and **13**.

In contrast to the samples **4**/AlMe$_3$ and **4**/AlEt$_3$, the formation of Ti^{II} species was not observed in the reaction of **4** with Al^{i}Bu$_3$. The greater ability of AlEt$_3$ to 'over-reduce' Ti^{IV} into Ti^{II} compared to that of Al^{i}Bu$_3$ was previously reported for the MgCl$_2$/ethylbenzoate/TiCl$_4$-AlR$_3$ catalyst systems.[24]

The addition of ethylene to the NMR tubes containing complexes **9**, **10** or **11** showed that they are not able to perform either trimerization or polymerization of ethylene. It was proposed previously, that ion pairs [LTi^{II}]$^+$[MeMAO]$^-$ can be responsible for trimerization of ethylene.[9] We have attempted a search of species of this type in the catalyst system **4**/MAO and **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$.

Cationic Ti^{II} species formed upon the interaction of 4 with AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, MAO and MMAO. It was found that after mixing **4** and AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ for 5 min at 25 °C, the spectrum of the sample **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ([Ti]:[Al]:[B] = 1:10:1.3) displayed resonances of, **4a′**, **9**, and those of a new complex **14** (Figure 5a). **14** exhibited a broad resonance near δ -6.7, and weaker resonances at δ -9.2. Upon storing the sample for 30 min at 25 °C (Figure 5b), resonances of **14** dropped in intensity, whilst those associated with **9** increased.

It is proposed that **14** is an ion pair of the type [LTi^{II}(S)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (S = solvent or vacancy) (Chart 6). The resonances at δ -6.7 can be assigned to Ar-CH_3 protons of **14**. In agreement with this assumption, the interaction of **4** with other cationizing reagents MAO and MMAO resulted in the formation of the complexes **14′** and **14″**, respectively. These complexes exhibited a broad Ar-CH_3

resonance at δ -6.7, resembling that of **14**. Complexes **14′** and **14″** can be assigned to the ion pairs

$[LTi^{II}(S)]^+[MeMAO]^-$ and $[LTi^{II}(S)]^+[MeMMAO]^-$ (Chart 6).
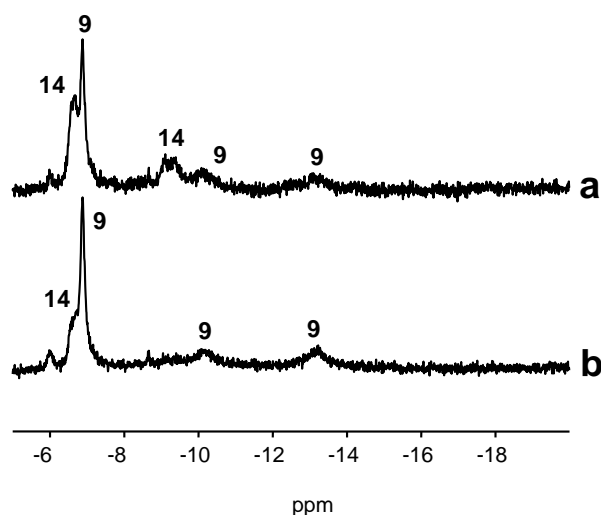
Figure 5. ^1H NMR spectra (25 °C, toluene-d^8) of the sample **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (([Ti]:[Al]:[B] = 1:10:1.3, [Ti] = 5×10^{-3} M): 5 min after reagents mixing at 25 °C (a); 30 min after reagents mixing at 25 °C (b).
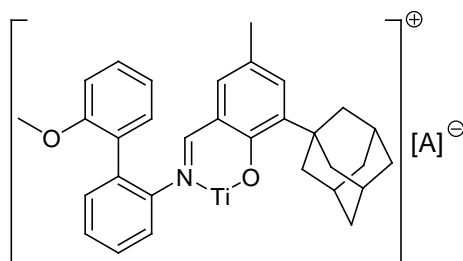
14	$[A]^- = [B(C_6F_5)_4]^-$
14′	$[A]^- = [MeMAO]^-$
14″	$[A]^- = [MeMMAO]^-$

Chart 6. Proposed structures of the complexes **14**, **14′**, and **14″**.

Trimerization and polymerization of ethylene with catalysts systems 4/MAO, 4/MMAO and 4/AlMe₃/[Ph₃C]⁺[B(C₆F₅)]₄⁻. The results of ethylene trimerization and polymerization studies of the catalyst **4** activated with various co-catalysts are presented in Table 3. When compared with MAO, the catalyst system **4**/MMAO produces a much larger amount of PE, and smaller amounts of 1-hexene (run 3, Table 3). The systems **4**/AlR$_3$ (R = Me, Et, ^{i}Bu) were almost inactive toward ethylene

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polymerization or trimerization (runs 6-8, Table 3). The catalyst systems **4**/MAO(20) and **4**/MAO, containing no Al^{i}Bu$_3$ (runs 1 and 2, Table 3), were the best for 1-hexene production.

Table 3. Ethylene trimerization and polymerization data for complex 4, activated with MAO, MMAO, and AlR$_3$ (R = Me, Et, ^{i}Bu)^a.

run	co-catalyst	m $_{1\text{-hexene}}$, g	m C$_{10}$, g ^{b}	m PE, g	1-hexene selectivity, %	1-hexene productivity, kg C$_6$/(g Ti·h)
1	MAO(20)^c	3.5	0.2	<0.1	92	32
2	MAO	3.5	0.2	0.6	82	35
3	MMAO	2.7	0.1	1.3	66	25
4	MAO^d	2.2	0.2	0.5	76	22
5	MMAO^d	0.7	0.1	1.0	29	6
6	AlMe$_3$	0	0	traces	0	0
7	AlEt$_3$	0	0	traces	0	0
8	Al^{i}Bu$_3$	0	0	traces	0	0
	AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$	Data will be added				
	Al^{i}Bu$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$	Data will be added				

^{a} Experimental conditions: 1.5-2.5 μmol Ti, [Al]/[Ti]= 500, 50 °C, 50 ml of the solvent (toluene the runs 1, 2, 4, 6, 7 and heptane in runs 3, 5, 8), ethylene pressure 10 bar. ^{b} 2-butyl-1-hexene, a side product of the ethylene trimerization.[13] ^{c} MAO(20) has been prepared by vacuum distillation of the commercial MAO sample at 20 °C. This co-catalyst contains ~10 mol. % of Al as AlMe$_3$. ^{d} Co-catalyst and complex **4** were preliminarily mixed and stored 20 min before injection into the reactor.

As shown above, in the catalyst system **4**/MMAO, the major part of the titanium exists in the reaction solution in the form of Ti(III) species, whereas in the system **4**/MAO, the concentration of Ti(III) species is low. Cationic, tetravalent group 4 metallocene and post-metallocene complexes of the type [L$_2$Ti^{IV}Me]$^+$[MeMAO]$^-$ are now well established as active α-olefin polymerization catalysts. Ti^{III} species formed upon activation of titanocene or post-titanocene polymerization catalysts L$_2$TiCl$_2$ with MAO are apparently inactive in such processes.[25, 26] For half-sandwich complexes Cp*TiCl$_3$, the mechanistic landscape is more controversial. Indeed, both Ti(III) and Ti(IV) cationic complexes were proposed as active species of styrene polymerization.[27-30]

Our NMR-tube experiments show that ethylene addition (~500 eq.) at 25 °C to the sample **4**/MMAO containing predominantly Ti(III) complexes of the type **7** and **8** (Figure 3c, Chart 5) leads to immediate ethylene polymerization, and only traces of 1-hexene are formed. Therefore, the assumption that Ti^{III} species $[LTi^{III}(\mu\text{-H})(\mu\text{-Cl})Al^iBu_2]^+[A]^-$ and $[LTi^{III}(\mu\text{-Me})(\mu\text{-Cl})Al^iBu_2]^+[A]^-$ ($[A]^-$ = $[MeMAO]^-$ and $[MeMMAO]^-$) can promote the generation of PE by the catalyst system **4**/MMAO seems to be plausible.

The proposed mechanism of the 1-hexene formation assumes shuttling between cationic Ti^{II} and Ti^{IV} species (Scheme 1). For the catalyst systems **4**/MAO and **4**/MMAO, we have reliably characterized only the starting ion pairs $[LTi^{IV}Me_2]^+[MeMAO]^-$ (**4a**) and $[LTi^{IV}Me_2]^+[MeMMAO]^-$ (**4a″**). At 25 °C, the ion pair **4a** is stable over 1 h, whereas **4a″** rapidly converts into Ti^{III} species. To confirm the participation of $[LTi^{IV}Me_2]^+$ species in the selective trimerization of ethylene, we have carried out catalytic experiments by premixing **4** with activator (20 min at 25 °C, runs 4 and 5, Table 3). The premixing leads to a decrease in 1-hexene yield (by a factor of 4 for the system **4**/MMAO, and by a factor of 1.6 for the **4**/MAO analogue), with the more pronounced negative effect of premixing observed for the **4**/MMAO system correlating with a more rapid decay of the $[LTi^{IV}Me_2]^+$ species. The NMR-tube experiments have shown that addition of ethylene to the samples **4**/MAO and **4**/AlMe₃/$[Ph_3C]^+[B(C_6F_5)_4]^-$ leads to the rapid decrease of the concentration of **4a** and **4a'**, and formation of 1-hexene even at -30 °C.

The results herein indicate that ion pairs **4a**, **4a′** and **4a″** are the likely precursors of the active sites for ethylene trimerization. It is assumed that in the course of the reaction, these ion pairs transform into ion pairs of the type $[LTi^{II}]^+[MeMAO]^-$, which operate in the catalytic cycle of ethylene trimerization (Scheme 1).[10] In this work, we have observed Ti^{II} complexes **14′** of proposed structure $[LTi^{II}(S)]^+[MeMAO]^-$ (S = solvent or vacancy). Further studies are needed to verify the key role of this type of species in the selective trimerization of ethylene.

Conclusions

The interaction of 'pendant-arm' complexes $LTi^{IV}Cl_3$, capable of efficient and selective ethylene trimerization to 1-hexene, with various activators was studied using NMR and EPR spectroscopy. At the initial stage of the interaction of $LTi^{IV}Cl_3$ with $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$, MAO or MMAO, outer-sphere ion pairs $[LTi^{IV}Me_2]^+[A]^-$ are formed ($[A]^- = [B(C_6F_5)_4]^-$, $[MeMAO]^-$ and $[MeMMAO]^-$) that further partially transform into Ti^{III} and Ti^{II} species. In the catalyst systems $LTi^{IV}Cl_3/AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ and $LTi^{IV}Cl_3/MAO$, complexes with proposed structures $LTi^{III}Me_2$, $LTi^{II}Cl$ and $[LTi^{II}(S)][A]^-$ ($[A]^- = [B(C_6F_5)_4]^-$ or $[MeMAO]^-$) were found. In the system $LTi^{IV}Cl_3/MMAO$, complexes with proposed structures $[LTi^{III}(\mu\text{-}H)(\mu\text{-}Cl)Al^iBu_2]^+[MeMMAO]^-$, $LTi^{II}Cl$ and $[LTi^{II}(S)][MeMMAO]^-$ were observed. In the first two systems, the concentration of Ti^{III} species ($LTi^{III}Me_2$) was smaller than the concentration of Ti^{II} species ($LTi^{II}Cl$ and $[LTi^{II}(S)]^+[A]^-$), whereas in the latter system, the concentration of Ti^{III} species ($[LTi^{III}(\mu\text{-}H)(\mu\text{-}Cl)Al^iBu_2]^+[MeMMAO]^-$) was much higher than that of the Ti^{II} counterparts ($LTi^{II}Cl$ and $[LTi^{II}(S)]^+[MeMMAO]^-$). The system $LTi^{IV}Cl_3/MMAO$ demonstrates a lower ethylene trimerization activity than the system $LTi^{IV}Cl_3/MAO$, which correlates with the lower concentration of Ti^{II} species in the former system. It is likely that cationic cationic Ti^{II} species of the type $[LTi^{II}(S)][A]^-$ are responsible for ethylene trimerization.

EXPERIMENTAL SECTION

General experimental data

All manipulations of air- and/or moisture-sensitive compounds were performed under an atmosphere of argon using glovebox, break-sealed or standard Schlenk techniques. Toluene and hexanes were dried over molecular sieves (4 Å) and distilled over sodium metal under argon. CH_2Cl_2 was dried over P_2O_5 and distilled under argon. Toluene-d^8 was dried over molecular sieves (4 Å) and distilled under argon. Complex **4** was synthesized according to published procedures with minor deviations.[13] A commercial sample of MAO was purchased from Crompton as toluene solution with a

total Al content 1.8 M and Al as $AlMe_3$ 0.5 M, MMAO purchased from AKZO as heptane solution (total Al content 7.1 wt.%), Al^iBu_3 (1.1 M toluene solution), $AlMe_3$ (100 %), $AlEt_3$ (100 %), and $[CPh_3]^+[B(C_6F_5)_4]^-$ were purchased from Aldrich. $AlMe_3$ and $AlEt_3$ toluene solutions used for spectroscopic and trimerization experiments were prepared by dilution of the neat $AlMe_3$ and $AlEt_3$. For the NMR and EPR experiments, solid MAO(20) with a total Al content of 40 wt % and ca. 10 % (mol.) of Al as $AlMe_3$ (obtained by removal of the solvent under vacuum at 20 °C from the commercial MAO) was used.

NMR and EPR experiments

Samples for NMR and EPR experiments were prepared in the glovebox. For the NMR-tube ethylene trimerization experiments the break-sealed technique was used.

^1H and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz NMR spectrometer at 400.130 and 100.613 MHz, respectively, using 5 mm o.d. glass NMR tubes. Chemical shifts were referenced to residual solvent peak, 2.09 ppm for CD_2H proton resonance of toluene. EPR spectra were measured on a Bruker ER-200D spectrometer at 9.3 GHz, modulation frequency 100 kHz, modulation amplitude 4 G. Periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+}, which served as a side reference, was placed into the second compartment of the dual cavity. EPR spectra were quantified by double integration with $Cu(acac)_2$ toluene/chloroform (3:2) solution as standard. The relative accuracy of the quantitative EPR measurements was ±30 %.

Formation of the complex **4a** during interaction of **4** with MAO(20).

MAO(20) (6.0 mg, 80 µmol) was suspended in the dry toluene-d^8 (0.5 ml). After addition of **4** (1.2 mg, 2.0 µmol), the sample was mixed and immediately placed in the NMR probe. ^1H NMR (δ, toluene-d^8, 25 °C): 7.46 (s, 1H, HC=N), 7.4-6.9 (m, 7H, Ar-H), 6.00 (d, 1H, Ar-H, J_{HH} = 7.5 Hz), 3.84 (s, 3H, O-CH_3), 2.28-1.91 (m, 15H, Ada-H), 2.19 (s, 3H, Ar-CH_3) 1.78 (s, 3H, Ti*Me*Me'), 1.66 (s, 3H, TiMe*Me'*). $^{13}C\{^1H\}$ NMR (δ, toluene-d^8, 25 °C): 174.26 (1C, HC=N), 160-120 (18C, Ar-C), 85.31 (1C, TiMe*Me'*), 82.02 (1C, Ti*Me*Me'), 71.03 (1C, O-CH$_3$), 41.56 (3C, Ada-C), 37.84 (1C, Ada-C),

37.20 (3C, Ada-C), 29.42 (3C, Ada-C). The Ar-CH_3 resonance was not observed due to overlapping with the resonances of the toluene-d^8 CD$_3$-group.

Formation of the complex **4a'** during interaction of **4** with AlMe$_3$ and [CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$.

[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (2.8 mg, 3.0 µmol) and pure AlMe$_3$ (2.5 µl, 25 µmol) were mixed in dry toluene-d^8 (0.5 ml). After addition of **4** (1.5 mg, 2.5 µmol), the sample was mixed and immediately placed in the NMR probe. ^{1}H NMR (δ, toluene-d^8, 25 °C): 7.58 (s, 1H, HC=N), 7.3-6.7 (m, 7H, Ar-H), 6.00 (d, 1H, Ar-H, J_{HH} = 7.5 Hz), 3.75 (s, 3H, O-CH_3), 2.26-1.84 (m, 15H, Ada-H), 1.73 (s, 3H, TiMeMe'), 1.56 (s, 3H, TiMeMe'). ^{13}C{^{1}H} NMR (δ, toluene-d^8, 25 °C): 174.30 (1C, HC=N), 84.35 (1C, TiMeMe'), 80.44 (1C, TiMeMe'), 71.65 (1C, O-CH$_3$), 41.44 (3C, Ada-C), 37.78 (1C, Ada-C), 37.19 (3C, Ada-C), 29.44 (3C, Ada-C). The Ar-C were not readily assigned due to overlapping with the CPh$_3$CH$_3$ resonances. The Ar-CH_3 resonance was not observed due to overlapping with the resonances of the toluene-d^8 CD$_3$-group.

Formation of the complex **4a''** during interaction of **4** with MMAO.

The interaction of **4** with MMAO at room temperature leads to the immediate reduction of Ti(IV) to the trivalent state. Given this, the interaction of **4** with MMAO was studied at −30 °C. Complex **4** (1.2 mg, 2.0 µmol) was placed into the NMR tube and carefully (without mixing!) covered by dry toluene-d^8. A 1.8 M solution of MMAO in heptanes (44 µl, 20 µmol) was added, and the NMR tube was covered by a rubber septa, and cooled in liquid N$_2$. The sample was mixed at low temperature and placed in the NMR probe, cooled to −30 °C. The concentration of the complex **4a''** was very low, and only resonances of HC=N and O-CH_3 were observed. ^{1}H NMR (δ, toluene-d^8, −30 °C): 7.41 (s, 1H, HC=N), 3.74 (s, 3H, O-CH_3).

Formation of the complexes **6-R$_2$** during interaction of **4** with AlR$_3$ (R = Me, Et, ^{i}Bu).

Complex **4** (1.2 mg. 2.0 µmol) was added to a toluene solution of AlR$_3$ (20 µmol). The sample was mixed, placed in the EPR spectrometer, and the EPR spectra were recorded at 25 °C. The EPR parameters were as follows: g$_0$ = 1.954 for **6-Me$_2$** and **6-Et$_2$**, and g$_0$ = 1.953 for **6-^{i}Bu$_2$**.

Formation of the complex **7** during interaction of **4** with Al^{i}Bu$_3$ and [CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$.

[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (2.2 mg, 2.4 µmol) and a 1.1 M Al^{i}Bu$_3$ solution in toluene (18 µl, 20 µmol) were mixed in dry toluene (0.5 ml). After addition of **4** (1.2 mg, 2.0 µmol), the sample was mixed and placed in the EPR spectrometer. EPR (25 °C): g_0 = 1.975, a_H = 5 Gs.

Formation of the complexes **7'** and **8** during interaction of **4** with Al^{i}Bu$_3$ and MAO(20).

MAO(20) (6.0 mg, 80 µmol) and a 1.1 M Al^{i}Bu$_3$ solution in toluene (18 µl, 20 µmol) were suspended in dry toluene (0.5 ml). After addition of **4** (1.2 mg, 2.0 µmol), the sample was mixed and placed in the EPR spectrometer. EPR parameters are as follows (25 °C): complex **7'**: g_0 = 1.975 (unresolved hfs from H); complex **8**: g_0 = 1.986.

Ethylene trimerization experiments

Ethylene trimerization was performed in a steel 0.3 L reactor. Complex **4** was introduced into the autoclave in an evacuated sealed glass ampoule. The reactor was evacuated at 80 °C, cooled down to 20 °C and then charged with the freshly prepared solution of the desired co-catalyst in toluene or hexanes (50 ml). After setting up the polymerization temperature (50 °C) and the ethylene pressure (10 bar), the reaction was started by breaking of the ampoule containing complex **4**. During the polymerization (60 min), the temperature, stirring speed and ethylene pressure were maintained (constant) by using an automatic computer-controlled system; the ethylene consumption was recorded a few seconds apart.

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