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Selective Ethylene Trimerization by Titanium Complexes Bearing Phenoxy-Imine Ligands: NMR and EPR Spectroscopic Studies of the Reaction Intermediates

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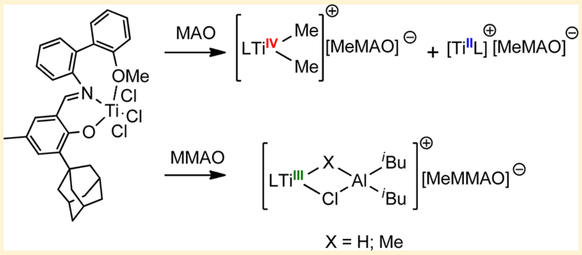
ABSTRACT: The catalyst systems (FI)$TiCl_3$/MAO (FI = phenoxyimine ligand with an additional aryl−O−CH_3 donor) display exceptionally high activity in selective ethylene trimerization. By means of NMR and EPR spectroscopy, the nature of the Ti species formed in the catalyst systems (FI)$TiCl_3$/MAO, (FI)$TiCl_3$/MMAO, and (FI)$TiCl_3$/AlR_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ (R = Me, Et, ^{i}Bu) has been studied. It was shown that outer-sphere ion pairs of the type $[(FI)Ti^{IV}Me_2]^+[A]^-$ ($[A]^-$ = $[MeMAO]^-$, $[MeMMAO]^-$, $[B(C_6F_5)_4]^-$) are formed at the initial stage of the reaction of (FI)$TiCl_3$ 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 (FI)$TiCl_3$/MAO and (FI)$TiCl_3$/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$, complexes with the proposed structures $(FI)Ti^{III}Me_2$, $(FI)Ti^{II}Cl$, and $[(FI)Ti^{II}(S)]^+[A]^-$ ($[A]^-$ = $[MeMAO]^-$, $[B(C_6F_5)_4)]^-$, S = solvent, vacancy) were observed (concentrations of Ti^{III} species was lower than those of the Ti^{II} congeners). In contrast, in the system (FI)$TiCl_3$/MMAO, the concentrations of Ti^{III} species (ion pairs of the type $[(FI)Ti^{III}(\mu\text{-}H)(\mu\text{-}Cl)Al^iBu_2]^+[MeMMAO]^-$) were higher than those of the Ti^{II} counterparts (ion pairs $[(FI)Ti^{II}(S)]^+[MeMMAO]^-$). The system (FI)$TiCl_3$/MMAO displays lower activity and selectivity in 1-hexene formation, in comparison to (FI)$TiCl_3$/MAO, due to undesirable PE generation. Probably, Ti^{II} and Ti^{IV} ion pairs are those participating 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 selective trimerization and tetramerization of ethylene,[4−7] the Phillips trimerization process remains the only example of the commercial selective trimerization of ethylene.

Hessen and co-workers 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 co-workers prepared the titanium(IV) complex **4** bearing a phenoxy-imine ligand with an additional aryl-OCH_3 donor for selective ethylene trimerization (Chart 1). When it was activated with MAO, this complex produced 1-hexene with exceptionally high activity (up to 132 kg of 1-hexene (g of Ti)$^{-1}$ h^{-1} bar^{-1}).[13] Very recently, a series of half-sandwich indenyl titanium(IV) complexes bearing an additional 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

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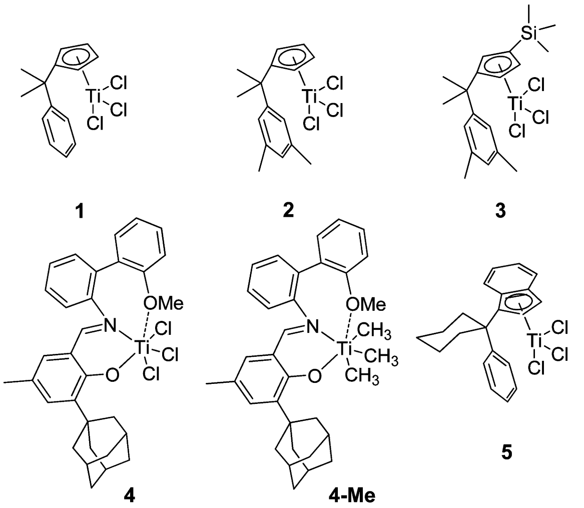
Chart 1. Structures of Complexes 1−5

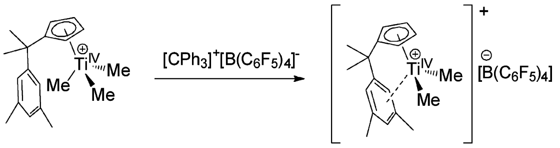


nature of the activator has a dramatic effect on the 1-hexene/PE ratio. It was found that, for the catalyst system **3**/MAO/C_2H_4, the C_6/PE ratio is 44, whereas for the catalyst system **3**/MAO/Al^iBu_3/C_2H_4 this ratio is 17.[10] Thus, additives such as Al^iBu_3 tend to promote undesirable PE 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]

It is assumed that at the initial stage of the reaction of **1** or **4** with Me-abstracting reagent, a cationic species of the type $[LTiMe_2]^+$ is formed (L is the corresponding ligand) (Scheme 1). 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 co-workers.[15] Hessen and co-workers 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 center (Scheme 2).

Scheme 2. Preparation of $[(\eta^5:\eta^6\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)TiMe_2]^+[B(C_6F_5)_4]^-$

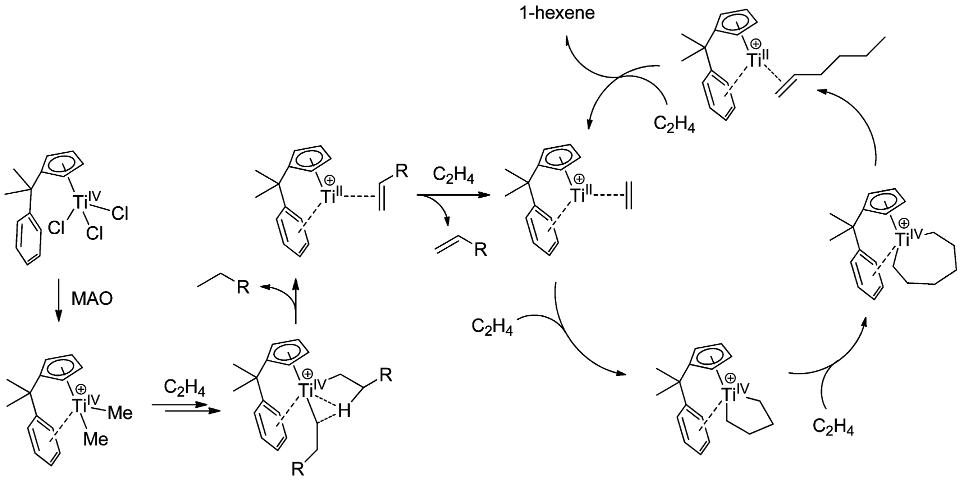


Very recently, Sattler et al. have shown that the reaction of **4-Me** (Chart 1) with 1 equiv of $B(C_6F_5)_3$ gives the outer-sphere (solvent-separated) ion pair $[(FI)Ti^{IV}Me_2]^+[MeB(C_6F_5)_3]^-$ (FI = phenoxy-imine), which is an effective precatalyst for the selective trimerization of ethylene.[16] However, no spectroscopic data on the structure of the intermediates formed upon the activation of titanium ethylene trimerization precatalysts with MAO were reported.

Previously, it was reported 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 postmetallocene ligands) leads to the formation of ion pairs of the type $[L_2TiMe^+\cdots MeMAO^-]$ (**A**), $[L_2TiMe(S)]^+[MeMAO]^-$ (**B**; S = solvent, vacancy), and $[L_2Ti(\mu\text{-}Me)_2AlMe_2]^+[MeMAO]^-$ (**C**), depending on the structure of L_2.[17,18] In the inner-sphere pairs of the type **A**, the nonuniform $MeMAO^-$ counteranions 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 relatively 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 postmetallocene ligand) are 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 broad and poorly resolved.

Scheme 1. Proposed Metallacyclic Mechanism of the Selective Ethylene Trimerization[10]



In previous studies of titanium-based catalyst systems for selective ethylene trimerization, only ion pairs of the type $[LTi^{IV}Me_2]^+[A]^-$ ($[A]^-$ = $[B(C_6F_5)_4]^-$, $[MeB(C_6F_5)_3]^-$) were observed. In the present work we have found that the activation of **4** with $[Ph_3C]^+[B(C_6F_5)_4]^-$, MAO, and MMAO results in the formation of outer-sphere ion pairs of type **B** $[(FI)Ti^{IV}Me_2]^+[A]^-$ ($[A]^-$ = $[B(C_6F_5)_4]^-$, $[MeMAO]^-$, $[MeMMAO]^-$), displaying sharp and characteristic NMR resonances. These ion pairs convert with time into Ti(III) and Ti(II) species. The possible role of the observed titanium species in the ethylene trimerization and polymerization is discussed.

■ RESULTS AND DISCUSSION

Formation of Outer-Sphere Ion Pairs $[(FI)Ti^{IV}Me_2]^+[MeMAO]^-$ and $[(FI)Ti^{IV}Me_2]^+[B(C_6F_5)_4]^-$ upon Reaction of the Precatalyst 4 with MAO and $AlMe_3$/$[CPh_3]^+[B(C_6F_5)_4]^-$. The starting complex **4** displays sharp ^1H and ^{13}C NMR resonances typical for diamagnetic titanium(IV) species (Figure 1a and Tables 1 and 2). The ^1H resonances for the *H*C═N and OC*H*$_3$ 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 the reaction 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 $[(FI)Ti^{IV}Me_2]^+[MeMAO]^-$ (**4a**) (Figure 1b, Tables 1 and 2, and Chart 2). The similar ion pair $[(FI)Ti^{IV}Me_2]^+[B(C_6F_5)_4]^-$ (**4a′**) was observed upon the reaction of **4** with $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ (Figure 1c, Tables 1 and 2, and Chart 2). **4a** and **4a′** exhibit the ^1H and ^{13}C NMR resonances of two nonequivalent Ti−C*H*$_3$ groups (Figure 1b,c and Tables 1 and 2).

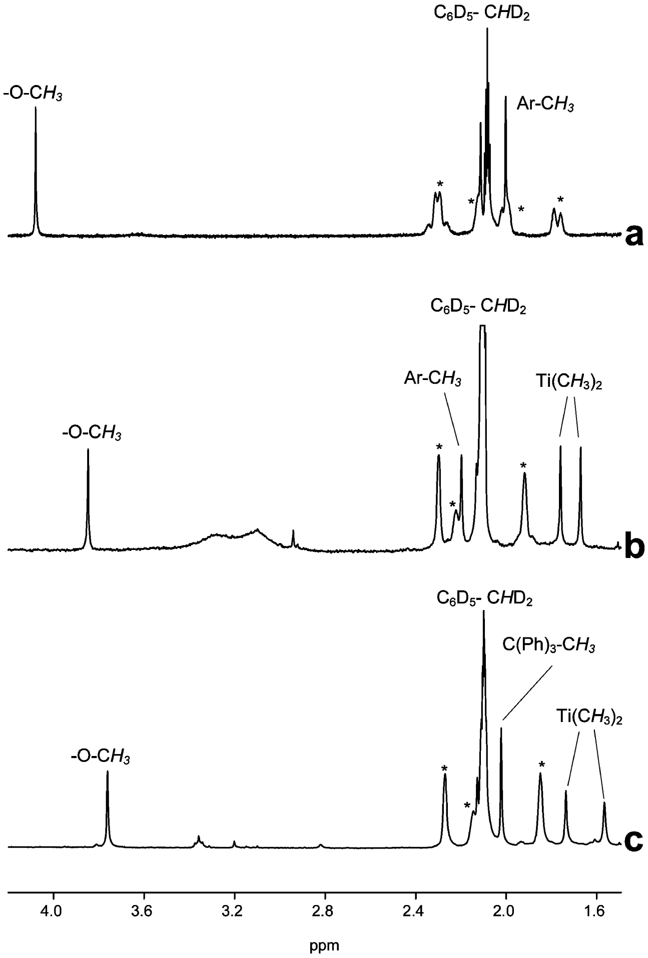


Figure 1. ^1H NMR spectra (25 °C, toluene-d_8) of (a) **4** and the samples (b) **4**/MAO ([Al]/[Ti] = 40, [Ti] = 5 × 10^{-3} M) and (c) **4**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ ([Al]/[Ti]/[B] = 10/1/1.2, [Ti] = 5 × 10^{-3} M). The aromatic region is omitted for clarity. Asterisks mark Ada-*H* signals. The region 2.8−3.5 ppm in (b) and (c) contains the signals of MAO and $AlMe_3$ oxidation products.

When MMAO (MAO modified by Al^iBu_3 additive) was used as an activator, the diamagnetic Ti(IV) species **4a″** was observed only at low temperatures (−30 °C). At higher temperatures, rapid reduction of the Ti(IV) into a lower-valence compound was observed. The ^1H chemical shifts of the *H*C═N and O-C*H*$_3$ protons of **4a″** (δ 7.41 and 3.74, respectively) are very close to those of **4a** and **4a′** (Table 1). The Ti-C*H*$_3$ 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 $[(FI)Ti^{IV}Me_2]^+[MeMMAO]^-$ (Chart 2).

The ion pairs $[(FI)Ti^{IV}Me_2]^+[B(C_6F_5)_4]^-$ (**4a′**) and $[(FI)Ti^{IV}Me_2]^+[MeMAO]^-$(**4a**) prevail in the systems **4**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ and **4**/MAO only at the initial stage of the reaction 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 reaction of **4** with AlR_3 and $AlR_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ (R = Me, Et, ^{i}Bu).

Ti^{III} Species Formed upon the Reaction 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 and $\Delta\nu_{1/2}$= 10 G, typical for Ti(III) species (Figure 2a,b). In the EPR spectrum of the sample **4**/Al^iBu_3 ([Al]/[Ti] = 10), a similar resonance at g_0 = 1.953 was observed (Figure 2c).

The maximum content 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^iBu_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 $(FI)Ti^{III}R_2$ (**6-R$_2$**).

Ti^{III} Species Formed upon Reaction of 4 with AlR_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ and AlR_3/MAO (R = Me, Et, ^{i}Bu). The addition of cationizing reagent 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**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ and **4**/$AlEt_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ ([Al]/[Ti]/[B] = 10/1/1.2, [Ti] = 5 × 10^{-3} M) displayed an intense multiline signal of the free radical $Ph_3C^\bullet$ 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**/$AlR_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ (R = Me, Et) did not exceed 10% of the titanium content.

In contrast, the addition of $[Ph_3C]^+[B(C_6F_5)_4]^-$ to the sample **4**/Al^iBu_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 multiline signal for the triphenylmethyl radical $Ph_3C^\bullet$ and an intense signal at g_0 = 1.975 from the new complex **7** (Figure 3a). The EPR signal of **7** exhibits a hyperfine

Table 1. ^{1}H NMR Parameters for the Ti(IV) Complexes Formed at the Initial Stage of the Reaction of 4 with MAO, AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, and MMAO^a

entry	species	*H*C=N	Ar-*H*	O-C*H*$_3$	Ada-*H* (15H)	Ar-C*H*$_3$	Ti(C*H*$_3$)$_2$
1	(FI)TiCl$_3$ (**4**)^b	8.20 s	7.63−7.17 m, 10H	4.42 s	2.33−1.83 m	2.41 s	
2	(FI)TiCl$_3$ (**4**)	7.44 s	7.2−6.7 m, 8H	4.08 s	2.31−1.78 m	2.01 s	
3	[(FI)TiMe$_2$]$^+$[MeMAO]$^-$ (**4a**)	7.46 s	7.4−6.9 d, 1H; 6.00 m, 7H (J^1_{HH} = 7.5 Hz)	3.84 s	2.28−1.91 m	2.19 s	1.78 s; 1.66 s
4	[(FI)TiMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**4a′**)	7.58 s	7.3−6.7 d, 1H; 6.00 m, 7H (J^1_{HH} = 7.5 Hz)	3.75 s	2.26−1.84 m	N/A	1.73 s; 1.56 s
5	[(FI)TiMe$_2$]$^+$[MeMAO]$^-$ (**4a**)^c	7.38 s	N/A	3.59 s	2.32−1.85 m	2.21 s	1.74 s; 1.59 s
6	[(FI)TiMe$_2$]$^+$[MeMMAO]$^-$ (**4a″**)^c	7.41 s	N/A	3.74 s	N/A	N/A	N/A

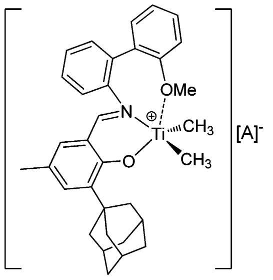
^{a}In toluene-d_8 at 25 °C, unless otherwise stated. N/A = not assigned. ^{b}In CH$_2$Cl$_2$. ^{c}Recorded at −30 °C.

Table 2. ^{13}C NMR Parameters for the Ti(IV) Complexes Formed at the Initial Stage of the Reaction of 4 with MAO and AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ in Toluene^a

no.	species	HC=N	Ar-C	O-CH$_3$	Ada-C	Ar-CH$_3$	Ti(CH$_3$)$_2$
1	(FI)TiCl$_3$ (**4**)^b	168.87	160−120 (18C)	72.12	29.11 (3C) 36.72 (1C) 36.75 (3C) 40.67 (3C)	20.67	
2	[(FI)TiMe$_2$]$^+$[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 ($^1J_{CH}$ = 126 Hz)^c 82.02 ($^1J_{CH}$ = 125 Hz)^c
3	[(FI)TiMe$_2$]$^+$[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}In toluene-d_8 at 25 °C, unless otherwise stated. N/A = not assigned. ^{b}Solution in CH$_2$Cl$_2$. ^{c}Determined using ^{13}C NMR gated decoupling experiment.

Chart 2. Proposed Structures of the Cationic Ti(IV) Species Formed upon the Activation of 4 with MAO, AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, and MMAO



4a [A]$^-$ = [MeMAO]$^-$
4a′ [A]$^-$ = [B(C$_6$F$_5$)$_4$]$^-$
4a″ [A]$^-$ = [MeMMAO]$^-$

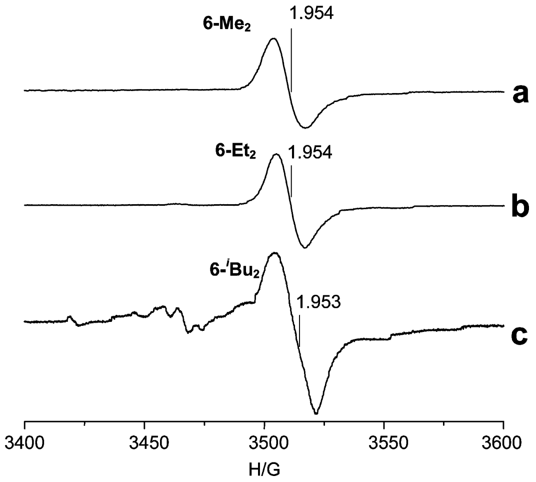


Figure 2. EPR spectra (25 °C, toluene) of various systems: (a) **4**/AlMe$_3$ ([Al]:[Ti] = 10, [Ti] = 5 × 10^{-3} M); (b) **4**/AlEt$_3$ ([Al]:[Ti] = 10, [Ti] = 5 × 10^{-3} M); (c) **4**/Al^{i}Bu$_3$ ([Al]/[Ti] = 10, [Ti] = 5 × 10^{-3} M).

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 [(FI)-Ti^{III}(μ-H)(μ-Cl)Al^{i}Bu$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ for the titanium hydride cationic species **7**; 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 [(FI)Ti^{III}(μ-H)(μ-Cl)Al^{i}Bu$_2$]$^+$[MeMAO]$^-$ (**7′**). The resonance at g_0 = 1.986 belongs to the 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 [(FI)Ti^{III}(μ-Me)(μ-Cl)-Al^{i}Bu$_2$]$^+$[MeMAO]$^-$. 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 those of **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.

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$_5$)$_4$]$^-$, **4**/AlMe$_3$/MAO, and **4**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ sharply differ in the nature and

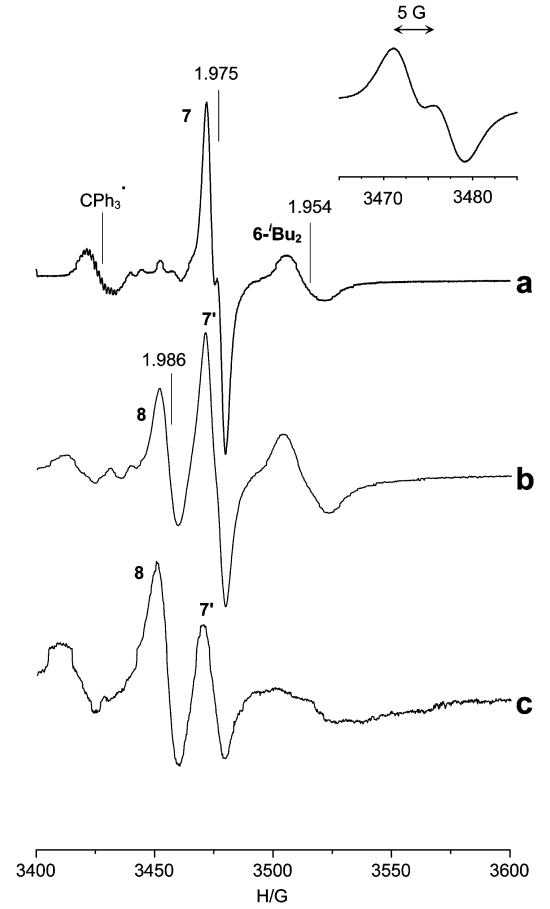


Figure 3. EPR spectra (25 °C, toluene) of the samples (a) **4**/Al^{i}Bu$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)]$_4^-$ ([Ti]/[Al]/[B] = 1/10/1.2, [Ti] = 5 × 10^{-3} M), (b) **4**/Al^{i}Bu$_3$/MAO ([**4**]/[Al^{i}Bu$_3$]/[MAO] = 1/10/40, [Ti] = 5 × 10^{-3} M), and (c) **4**/MMAO ([Al]/[Ti] = 10, [Ti] = 5 × 10^{-3} M). The insert shows the expanded resonance of **7**.

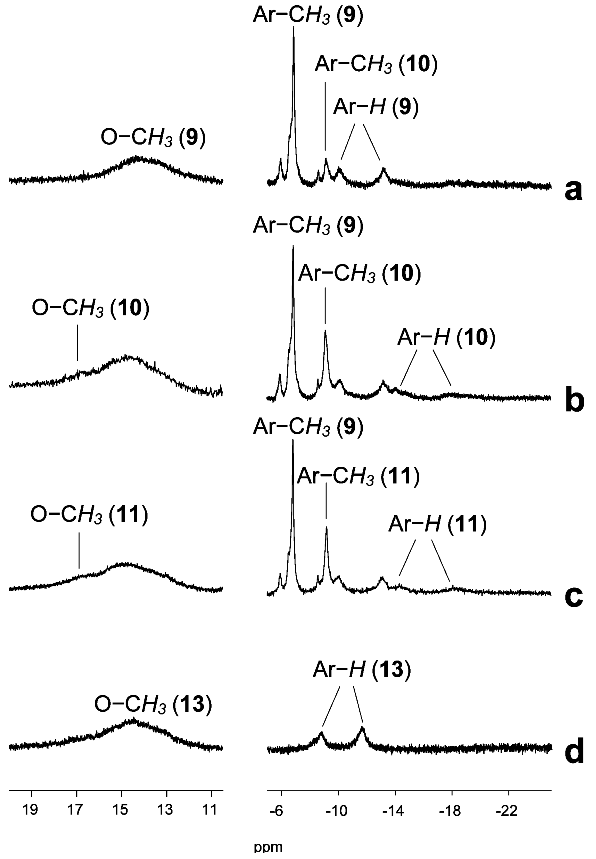


Figure 4. ^{1}H NMR spectra (25 °C, toluene-d_8) of the samples (a) **4**/AlMe$_3$ ([Al]/[Ti] = 5, [Ti] = 5 × 10^{-3} M), (b) **4**/AlMe$_3$ ([Al]/[Ti] = 15, [Ti] = 5 × 10^{-3} M), (c) **4**/AlEt$_3$ ([Al]/[Ti] = 5, [Ti] = 5 × 10^{-3} M), and (d) **12**/AlMe$_3$ ([Al]/[Ti] = 5, [Ti] = 5 × 10^{-3} M).

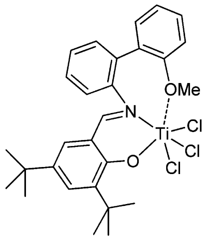
concentration of the Ti^{III} species present in the reaction solution. In the first two systems, the total concentration of Ti^{III} species (ion pairs **7**, **7′**, and **8**) is more than 50% of the total titanium content. In the second two systems, only a minor part of the titanium (less than 10%) exists in the reaction solution in the form of Ti^{III} species (neutral complex **6-Me$_2$**), the rest retaining the Ti^{IV} oxidation state.

Ti^{II} Species Formed upon Reaction 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 (S = 1) 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 to +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 (see the Experimental Section), we have assigned the broad resonance at δ 2 (15H, $\Delta\nu_{1/2}$ ≈ 100 Hz) to adamantyl protons of **9**. On the basis of integration, the resonances of **9** at δ 14.5 (3H, $\Delta\nu_{1/2}$ ≈ 800 Hz), −6.81 (3H, $\Delta\nu_{1/2}$ = 90 Hz), −10.1 (1H, $\Delta\nu_{1/2}$ = 300 Hz), and −13.1 (1H, $\Delta\nu_{1/2}$ = 230 Hz) were assigned to O-CH_3, Ar-CH_3, and aromatic protons (Ar-H) of the phenolic moiety of the phenoxyimine ligand (Figure 4a), respectively. When the [Al]/[Ti] ratio is increased to 15/1, resonances of the new complex **10** grew up at the expense of those of **9** (Figure 4b). As in the case of **9**, the resonances at δ 17.0 ($\Delta\nu_{1/2}$ ≈ 800 Hz), −9.1 ($\Delta\nu_{1/2}$ ≈ 110 Hz), −14.3 ($\Delta\nu_{1/2}$ = 400 Hz), and −18 ($\Delta\nu_{1/2}$ = 310 Hz) can be assigned to O-CH_3, Ar-CH_3, and Ar-H protons of **10**, respectively. Most probably, **9** and **10** are the complexes (FI)Ti^{II}Cl and (FI)Ti^{II}Me, respectively.

It could be expected that the system **4**/AlEt$_3$, similar to the system **4**/AlMe$_3$, would display resonances of the complexes (FI)Ti^{II}Cl and (FI)Ti^{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 with the resonances of **10**, which can be ascribed to complex **11** (Figure 4c). Not surprisingly, the replacement of Ti-Me by Ti-Et (when passing from **10** to **11**) would not essentially change the chemical shifts of the protons which are rather far from the Ti-R moiety.

To support the assignment of the resonance at δ −6.81 to Ar-CH_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 3). The ^{1}H NMR spectrum of the sample **12**/AlMe$_3$ ([Al]/[Ti] = 5) in the range −15 to 0 ppm displayed only resonances at δ −8.75 (1H, $\Delta\nu_{1/2}$ = 290 Hz) and −11.8 (1H, $\Delta\nu_{1/2}$ = 360 Hz), which can be assigned to aromatic protons of the phenolic moiety of L$_1$Ti^{II}Cl (**13**) (Figure 4d).

Chart 3. Structure of Complex 12



12

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^iBu_3. The greater ability of $AlEt_3$ to "over-reduce" Ti^{IV} into Ti^{II} in comparison to that of Al^iBu_3 was previously reported for the $MgCl_2$/ethyl benzoate/$TiCl_4$–AlR_3 catalyst systems.[24]

Cationic Ti^{II} Species Formed upon the Reaction of 4 with $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$, MAO, and MMAO. It was found that, without cationizing agents, injected ethylene was not consumed in NMR samples containing the complexes **9**–**11**. It was proposed previously that ion pairs $[LTi^{II}]^+[MeMAO]^-$ could be responsible for the trimerization of ethylene.[9] We have attempted a search for species of this type in the catalyst systems **4**/MAO and **4**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$.

It was found that after mixing **4** and $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ for 5 min at 25 °C, the spectrum of the sample **4**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ ([Ti]/[Al]/[B] = 1/10/1.3) displayed resonances of, **4a′** and **9** and those of the new complex **14** (Figure 5a). **14** exhibited a broad resonance near δ −6.7 ($\Delta\nu_{1/2} \approx$ 150 Hz) and weaker resonances at δ −9.2 ($\Delta\nu_{1/2} \approx$ 400 Hz). When the sample was stored for 30 min at 25 °C (Figure 5b), resonances of **14** decreased in intensity, while those associated with **9** increased.

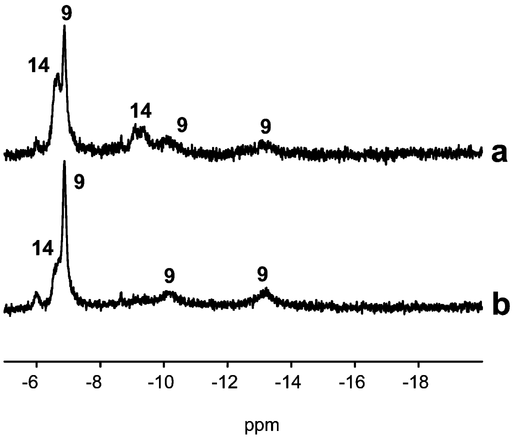
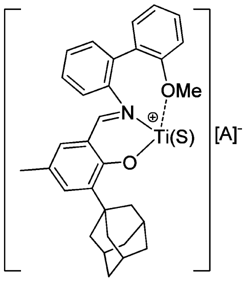


Figure 5. ^1H NMR spectra (25 °C, toluene-d_8) of the sample **4**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ (([Ti]/[Al]/[B] = 1/10/1.3, [Ti] = 5×10^{-3} M): (a) 5 min after mixing of the reagents at 25 °C; (b) 30 min after mixing of the reagents at 25 °C.

It is proposed that **14** is an ion pair of the type $[(FI)Ti^{II}(S)]^+[B(C_6F_5)_4]^-$ (S = solvent, vacancy) (Chart 4). The resonances at δ −6.7 can be assigned to Ar-CH_3 protons of **14**. In agreement with this assumption, the reaction of **4** with the other cationizing reagents MAO and MMAO resulted in the formation of 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 $[(FI)Ti^{II}(S)]^+[MeMAO]^-$ and $[(FI)Ti^{II}(S)]^+[MeMMAO]^-$ (Chart 4).

Chart 4. Proposed Structures of the Complexes 14, 14′, and 14″



14 $[A]^- = [MeMAO]^-$
14' $[A]^- = [B(C_6F_5)_4]^-$
14" $[A]^- = [MeMMAO]^-$

Trimerization and Polymerization of Ethylene with the Catalyst Systems 4/MAO, 4/MMAO, and 4/$AlMe_3/[Ph_3C]^+[B(C_6F_5)]_4^-$. The results of ethylene trimerization and polymerization studies of the catalyst **4** activated with various cocatalysts are presented in Table 3. In comparison with MAO, the catalyst system **4**/MMAO produces a much larger amount of PE and a smaller amount of 1-hexene (run 3, Table 3). The systems **4**/AlR_3 (R = Me, Et, ^iBu) were almost inactive toward ethylene polymerization or trimerization (runs 6–8, Table 3). The catalyst systems **4**/MAO(20) and **4**/MAO, containing no Al^iBu_3 (runs 1 and 2, Table 3), were the best for 1-hexene production.

As was shown above, in the catalyst system **4**/MMAO, the major part of 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 postmetallocene complexes of the type $[L_2Ti^{IV}Me]^+[MeMAO]^-$ are now well established as active α-olefin polymerization catalysts. Ti^{III} species formed upon the activation of titanocene or post-titanocene polymerization catalysts L_2TiCl_2 with MAO are apparently inactive in such processes.[25,26] For half-sandwich complexes Cp^*TiCl_3, however, the mechanistic landscape is more controversial. Indeed, both Ti(III) and Ti(IV) cationic complexes were proposed to be active in styrene polymerization.[27−30]

Our NMR-tube experiments show that ethylene addition (~500 equiv) at 25 °C to the sample **4**/MMAO containing predominantly Ti(III) complexes of the type **7** and **8** (Figure 3c) leads to immediate ethylene polymerization, and only traces of 1-hexene are formed. Therefore, the assumption that Ti^{III} species $[(FI)Ti^{III}(\mu\text{-}H)(\mu\text{-}Cl)Al^iBu_2]^+[A]^-$ and $[(FI)Ti^{III}(\mu\text{-}Me)(\mu\text{-}Cl)Al^iBu_2]^+[A]^-$ ($[A]^-$ = $[MeMAO]^-$, $[MeMMAO]^-$) promote the generation of PE by the catalyst system **4**/MMAO cannot be excluded.

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 $[(FI)Ti^{IV}Me_2]^+[MeMAO]^-$ (**4a**) and $[(FI)Ti^{IV}Me_2]^+[MeMMAO]^-$ (**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 $[(FI)Ti^{IV}Me_2]^+$ species in the

Table 3. Ethylene Trimerization and Polymerization Data for Complex 4, Activated with MAO, MMAO, and AlR_3 (R = Me, Et, ^{i}Bu)[a]

run	cocatalyst	m(1-hexene), g	$m(C_{10})$, g[b]	m(PE), g	1-hexene selectivity, %	1-hexene productivity, kg of C_6 (g of Ti)$^{-1}$ h^{-1}
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

[a] Experimental conditions: 1.5–2.5 μmol of Ti, [Al]/[Ti] = 500, 50 °C, 50 mL of the solvent (toluene for runs 1, 2, 4, 6,and 7 and for in runs 3, 5, and 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 cocatalyst contains ~10 mol % of Al as $AlMe_3$. [d] Cocatalyst and complex **4** were preliminarily mixed and stored 20 min before injection into the reactor.

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 $[(FI)Ti^{IV}Me_2]^+$ species. The NMR-tube experiments demonstrated that addition of ethylene to the samples **4**/MAO and **4**/$AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ 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 $[(FI)Ti^{II}]^+[MeMAO]^-$, which were proposed to be the key species of the catalytic cycle for ethylene trimerization (Scheme 1).[10] In this work, we have observed Ti^{II} complexes **14′** of the proposed structure $[(FI)Ti^{II}(S)]^+[MeMAO]^-$ (S = solvent, vacancy). Further studies are needed to verify the key role of species of this type in the selective trimerization of ethylene.

CONCLUSIONS

The reaction of phenoxy-imine complexes $(FI)Ti^{IV}Cl_3$, 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 reaction of $(FI)Ti^{IV}Cl_3$ with $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$, MAO, or MMAO, outer-sphere ion pairs $[(FI)Ti^{IV}Me_2]^+[A]^-$ are formed ($[A]^-$ = $[B(C_6F_5)_4]^-$, $[MeMAO]^-$, $[MeMMAO]^-$) that partially transform into Ti^{III} and Ti^{II} species upon storing at room temperature. In the catalyst systems (1) $(FI)Ti^{IV}Cl_3/AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ and (2) $(FI)Ti^{IV}Cl_3$/MAO, complexes with the proposed structures $(FI)Ti^{III}Me_2$, $(FI)Ti^{II}Cl$, and $[(FI)Ti^{II}(S)][A]^-$ ($[A]^-$ = $[B(C_6F_5)_4]^-$, $[MeMAO]^-$) were found. In the system (3) $(FI)Ti^{IV}Cl_3$/MMAO, complexes with the proposed structures $[(FI)Ti^{III}(\mu\text{-}H)(\mu\text{-}Cl)Al^{i}Bu_2]^+[MeMMAO]^-$, $(FI)Ti^{II}Cl$, and $[(FI)Ti^{II}(S)][MeMMAO]^-$ were observed. In the first two systems, the concentration of Ti^{III} species ($(FI)Ti^{III}Me_2$) was smaller than the concentration of Ti^{II} species ($(FI)Ti^{II}Cl$ and $[(FI)Ti^{II}(S)]^+[A]^-$), whereas in the latter system, the concentration of Ti^{III} species ($[(FI)Ti^{III}(\mu\text{-}H)(\mu\text{-}Cl)Al^{i}Bu_2]^+[MeMMAO]^-$) was much higher than that of the Ti^{II} counterparts ($(FI)Ti^{II}Cl$ and $[(FI)Ti^{II}(S)]^+[MeMMAO]^-$). The system $(FI)Ti^{IV}Cl_3$/MMAO demonstrates a lower ethylene trimerization activity than the system $(FI)Ti^{IV}Cl_3$/MAO; this behavior correlates with the higher concentration of Ti^{III} species in the former system. Thus, one can exclude the participation of Ti^{III} species in selective ethylene trimerization in the presence of catalyst **4**. In contrast, our observations indicate that ion pairs **4a, 4a′**, and **4a″** ($[(FI)Ti^{IV}Me_2][A]^-$) are the most plausible precursors of the active sites for ethylene trimerization. As the reaction proceeds, these titanium(IV) ion pairs transform into ion pairs of the type $[(FI)Ti^{II}]^+[MeMAO]^-$, which were previously proposed to operate in the catalytic cycle of ethylene trimerization (Scheme 1).[10]

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 a toluene solution with a total Al content 1.8 M and Al as $AlMe_3$ 0.5 M, MMAO was purchased from AKZO as a heptane solution (total Al content 7.1 wt %), and $Al^{i}Bu_3$ (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-seal technique was used. ^{1}H 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 the residual solvent peak: 2.09 ppm for the CD_2H proton resonance of toluene. The pulse program **t1ir1d** was used for the inversion–recovery NMR experiments. EPR spectra were measured on a Bruker ER-200D spectrometer at 9.3 GHz, modulation frequency 100 kHz, and 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 the Reaction of 4 with MAO(20). MAO(20) (6.0 mg, 80 μmol) was suspended in 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. ^{1}H NMR (δ, toluene-d_8, 25 °C): 7.46 (s, 1H, *H*C═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-C*H*$_3$), 2.28–1.91 (m, 15H, Ada-*H*), 2.19 (s, 3H, Ar-C*H*$_3$), 1.78 (s, 3H, Ti*Me*Me′), 1.66 (s, 3H, TiMe*Me*′). ^{13}C{^{1}H} 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 the Reaction 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, *H*C═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-C*H*$_3$), 2.26–1.84 (m, 15H, Ada-*H*), 1.73 (s, 3H, Ti*Me*Me′), 1.56 (s, 3H, TiMe*Me*′). ^{13}C{^{1}H} NMR (δ, toluene-d_8, 25 °C): 174.30 (1C, HC═N), 84.35 (1C, TiMe*Me*′), 80.44 (1C, Ti*Me*Me′), 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* atoms were not 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 the Reaction of 4 with MMAO. The reaction of **4** with MMAO at room temperature leads to the immediate reduction of Ti(IV) to the trivalent state. Given this, the reaction 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 with dry toluene-d_8. A 1.8 M solution of MMAO in heptanes (44 μL, 20 μmol) was added, and the NMR tube was closed by a rubber septum and then 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 complex **4a″** was very low; only resonances of *H*C═N and O-C*H*$_3$ were observed. ^{1}H NMR (δ, toluene-d_8, −30 °C): 7.41 (s, 1H, *H*C═N), 3.74 (s, 3H, O-C*H*$_3$).

Formation of the Complexes 6-R$_2$ during the Reaction 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 and 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 the Reaction 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 G.

Formation of the Complexes 7′ and 8 during the Reaction 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 ampule. The reactor was evacuated at 80 °C, cooled to 20 °C, and then charged with the freshly prepared solution of the desired cocatalyst in toluene or hexanes (50 mL). After the polymerization temperature (50 °C) and the ethylene pressure (10 bar) were set, the reaction was started by breaking of the ampule 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; ethylene consumptions were recorded a few seconds apart.

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Notes

The authors declare no competing financial interest.

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