Synthesis and Characterization of Dichlorotitanium Alkoxide Complex and Its Activity in the Polymerization of α-Olefins

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ABSTRACT: We present the synthesis, characterization, X-ray molecular structure, and catalytic activity of a $[(HOEt)Ti(\mu\text{-}OEt)OEt(Cl)_2]_2$ (**1**) dimeric complex. Complex **1** was found to undergo, in solution, a succession of fluxional processes involving the rotation of the ligands, rapid exchange between the anionic ethoxide ligands, and exchange of the hydroxylic hydrogen. The complex, when activated by methylalumoxane (MAO), undergoes an abstraction of the ligands through a heterobimetallic intermediate with ethoxide bridges between the aluminum and titanium atoms. We propose that this intermediate is the active species in the polymerization of α-olefins. The complex displays unexpectedly a single site behavior in contradiction to other titanium alkoxide complexes. The resulting polymers were found to show elastomeric properties with intermediate tacticities.

Introduction

Since the discovery of the Ziegler −Natta systems for the polymerization of olefins in the 1950s,[1−3] an enormous amount of research has been directed toward understanding and improving these systems. The research has focused on the development of homogeneous single-site polymerization catalysts that allow a better control over the primary properties of the polymers. Metallocene complexes of group 4 transition metals were widely studied for this purpose, essentially in the 1980s.[4] The nature of the Cp ligand can be modified by the appropriate addition of substituents on the ring, thus changing in a predictable way both sterically and electronically the properties of the metallocene complex.[5−10] Since the first half of the 1990s the research has focused on non-metallocene-related complexes such as constrained geometry complexes (CGC),[11−14] diamides,[15−17] phenoxyimine (FI),[18,19] and amidinates.[20,21] The scope of these systems has expanded from both point of views of the ligands and the metals[22] (iron[23−25] and late transition metals such as nickel[26−29]). The symmetry of the complex was found to bear a deep influence of the stereoregularity of the obtained polymer, when complexes exhibiting C_2 symmetry usually produce stereoregular isotactic polypropylene,[30] and higher symmetries will induce atactic polymers.[31]

High activities in the polymerization of α-olefins are achieved in the presence of a proper coactivator. Extensive studies has focused on improving these coactivators; good results have been reported for methylalumoxane (MAO),[32] perfluoroarylboranes,[33,34] perfluoroarylborates and aluminates,[35,36] or mixtures of alkylaluminum and perfluoroarylborane and borates.[37−39]

Alkoxides have been considered as alternatives for Cp ligands. The titanium complexes based on these ligands, and among them, those with the general formula $Ti(OR)_2Cl_2$ or $Ti(OR)_4$ have been known for a while and are used as Lewis acid catalysts or at stoichiometric amounts for a wide scope of organic reactions such as hetero-Diels−Alder reactions, Michael additions, and others.[40] Simple titanium alkoxide complexes are used as well in the epoxidation of olefins.[41] The complexes in which R shows a specific chirality are of particular interest for enantioselective transformations.[42−44]

Alkoxide complexes of tin[45] and aluminum[46] are also known for their ability to polymerize cyclic aliphatic esters such as ϵ-caprolactone and lactide.

Sophisticated alkoxide complexes of group 4 metals have been studied since the 1990s for the polymerization of ethylene and propylene, where they show relatively good activities. The ligands are generally chelating alkoxides or aryloxides either with two oxygen donors in the ligands such as in maltol or guaiacol[47] or where the additional donor atom bonded to the metal is nitrogen[48−51] or sulfur.[52] The activity of these complexes usually shows a strong dependence on the size of the substituents at the ligands.[53]

Simple aliphatic alkoxide complexes of group 4 metals have rarely been used for the polymerization of olefins in the presence of aluminum-based cocatalysts. $Ti(OBu)_4$ has been known for its ability to produce oligomers from ethylene when reacted in the presence of $Et_3Al_2Cl_3$.[54] Other systems using tandem copolymerization to form LLDPE have been successfully used.[55] In these one-pot systems, $Ti(OBu)_4$ or $Ti(O^iPr)_4$ is activated by Et_3Al and affords small oligomers (α-olefins); these small oligomers and ethylene are further copolymerized by heterogeneous MAO-activated metallocenes to give a tailor-branched polyethylene.

There are only a few works presented for the polymerization of ethylene or propylene with advanced titanium alkoxide complexes as precatalysts.[52,56−58] Whereas, there are nearly no reports for simple aliphatic alkoxide precatalysts. Pellecchia and co-workers have shown that alkoxide achiral complexes of type $Ti(OBu)_4$ induce the formation of a mixture of isotactic (up to 80% isotacticity) and atactic polypropylene in the presence of MAO−$Al(Me)_3$ as cocatalysts.[59] In these systems the molecular weight polydispersities are high (7−15) and correspond to multiple active species. Pellecchia postulated that stereorigid complexes bearing some degree of symmetry arise from the interaction of MAO and the achiral catalysts.

We report here the synthesis, characterization, and X-ray diffraction structures of a dichlorotitanium alkoxide dimer complex. The complex shows excellent catalytic activity for

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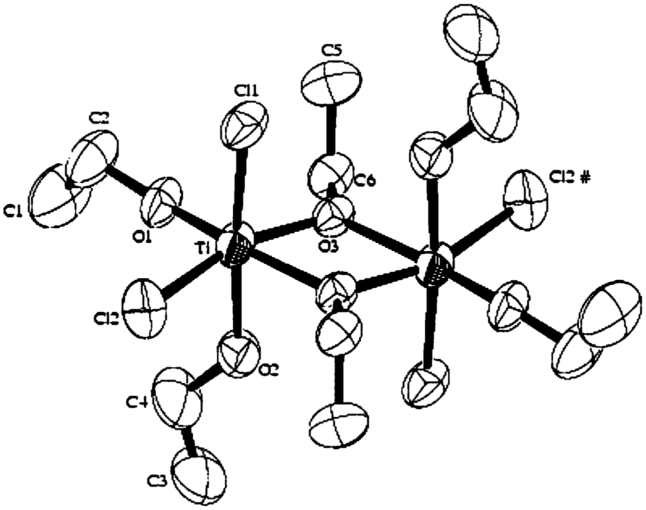


Figure 1. ORTEP diagram (50% probability ellipsoid) of the titanium complex **1**. Hydrogen atoms were omitted for clarity.

the polymerization of ethylene and propylene in the presence of methylalumoxane (MAO) as cocatalyst, producing high molecular weight polyethylene and elastomeric polypropylene, respectively.

Results and Discussion

The goal of this investigation was to synthesize a simple alkoxide complex bearing two *cis*-chloro ligands allowing the formation of an active species toward olefin polymerization when reacted with Lewis-acidic MAO, while retaining a single site catalyst character. We tested the influence of the chloride ligands on the formation of the active species as compared to known pure alkoxide complexes.[59]

Complex **1** was prepared in dry ethanol by the reaction of 2 equiv of fresh sodium ethoxide with $TiCl_4$ in ethanol (see Scheme 1) and was found to be soluble in polar nonaromatic organic solvents as well as in toluene and benzene but insoluble in nonpolar hydrocarbons such as *n*-hexane.

The complex was characterized by variable temperature ^1H NMR, ^{13}C NMR, $^1H-^1H$ correlation experiment (COSY), diffusion ^1H NMR (DOSY), elemental analysis, and X-ray crystallography. In Figure 1, the crystalline structure of the complex is presented. The complex in the solid state is dimeric; both metals are pseudo-octahedral and related by an inversion center. Each metal is connected to two *cis*-chloro ligands (Cl(2)−Ti−Cl(1) = 92.86°), two ethoxide bridges, one ethoxide (C(2)−O(1)−Ti = 162.8°), and one neutral ethanol (C(4)−O(2)−Ti = 132.6°). The C(2)−O(1)−Ti angle indicates that at least four electrons are donated by the ethoxide ligand to the metal center, making the molecule a 14-electron complex. The complex exhibits three different Ti−O bond lengths corresponding to the different charges of the ligands (anionic ethoxide (Ti−O(1) = 1.727 Å), bridging anionic ethoxide (Ti−O(3) = 1.9462 Å), and coordinative ethanol (Ti−O(2) = 2.084 Å)), very similar to the corresponding isopropoxide complex[60] and other titanium ethoxide clusters.[61,62] The equatorial plane of the dimer is defined by the two titanium atoms, two oxygen atoms (O1 and O3) and a chlorine atom (Cl2), whereas the apical positions are taken by Cl(1) and O(2). Representative values of bond lengths and angles are presented in Table 1 and the measurement parameters in Table 2. Interestingly, a monomeric form of the complex, prepared in excess ethanol, was proposed 71 years ago, although no structural data were suggested.[63]

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Ti Complex 1

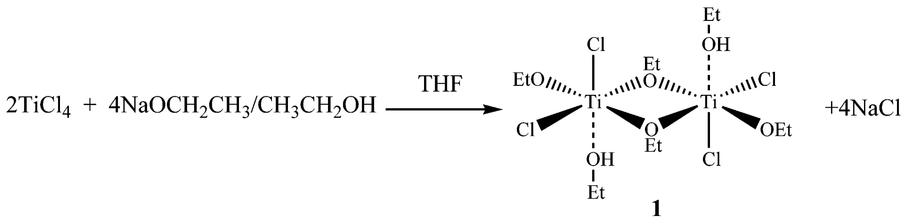
Ti−O(1)	1.727(2)
Ti−O(2)	2.084(3)
Ti−O(3)	1.9462(19)
Cl(2)−Ti−Cl(1)	92.86(4)
O(1)−Ti−O(3)	98.80(9)
O(1)−Ti−O(2)	92.28(11)
O(3)−Ti−O(2)	84.55(10)
O(1)−Ti−Cl(2)	96.63(7)
O(3)−Ti−Cl(2)	162.77(7)
C(2)−O(1)−Ti	162.8(2)
C(4)−O(2)−Ti	132.6(3)
C(6)−O(3)−Ti	123.74(17)

Table 2. Crystal Data and Refinement Details for Complex 1

identification code	complex **1**
empirical formula	$C_6H_{16}Cl_2O_3Ti$
formula weight	254.99
T (K)	230.0(2)
wavelength Å	0.71073
crystal system	triclinic
space group	P-1
unit cell dimensions	
a (Å)	7.1860(10)
b (Å)	9.5460(10)
c (Å)	9.8940(12)
α (deg)	63.082(10)
β (deg)	86.770(5)
γ (deg)	80.046(6)
vol (Å^3)	595.88(13)
Z	2
D_{calc} (mg/m^3)	1.421
absorption coefficient (mm^{-1})	1.139
F(000)	264
crystal size (mm)	0.03 × 0.18 × 0.18
θ range for data collection (deg)	2.31−25.05
limiting indices	$-8 \leq h \leq 7, -11 \leq k \leq 11, -11 \leq l \leq 11$
reflections collected/unique (R_{int})	3567/2099 (0.0366)
completeness to θ	99.6% (θ = 25.05)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2099/0/128
goodness-of-fit on F^2	0.867

Most of the known $Ti(OR)_4$ (R = Me, Et, ^{n}Bu) complexes are found in the solid state and in solution as mixtures of mono-, di-, and trimers,[64−66] when for the more bulky ligands (R = ^{i}Pr, ^{i}Bu) the main species are found to be monomeric.[67] The proton NMR spectra of complex **1** in toluene-d_8 displayed well-defined but broadened signals, indicating that a dynamic process was taking place. We have excluded intermolecular equilibrium between the dimer and other species by performing a diffusion proton NMR experiment (DOSY), which separates signals

Scheme 1. Synthesis of Complex 1



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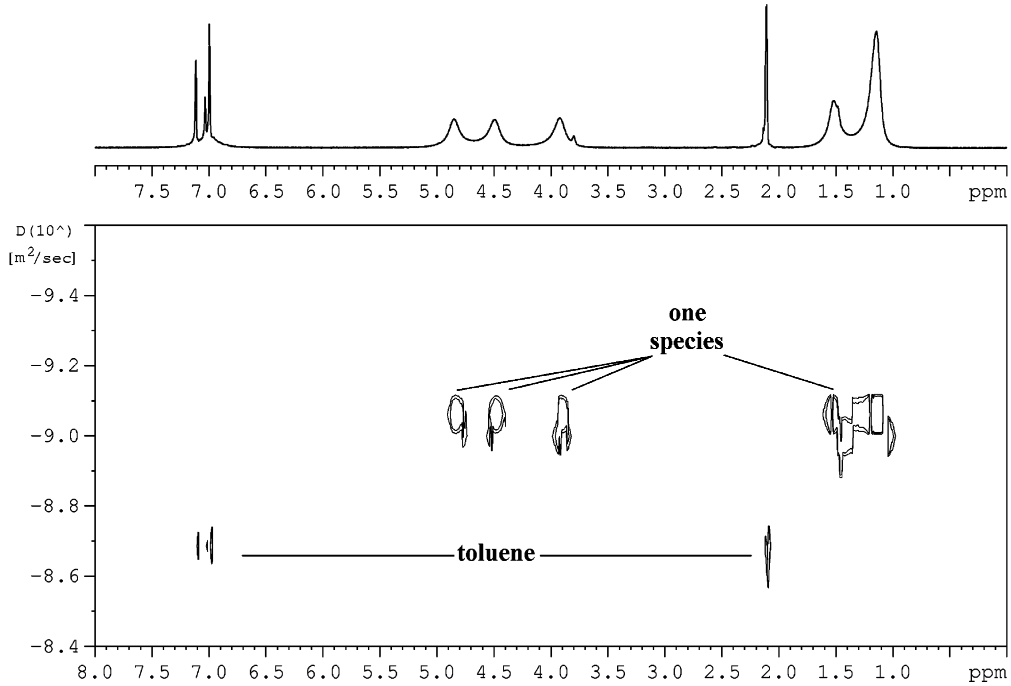

Figure 2. DOSY spectrum for complex **1** in toluene.

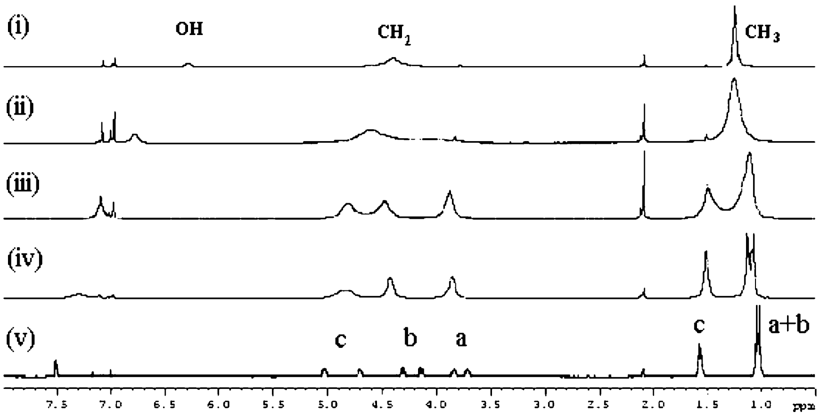

Figure 3. Variable temperature ^{1}H NMR spectra of complex **1** in toluene at (i) 337, (ii) 317, (iii) 297, (iv) 276, and (v) 205 K.

according to their diffusion coefficients (Figure 2). This experiment was conclusive about the presence of one unique form of the complex. Hence, complex **1** exhibited a different behavior than to other simple mononuclear titanium alkoxide complexes and was found to exist as a stable dimer in toluene having similar diffusion coefficients as to dinuclear titanium complexes.

The ^{1}H NMR spectra at room temperature of complex **1** displayed well-defined resonances with the expected integrations for the dimer **1**. Three broad signals of methylene groups corresponding to the three different ethanol/ethoxide ligands (4.83, 4.48, and 3.87 ppm), two broad signals in the methyl region (1.50 and 1.11 ppm) and one broad signal corresponding to the OH group of the ethanol, were found to overlap the toluene signals (7.10 ppm) at room temperature. Variable temperature ^{1}H NMR experiments have shown that the three ligands coexist in a dynamic system, as can be seen in Figure 3. It is important to note that the presence of three different signals for the methylene hydrogens excludes the existence of a monomeric form of the complex and corroborates our claim that the complex retains its dimeric form in solution at room temperature.

The centrosymmetric structure of the complex lead us to expect that on the NMR time scale, at low temperature, the six hydrogens of the methylene groups should be nonequivalent, when the methyl groups were expected to be less differentiated. Thus, upon cooling to 205 K six different resonances could clearly be differentiated in the methylene region (δ 5.01, 4.69, 4.29, 4.12, 3.82, 3.70) while only two could be differentiated in the methyl region (δ 1.55, 1.03) (Figure 3, spectrum v). Three fluxional processes were observed at different temperatures. We will focus on the methylene region of the spectrum to describe these processes. At 240 K two pairs of signals (4.29 and 4.12 ppm; 3.82 and 3.70 ppm) merged into two broad bands (at 4.40 and 3.85 ppm, respectively). At 250 K the last pair found at lowest field (5.01 and 4.69 ppm) coalesces into a broad signal at 4.82 ppm. These three new signals are observed in spectra iii and iv in Figure 3. The second exchange process takes place at $T = 305$ K, where the two new signals at low field (4.82 and 4.40 ppm) coalesce at 4.61 ppm (spectrum ii, Figure 3). At 325 K a third process was observed, affording a single signal in the methylene region at temperatures higher than 325 K (4.42 ppm), as shown in spectrum i in Figure 3. The OH hydrogen of the ethanol ligand moved along the spectra with heating, affording

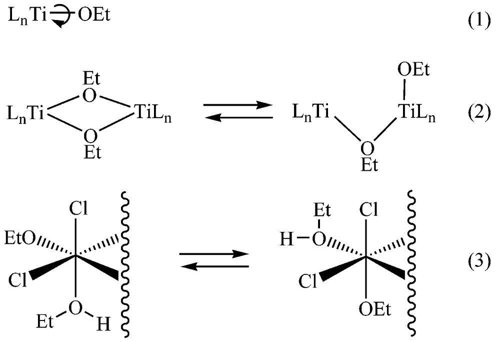

Figure 4. Three dynamic process taking place in complex **1** at various temperatures in toluene-d_8.

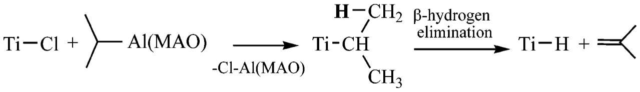

Figure 5. Formation of isobutylene in the presence of MAO.

a broad signal at 337 K (6.30 ppm) and a sharp signal at 205 K (7.49 ppm).

The assignment of the signals was made according to a ^{1}H−^{1}H correlation NMR experiment (COSY) at 205 K. The COSY spectrum displayed several correlations: the methyl signal found at 1.03 ppm correlated with four methylene hydrogens found in the range 3.70−4.29 ppm; the methyl signal at 1.55 ppm correlated to the hydrogens at 4.69 and 5.01 ppm, and the hydroxyl hydrogen (7.49 ppm) correlated to the 3.82 and 3.70 ppm signals. The signals at 7.49, 3.82, 3.70, and 1.03 ppm were therefore assigned to the neutral ethanol ligand.

The assignment of the other signals required some further insight into the structure of the complex. One set of methylene signals (b) merged at 240 K, while the signals labeled c merged at 250 K, thus implying a stronger disturbance in the rotation of the methylene hydrogens (c). A close observation of the X-ray structure of the complex including the hydrogen atoms showed that a steric hindrance to the rotation of the methylene hydrogen is observed for the bridging ethoxide ligand. The distances of the atoms O1 and Cl2# from the relevant hydrogen (H6A−O1 = 2.62 Å and H6B−Cl2# = 2.72 Å) are shorter than the sum of the corresponding van der Waals radii of the involved atoms, thus indicating some interactions impeding the free rotation of the ligand. This steric hindrance was not encountered for the nonbridging ethoxide ligands. We therefore assigned the signals b and c to the ethoxide and bridging ethoxide, respectively.

The VT-NMR analysis leads us to the conclusion that at high temperatures three rapid exchanges occur in the complex (see Figure 4). First, an internal rotation around the Ti−OCH$_2$ bonds in all the ligands, as shown in (1). The rotation has a low-energy barrier at room temperature and long enough residence time leading to six different resonance signals which can be observed only at temperatures below 240−250 K where the signals coalesce (see signals a, b, c in Figure 3). The second exchange process taking place is the opening of the bridged ethoxide, giving rise at T = 305 K to the coalescence of the signals belonging to the two different ethoxide (exchange of bridging ethoxide groups), as presented in (2). At 325 K a third process is observed where the proton of the neutral EtO*H* exchanges with the anionic ethoxides, thus affording a single signal in the methylene region at temperatures higher than 325 K. The rate of rotation of the ligands was calculated according to line shape analysis.[68] The calculated rates for these processes are presented in Table 3.

Table 3. Calculated Values for Rate Exchanges between Equally Populated Sites at Coalescence Temperatures

exchange process	$T_{\text{coalescence}}$ (K)	rate constant (Hz)
methylene rotation of the ethanol moiety HO*CH$_2$*CH$_3$	250	139.0
methylene rotation of the ethoxide moiety O*CH$_2$*CH$_3$	250	181.5
methylene rotation of the bridging moiety μ-O*CH$_2$*CH$_3$	240	235.9
bridging/terminal ethoxide exchange O*CH$_2$*CH$_3$ ↔ μ-O*CH$_2$*CH$_3$	305	655.0

Reaction of Complex 1 with MAO. In an attempt to characterize the active species for the polymerization of propylene, we have studied the reaction of complex **1** with small amounts of MAO. We observed at a **1**:MAO ratio of 1:30 and 1:50 that, upon addition of MAO, all the signals corresponding to the various ethyl groups in complex **1** disappeared and four new signals appeared at a higher magnetic field (3.64, 3.37, 0.98, and 0.92 ppm). These signals were found to correlate as two ethoxide pairs under a COSY experiment (3.64, 0.98 and 3.37, 0.92 ppm) and correlate as well to signals in the carbon NMR (59.75, 17.71 and 58.22, 17.42 ppm), respectively.

As expected, the signal corresponding to the hydroxyl proton of the neutral ethanol ligand disappeared as well, forming methane. These results are in agreement with the formation of two new ethoxide groups, where the signals corresponding to the methyl groups (0.98 and 0.92 ppm) fall in the range of broad signals belonging to MAO. The intensity of the signals was found to vary with the reaction time. Five minutes after the MAO was added, the 3.64 ppm:3.37 ppm ratio was 1:2 among the methylene signals, and then this ratio was reversed. After 72 h, the ratio among the signals was stabilized at 4:1. The overall integrations of the methylene (3.3−3.7 ppm) and methyl (0.8−1.1 ppm) regions did not vary with reaction time when compared to the intensities of an internal standard or that of the solvent.

Interestingly, after the addition of the MAO to the complex, we have observed the formation of small amounts of free isobutylene in the solution which concentration remained steady throughout the whole reaction time frame. We have found that the formation of isobutylene was elucidated by the existence of small amounts of isobutyl groups from the purchased MAO; the isobutyl groups exchange to some extent with the chloride atoms or ethoxide groups in the complex. This reaction followed by β-hydrogen elimination liberates the isobutylene molecule and leaves a new titanium hydride complex, which is known to induce the insertion of monomer and further catalysis (Figure 5).[69] The isobutylene was not expected to react under these conditions, since the polymerization of isobutylene is achieved under cationic polymerization conditions.[70−72] Interestingly, MAO was found to be a good precatalyst for the polymerization of isobutylene but only when dichloromethane was used as a solvent, via a transfer of a chloride from the solvent to MAO affording the active cationic species. The reaction in toluene displayed an extremely low reaction rate.[73]

The blank reaction of ethanol (2 mmol) with MAO (2 mmol) in toluene-d_8 has given us an interesting insight into the bonding of the ligands. The signals corresponding to free ethanol disappeared both in the proton and in the carbon NMR. The proton spectra displayed new broad signals (0.7−1.7 and 3.4−4.5 ppm). Thus, the reaction of ethanol with MAO produced a large variety of ethyl species among which we recognized one set of signals corresponding to the spectra of complex **1** with MAO (0.98 and 3.64 ppm). These results show that the ethanol and/or ethoxide ligands react directly with the aluminum atoms

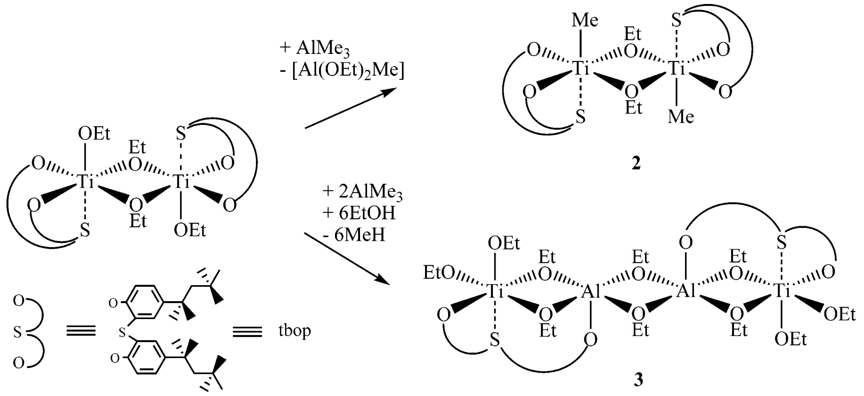

Figure 6. Heterometallic aluminum and titanium complex of tridentate tbop ligand.[75]

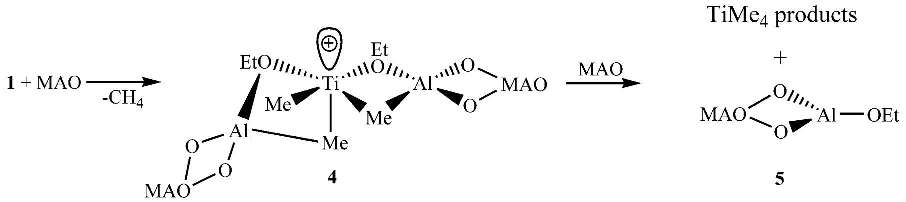

Figure 7. Putative active species in the reaction of complex **1** with MAO.

of MAO, thus implying that a ligand abstraction is taking place and that at least one ethyl species is no more connected to the titanium atom. The formation of aluminum ethoxide species is supported by the known stability of aluminum alkoxide compounds which are commercially available; moreover, clusters such as $[Al\{(\mu\text{-}OEt)_2AlMe_2\}_3]$ have been isolated and fully characterized.[74]

An additional insight into the reaction of complex **1** and MAO was obtained by the reaction of complex **1** with trimethylaluminum in an attempt to provide a simpler model for the reaction. The resulting signals obtained show the formation of three new ethyl species at higher field than in complex **1**. Two of the ethyl groups correspond to the signals observed in the reaction of complex **1** and MAO, whereas the third ethyl was found at a higher field (3.19 and 0.78 ppm) and most probably corresponds to some EtO−Al−Cl moieties, which cannot be formed on the polymeric backbone of MAO. We could observe as well the presence of at least four new methyl species bound to aluminum atoms, thus confirming the multiple nature of the bonding of this group in the model reaction (bridging and nonbridging). Recently, Janas and co-workers have isolated several homo- and Ti−Al heterobimetallic containing tbop ligands complexes (see **2** and **3**, respectively, in Figure 6).[75] Interestingly, the proton NMR of these complexes displays remarkably similar resonances to the unassigned signals we have encountered for complex **1** and MAO.

The existence of heterobimetallic complexes such as **3** cannot be proven at this point in the reaction of complex **1** with MAO, but the results of the polymerization reactions that are presented below indicate a single site catalysis (low polydispersity) by a well-defined octahedral active species (relatively high degrees of isotactcity—mmmm > 23%), as opposed to common titanium alkoxides with fluxional structures.[59] Moreover, the work performed by Janas confirms that the ethoxide ligands on titanium can either be abstracted by the aluminum atom or bridge between aluminum and titanium atoms. Finally, we could observe in the proton NMR, as we did in the model reaction with Me_3Al, signals corresponding to new methyl groups within the range of MAO and therefore connected to aluminum atoms (but not in the form of MAO). Methyl groups have long been known as bridging groups between aluminum and titanium atoms[76−78] or between titanium atoms,[79] and similar NMR resonances as the ones observed in the reaction of **1** and MAO have been reported.[80] On the basis of these observations, we propose that the reaction of complex **1** with MAO proceeds in two steps (see **4** and **5** in Figure 7).

In a first step, an ethanol abstraction takes place, leading to the formation of methane and of a free coordination site in the complex. In parallel, the chloride ligands are replaced by methyl groups from MAO, as has been reported in numerous works.[4,81,82] A chelating process of the two ethoxide ligands with MAO allows the formation of a stable intermediate complex where both of the ethoxides from complex **1** and the methyl from the MAO bridge between the aluminum and the titanium atoms. The corresponding proton NMR signals for the bridging ethoxide are found at 3.37 and 0.92 ppm, similar to the complex proposed by Janas.[75] Ultimately, one of the methyl groups is abstracted by MAO to give the putative cationic complex **4**. We propose complex **4** as the plausible active species in the polymerization. The complex might be found as a mixture of structures where the methyl groups may possibly undergo changes in their bonding to the metal atoms (from μ-bridges to nonbridging ligation). The proposed fluxional structure of **4** is expected to deteriorate the single site character of the complex in the polymerization of α-olefins.

In a second step, the μ-ethoxide ligands in complex **4** are abstracted by the aluminum affording Al−ethoxide species bearing ^1H NMR resonances at 3.64 and 0.98 ppm, analogous to the signals found in the reaction of ethanol and MAO. The previously bridging methyl remains on the titanium atom, thus leading to the formation of $TiMe_n$ products which are known to decompose readily at room temperature[83−88] and therefore are not reactive toward the polymerization of α-olefins. Our claim for the decomposition of the active complex is reinforced by the polymerization results, which show that a faster deactivation is taking place with high amounts of MAO and long reaction times (vide infra).

In order to confirm that the Al−OEt species characterized by the reaction of ethanol and MAO (3.64 and 0.98 ppm) are not the active species in the polymerization process, we have

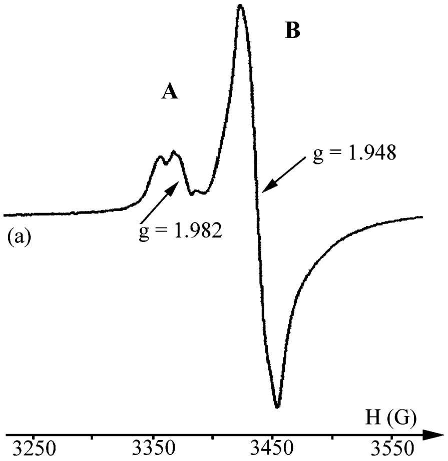

Figure 8. ESR spectrum of complex **1** activated by MAO at room temperature.

performed a blank polymerization of propylene with a 1: 200 ethanol:MAO solution in toluene. The reaction afforded no polymer, thus indicating that the polymerization proceeds via titanium species.

In order to establish if the proposed complex **4** is the active species in the polymerization, we have looked for reduced forms of the complex Ti(III)[89] by monitoring the reaction of the complex with the cocatalyst at a **1**:MAO ratio of 1:50 in toluene-d_8. The ESR spectra of the paramagnetic intermediates were measured at room temperature. When complex **1** was activated by MAO, the ESR spectrum at 290 K (Figure 8) showed a superposition of several signals (where two signals dominated, A and B) with upfield-shifted *g*-factors (compared to organic radicals) at $g = 1.982$ (A) and $g = 1.948$ (B). Such low values of *g*-factor are typically exhibited by paramagnetic Ti^{+3} complexes.[90−92]

Signals A (line width ~ 17 G) and B (line width ~ 28 G) were found to have a weak anisotropy of the *g*-factor in frozen glass (at 150 K) in contrast with typical Ti^{+3} paramagnetic complexes,[93−96] which is the result of an agglomeration of various titanium noncatalytic reactive species and spin-exchange processes within the agglomerate.[93,97]

When complex **1** was activated by MAO in a solution of C_{60}, a polyaddition of Me or EtO radicals to fullerene took place. We could observe the corresponding stable fullerenyl radicals $^{\bullet}C_{60}(Me)_x(OEt)_y$ (where $x + y = 3, 5, 7$, etc.) in the ESR spectrum (Figure 9a). MALDI-TOF analysis demonstrated the superposition products of the polyaddition of Me or OEt radicals to C_{60} (Figure 9b).

In the second experiment we reacted complex **1** and MAO for 6 h prior to the addition of the C_{60}. Interestingly, after this amount of time fullerene was still able to trap radicals. The irradiation of the reaction mixture in the cavity of ESR spectrometer by visible light ($\lambda > 600$ nm) gave rise only to the reversible dissociation of the dimer $MeC_{60}{-}C_{60}Me$ of fullerenyl radicals ($MeC_{60}{-}C_{60}Me \rightleftharpoons 2^{\bullet}C_{60}Me$), and the corresponding signal was observed with a low intensity (see $^{\bullet}C_{60}$-Me signal in Figure 9c). The MALDI-TOF data revealed methyl radicals trapped on fullerene (signals with mass 735 (720 + 15), 750 (very small), 765 (very small)) as well as a $C_{60}(OEt)_2$ signal with a mass of 810 (720 + 90)) (Figure 9d).

Considering that MAO gives no paramagnetic adducts when reacted with fullerene and that the polyaddition radicals trapped in the first experiment are not present in the second one, we propose that the radicals observed in the first experiments are the result of a partial reduction of the complex by MAO and subsequent formation of ethoxide and methyl radicals. When the reaction is allowed to react for 6 h prior to the addition of C_{60}, these radicals react to give stable organic compound that are not detected by NMR spectroscopy due to their low concentration. One of the stable organic compounds formed is a diethyl peroxide (EtO−OEt) for which a bond dissociation energy of $D_{O-O} = 150.3$ kJ/mol has been reported.[98] Interestingly, *tert*-butyl peroxides have been known to add to fullerene under irradiation conditions.[99] The $C_{60}(OEt)_2$ signal in Figure 9d most probably corresponds to the product of the heterolytic dissociation of the peroxide induced by the radiation of the complex during the ESR experiment. The methyl radicals trapped by fullerene and displayed in the MALDI-TOF spectrum

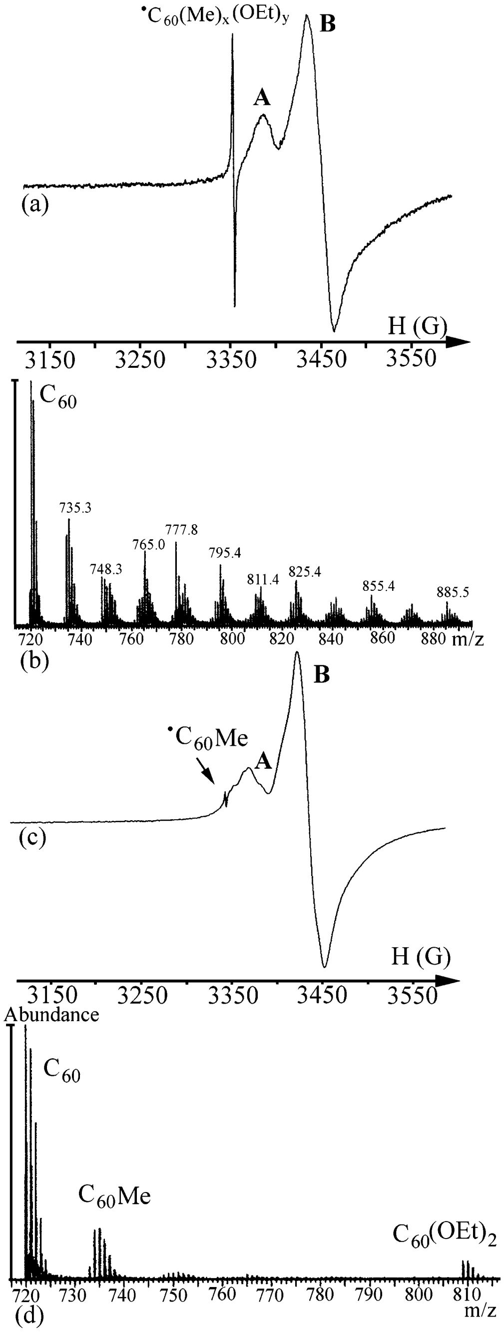

Figure 9. ESR and MALDI-TOF monitoring the mixture of complex **1** with fullerene C_{60} and MAO in toluene-d_8 at 290 K (**1**:MAO are at a 1:50 ratio): (a) ESR spectrum of **1** + MAO + C_{60}, (b) corresponding MALDI-TOF spectrum, (c) ESR spectrum of **1** + MAO reacted for 6 h, then addition of C_{60} [under visible light ($\lambda > 600$ nm)], (d) corresponding MALDI-TOF spectrum.

Table 4. Results of the Polymerization of Ethylene by Complex 1 Activated by MAO[a]

entry	**1**:MAO ratio	$P(C_2H_4)$ (atm)	time (min)	T (°C)	activity (g/(mol h))	M_n	M_w	MWD
1	1:200	1	15	25	101 000	39 000	60 000	1.56
2	1:200	10	15	25	259 500	46 000	69 000	1.52
3	1:200	20	15	25	650 000	281 000	467 000	1.67
4	1:200	30	15	25	680 000	725 000	1 356 000	1.87
5	1:200	30	5	25	756 000	681 000	1 216 000	1.99
6	1:200	30	60	25	334 000	806 000	1 354 000	1.68
7	1:20	30	60	25	7 000	1 379 000	1 998 000	1.45
8	1:100	30	60	25	247 000	906 000	1 611 000	1.78
9	1:400	30	60	25	148 000	1 060 000	1 825 000	1.72
10	1:200	30	15	−20	491 000	50 000	86 000	1.74
11	1:200	30	15	0	752 000	47 000	95 000	2.05
12	1:200	30	15	50	656 000	48 000	99 000	2.09
13[b]	1:200	30	15	25	203 000	40 000	96 000	2.39
14[c]	1:200	30	15	25	628 000	27 000	66 000	2.43
15[d]	1:20	30	15	25	39 000	49 000	128 000	2.64

[a] Polymerization conditions: **1** = 8 mg; solvent = 10 mL of toluene. [b] Reaction performed in the absence of solvent. [c] The complex and MAO were stirred in 10 mL of toluene for 5 min. The solvent was evacuated prior to the addition of ethylene. [d] $\mathrm{Al^iBu_3}$ as cocatalyst.

Table 5. Results of the Polymerization of Propylene by Complex 1 in the Presence of MAO as Cocatalyst[a]

entry	**1**:MAO ratio	time (h)	T (°C)	activity (g/(mol h))	%mmmm	M_n	M_w	MWD
1	1:400	1	25	50 000	27.5	33 000	113 000	3.40
2	1:400	2	25	44 000	24.3	39 000	117 000	3.06
3	1:400	4	25	33 000	23.9	43 000	118 000	2.92
4	1:400	18	25	11 000	22.4	51 000	147 000	3.11
5	1:200	1	25	33 000	26.3	72 000	252 000	3.52
6	1:800	1	25	87 000	22.7	22 000	77 000	3.87
7	1:400	1	−20	17 000	23.9	30 000	98 000	3.22
8	1:400	1	0	39 000	24.9	31 000	96 000	3.16
9	1:400	1	50	64 000	28.0	27 000	86 000	3.19
10[b]	1:400	1	−20	16 000	22.1	18 000	65 000	3.41
11[c]	1:200	1	25	30 000	23.7	17 000	59 000	3.47

[a] Polymerization conditions: **1** = 8 mg; solvent = 5 mL of toluene; propylene = 35 mL. [b] Reaction performed in the absence of solvent. [c] Reaction performed in the presence of 2.5 mL of toluene and 2.5 mL of fullerene (2 mg (fullerene) /mL (toluene)).

(Figure 9d) are the result of the slow reduction of the heterobimetallic complex **4** by MAO and release of methyl radicals.

The carbon NMR analysis of the polypropylene and polyethylene obtained in the polymerization reaction in the presence of complex **1** and MAO showed that the polymers were linear and that no major branching are observed during the reaction;[100] moreover, the polydispersity of the polymers was narrow. A radical polymerization initiated by the titanium(III) paramagnetic species is therefore unlikely. In order to exclude the occurrence of such a radical process, we have performed the polymerization of propylene under radical trapping conditions. A solution of fullerene (C_{60}) in toluene (2 mg of fullerene in 1 mL of toluene) was added to the complex and MAO mixture prior to the addition of the monomer. A large amount of weakly conjugated bonds in fullerene makes it an excellent radical trapping agent.[101−106] Furthermore, fullerene has been used successfully as inhibitor for radical polymerization processes.[107] The analysis of the polypropylene obtained under these conditions (see entry 11 in Table 5) confirms that the presence of the radical trap does not hold a major influence on the nature of the resulting polymer (% mmmm, MWD, M_n). Hence, the titanium paramagnetic species observed in the ESR spectrum are expected to play a negligible role in the polymerization reactions.

Polymerization of Ethylene. We have investigated the activity of complex **1** in the polymerization of ethylene in the presence of methylalumoxane (MAO) under various reaction conditions. The reactions were performed by varying one parameter at a time while maintaining the other parameters constant. The parameters we have studied are monomer pressure, reaction time, cat:MAO ratio, reaction temperature, and solvent. The results for the polymerization are presented in Table 4.

As opposed to the results for the polymerization of α-olefins by simple titanium alkoxide,[59] the values of the molecular weight distributions of the obtained polymers indicate a single site catalyst. The activities and molecular weights obtained are high although not approaching the values needed sometimes in the industry.[108]

We investigated the influence of monomer pressure on the polymer obtained by performing the reaction at a catalyst to MAO ratio of 1:200 for 15 min (see entries 1−4). We could observe that all the measured parameters (activity, molecular weight, and molecular weight distribution) increased with raise of monomer pressure. This result is in line with increased insertion rate of monomer with enhanced concentration. It is interesting to note that the reaction at atmospheric pressure of monomer yielded a polymer with high activity and reasonable molecular weight (see entry 1).

The effect of reaction time on the polymerization is a central issue. The concentration of the active species (which we propose is **4**) was found to decrease with time. The NMR analysis of complex **1** with MAO showed that the putative active species **4** is formed instantaneously, and its concentration decreases right from the first minutes of the reaction. We therefore expected a decrease in the rate of insertion of monomer with time. The insertion rates were calculated according to eq 1:

$$\mathrm{ri} = \frac{m/\mathrm{MW}}{t} \qquad \mathrm{rt} = \frac{m/M_n}{t} \tag{1}$$

where ri is the rate of insertion, rt the rate of termination, M_n the number-average molecular weight, m the mass of the polymer, MW the molecular weight of propylene = 42.08 g/mol, and t the polymerization time. The maximal insertion rate was observed after the first measurement (polymerization time = 5 min), thus strongly reinforcing our assumptions. We could not observe an increase in the activity during the first steps of the reaction as is usually expected from the induction time, for reaching optimal activation of the catalyst with MAO as cocatalyst.[109]

The activity of the catalyst, molecular weights, and polydispersities of the polymers were measured as a function of MAO concentration (entries 5−8). The maximum polymerization activity was reached when the catalyst:cocatalyst ratio used was 1:200. Higher concentrations of MAO did not improve the activity due to an earlier abstraction of the ethoxide ligands and subsequent decomposition of the active species. This effect is most probably enhanced by the known deactivation of catalysts in the presence of high amounts of MAO.[110] It is extremely important to point out that high activities are reached with relatively small amounts of MAO in contrast to metallocenes or other Ziegler−Natta type systems.[4]

Changes in the reaction temperature (compare entries 10−12) did not induce noticeable changes in the polymers apart from the expected increase in activity of the system.

Interestingly, a drastic drop in activity was observed when the reaction was performed in the absence of solvent, while the activity remained constant when the solvent was evaporated prior to the addition of ethylene (compare entries 4, 13, and 14). This result indicates that the presence of the solvent, even at minimal amounts, is necessary for the formation of the active species and for reaching good solubility of the olefin.

Polymerization of Propylene. We have investigated, as well, the activity of complex **1** with MAO as a cocatalyst in the polymerization of propylene. The influence of reaction time, cat:MAO ratio, reaction temperature, and solvent was studied, and the results for the polymerization are presented in Table 5.

The molecular weight polydispersities obtained under all the reaction conditions tested reveal that the reaction is not performed via a truly single site complex. The molecular weight distribution of the polymers obtained under all reaction conditions varied from 2.92 to 3.87, indicating that two probably active species at most are active in the polymerization of propylene. This result is in disagreement with the results obtained by Pellecchia for $Ti(OBn)_4$ (where MWD = 7−15).[59] In order to characterize the polymers obtained by the active species, we have performed a fractionation of the polymers in refluxing hexane, isolating two fractions (corroborating two active species). An insoluble fraction displayed an average tacticity of 30% mmmm, while a soluble fraction displayed a lower average tacticity (15% mmmm) when the molecular weights and polydispersities remained similar. Thus, the polymers obtained in the two fractions are very similar apart from their tacticities and indicate the presence of two similar active species varying only slightly in their symmetry. (This symmetry difference should not have made any change during the polymerization of ethylene; hence, we obtained as expected a single site active complex.) The two “cationic” species present in solution must differ by a slight change in symmetry, when the species with the lower symmetry induces the formation of the higher stereoregular polymer. The differentiation is only noticeable for propylene (but not in ethylene) due to the prochiral properties of the monomer. These species must emerge plausible from variations in the bonding properties of the methyl groups (bridging/nonbridging) in complex **4**.

Another feature that differed from the results of the polymerization of ethylene lies in the influence of the amount of MAO used on the resulting polymers (see entries 1, 5, and 6 in Table 5). We could observe a constant increase in activity with increase of MAO concentration up to a **1**:MAO of 1:800. Maximum activity was not reached at this ratio. Higher amounts of MAO are often needed in the polymerization of propylene than in the polymerization of ethylene.[111−113]

We observed a similar trend for the influence of reaction time as in the polymerization of ethylene (compare entries 1−4). Maximum insertion rate was calculated for the shortest reaction time measured, thus strengthening our claim for the decomposition of the active species right from the first steps of the reaction. Temperature changes in the polymerization of propylene induced no major changes in the resulting polymers except for an increase in activity, as was observed in the polymerization of ethylene (compare entries 1 and 7−9). The results obtained in the polymerization of propylene are in agreement with the proposed octahedral Ti−Al heterobimetallic active species (**4**).

Conclusions

Complex **1** was found to react with MAO to give mainly a heterobimetallic cationic monomethyl species with ethoxide bridges as the main active species for the polymerization of propylene and ethylene. The lifetime of this complex is sufficiently long to allow an effective polymerization. Moreover, this active species can be found with minor variations in the symmetry, the lowest symmetry inducing a slightly more stereoregular polypropylene. The reaction eventually gives rise to an abstraction of the ethoxide ligands by the aluminum atom in MAO and subsequent deactivation of the complex. The obtained polymers display intermediate tacticities and high molecular weight. The presence of the chlorine atoms in complex **1** have proven crucial for the formation and stabilization of an octahedral single site active species.

Experimental Section

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1−2 ppm of O_2). Argon and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under nitrogen from potassium benzophenone ketyl. Hydrocarbon solvents were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuo over Na/K alloy in resealable bulbs or freshly distilled prior to use.

NMR spectra were recorded on a Bruker Avance 300 spectrometer and a Bruker Avance 500 spectrometer. Chemical shifts for ^1H NMR and ^{13}C NMR are referenced to the internal solvent resonance and reported relative to tetramethylsilane.

Molecular weight determinations of the polymers were measured on a Waters Alliance 2000 GPC instrument using 1,2,4-trichlorobenzene as a solvent at 140 °C. Polystyrene standards were used for the standard calibration curve of the GPC.

ESR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.4 GHz) digital ESR spectrometer equipped with Bruker N_2-temperature controller. All spectra were recorded at microwave power 6.4 mW and 100 kHz magnetic field modulation of 1.0 G amplitude. Digital field resolution was 2048 points per spectrum, allowing all hyperfine splitting to be measured directly with an accuracy better than 0.1 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia Software.

Crystal Structure Determination: General Procedure. Single crystals immersed in Paraton-N oil were quickly fished with a glass rod and mounted on a KappaCCD diffractometer under a cold stream of nitrogen at 230 K. Data collection was carried out with monochromatized Mo Kα radiation using omega and phi scans to cover the Ewald sphere.[114] Accurate cell parameters were obtained with complete collections of intensities, and these were corrected in the usual way.[115,116] The structures were solved by direct methods and completed using successive Fourier difference maps.[117] Refinements were performed anisotropically with respect to the nonhydrogen atoms.[118,119] Hydrogens were placed at calculated positions and refined using the riding model until convergence was reached.

Synthesis of Complex 1. 2.3 g (0.1 mol) of Na was added gradually to 50 mL of dry ethanol and cooled to 0 °C. The mixture was stirred and allowed to reach room temperature. The reaction was continued until no metallic Na could be observed. The solvent was evaporated, and 50 mL of dry THF was added to the white solids. The solution was cooled to 0 °C, and 5.5 mL (0.05 mol) of $TiCl_4$ was syringed followed by the instantaneous formation of a white suspension. The reaction mixture was stirred for 2 days at room temperature and then filtered, and the solvent was removed. The product was purified by recrystallization from 80 mL of dry toluene and 1 mL of dry hexane at −60 °C. After 72 h, 4.4 g (0.009 mol) of complex **1** was collected (35% yield). A second recrystallization affords additional 4.3 g of complex **1**, allowing a total yield of 70%. Anal. Calcd for **1** ($Ti_2C_{12}H_{32}Cl_4O_6$): C, 28.26; H, 6.33. Found: C, 27.82; H, 6.05%. ^{1}H NMR [toluene-d_8, 294 K, δ]: 7.10 (broad, 1H, *H*OEt), 4.83 (broad,2H, μ-OCH_2CH_3), 4.48 (broad, 2H, OCH_2CH_3), 3.87 (broad, 2H, $HOCH_2CH_3$), 1.49 (broad, 3H, μ-OCH_2CH_3), 1.11(broad, 6H, $HOCH_2CH_3 + OCH_2CH_3$). ^{13}C NMR [toluene-d_8, 294 K, δ]: 81.62 (OCH_2CH_3), 75.63 (μ-OCH_2-CH_3), 65.21 ($HOCH_2CH_3\,C_5$), 17.32 (μ-OCH_2CH_3), 16.98 (OCH_2CH_3), 16.64 ($HOCH_2CH_3$).

Polymerization Procedures. The polypropylene and polyethylene samples were prepared in a stainless steel reactor equipped with a magnetic stirrer. The reactor was charged with 8 mg (1.6 × 10^{-2} mmol) of complex **1** and with the required amount of solvent and cocatalyst. For the polypropylene runs, purified propylene gas was condensed in excess (35 mL) into the reactor vessel. For the polyethylene runs, purified ethylene was pressurized in excess into the reactor to the desired pressure. The pressure was kept constant during the polymerization by addition of ethylene when needed. For both monomers the polymerization was conducted with strong stirring for the required reaction time and at the required temperature.

The polymerization was quenched by opening the reaction vessel in a well-ventilated hood and adding 30 mL of a 5:1 H_2O: acetylacetone solution. The solution was decanted (or filtered when needed), and the polymer was washed with three 30 mL portions of acetone. The polymers were vacuum-dried at 50 °C.

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Supporting Information Available: Crystallographic data (CIF) for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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