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Bis(1,3-di-*tert*-butylimidazolin-2-iminato) Titanium Complexes as Effective Catalysts for the Monodisperse Polymerization of Propylene

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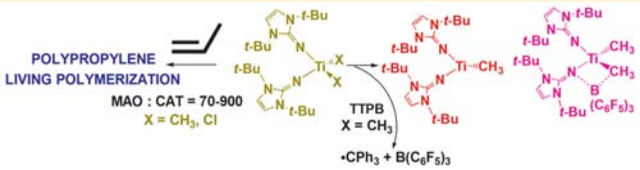
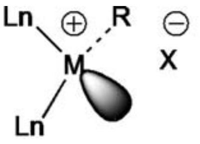
Supporting Information



ABSTRACT: The use of bis(1,3-di-*tert*-butylimidazolin-2-iminato) titanium dichloride (**1**) and dimethyl (**2**) complexes in the polymerization of propylene is presented. The complexes were activated using different amounts of methylalumoxane (MAO), giving in each case a very active catalytic mixture and producing polymers with a narrow molecular weight distribution (polydispersity = 1.10). The use of the cocatalyst triphenylcarbenium (trityl) tetra(pentafluorophenyl)borate totally inhibits the reaction, producing the corresponding bis(1,3-di-*tert*-butylimidazolin-2-iminato) titanium(III) methyl complex, the trityl radical ($^\bullet$CPh$_3$), the anionic MeB(C$_6$F$_5$)$_4^-$, B(C$_6$F$_5$)$_3$, and the bis(1,3-di-*tert*-butylimidazolin-2-iminato) titanium(IV) dimethyl·B(C$_6$F$_5$)$_3$ complex. The use of a combination of physical methods such as NMR, ESR-C$_{60}$, and MALDI-TOF analyses enabled us to propose a plausible mechanism for the polymerization of propylene, presenting that the polymerization is mainly carried out in a living fashion. In addition, we present a slow equilibrium toward a small amount of a dormant species responsible for 2,1-misinsertions and chain transfer processes.

1. INTRODUCTION

Since the discovery of Ziegler−Natta catalysts[1] in the 1950s the polymerization of α-olefins has remained one of the most successful and widely studied organometallic mediated catalytic processes. In the 1980s the "metallocene revolution" gave some of the most significant breakthroughs with the development of single site group 3 and 4 metallocene catalysts;[2] these findings helped us to understand various mechanistic aspects of such processes, as well as how the catalyst structure affects the polymer microstructure.[3] During this period, both academic and industrial researchers have devoted significant efforts to elucidate the essence of the active species and to gain control over the nature of the polyolefin products.[4] It was found that most of the time, there is a direct correlation between the catalyst symmetry and the poly-α-olefin tacticity, with C_2- and C_1-symmetric complexes producing isotactic polymers, C_S-symmetric catalysts producing mainly syndiotactic polymers, and C_{2v}-symmetric catalysts yielding atactic polymers.[5] Despite these general correlations, some transition metal complexes do not follow these expected reactivity patterns, thereby forming unique, unexpected materials which subsequently gave new impressive insights into the reaction mechanism for the polymerization of propylene.[2−6] The possibility of controlling the stereoregularity of the polyolefin products was elegantly demonstrated by the capacity of specific *ansa*-metallocenes to polymerize propylene with very high iso- or syndiotactic microstructures.[2−6] Recent evidence has been reported, which shows that the activator and the structures of the resulting ion pairs (**A**) can have a profound influence on the single-site polymerization catalyst activity, stability, lifetime, chain-transfer characterization, and possibly stereoregulation.[7]



(A)

R= alkyl group

Ln = ancillary group

In parallel to the 'metallocene revolution', a significant amount of research has been developed which focuses rather on new, nonmetallocene early and late transition-organometallic complexes.[8] Furthermore, the discovery of constrained-geometry catalysts brought about a great diversity of half-metallocene complexes and many other monocyclopentadienyl piano-stool type complexes as catalytic precursors.[9]

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We have been interested in non-Cp ancillary ligands, particularly those containing the chelating N-donor benzamidinate.[10] Benzamidinate ligands can be considered as a steric equivalent of the Cp or Cp* (Cp = C_5H_5; Cp* = C_5Me_5) moieties; however they possess unique electronic properties.[11] The anionic moiety $[\text{R-C(NSiMe}_3)_2]^-$ is a four electron donor, promoting a higher electrophilicity at the metal center, as compared to the six electrons of the cyclopentadienyl ligands. The activation of these systems has given vital insights toward the design of new ancillary ligands which are isolobal to cyclopentadienyl ligands, yet possess a higher level of coordinative unsaturation. Among the most interesting examples of such ligands thus far are imidazolin-2-iminato ligands.[12]

Recently, a general method for the synthesis of this class of 2-iminoimidazoline N-heterocyclic N-donor ligands, which behaves as a $2\sigma,4\pi$-electron donor, was introduced.[13] These imidazolin-2-iminato ligands can be described by the two limiting mesomeric structures shown in Figure 1, which in turn should lead to highly basic ligands with a strong electron donating capacity. The synthetic route exploits the propensity of stable carbenes of the imidazolin-2-ylidene type to undergo a Staudinger[14] reaction with trimethylsilyl azide forming *N*-silylated 2-iminoimidazolines. Moreover, the substituents at the ring may conveniently be altered to allow for the fine-tuning of both the steric and electronic properties of the ligands.

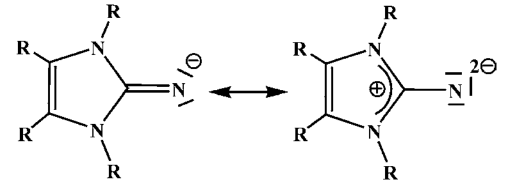


Figure 1. Mesomeric forms in the imidazoline-2-iminato ligand.

Interestingly, it has been shown that half sandwich complexes of titanium of the type $CpTi(L)X_2$ (L = imidazolin-2-imide, X = Cl, CH_3) were found to be active in the polymerization of ethylene and in the copolymerization of ethylene and 1-hexene.[15] These findings have prompted us to study complexes of the type L_2TiX_2 (L = imidazolin-2-imide, X = Cl, CH_3) and their potential as polymerization catalysts.

It has been previously shown that the catalytic and stoichiometric properties of organo-f-element complexes are dramatically influenced by the nature of the π ancillary ligands.[16] Regarding the structure of the overall complex, a significant opening of the metal coordination sphere (frontier orbitals)[17] at the σ-ligand equatorial girdle is attained by replacing the pentamethylcyclopentadienyl ligation in $Cp^*_2MR_2$ (Cp* = C_5Me_5, M = f-element metal, R = σ-bonded ligand) by a bridged ligation toward the corresponding *ansa*-$Me_2SiCp''_2MR_2$ (Cp″ = C_5Me_4).[18] In the respective organolanthanides, this change allows an increase (10−100-fold) in rates for the olefin insertion into the M−R bond,[19] whereas this effect is more pronounced in the analogous organoactinides, resulting in an increase by 3 orders of magnitude in their catalytic activity for the hydrogenation of 1-hexene or in the hydrosilylation of alkynes.[18a,d,20] Following the same rationale, we expected that the imidazolin-2-iminato complexes would result in an opening at the equatorial girdle as compared to the *ansa*-metallocene group 4 complexes.

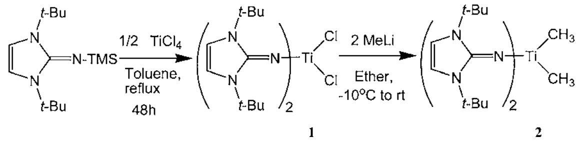
When the complex L_2TiX_2 (L = imidazolin-2-imide, X = CH_3) was studied in the polymerization of ethylene, a mild active catalyst was obtained producing high MW polyethylene, however in a very high multimodal fashion (polydispersity >16).[15] Our first attempts to compare the same systems in the polymerization of propylene showed vastly different results. Hence, we present herein highly active L_2TiX_2 (L = imidazolin-2-imide, X = Cl, CH_3) complexes as catalytic precursors in the polymerization of propylene. Furthermore, we present a detailed kinetic and mechanistic study showing that these complexes behave in a pseudo living manner and are catalytically active with a very low loading of the MAO cocatalyst. The effect of different cocatalysts was studied, and intermediate compounds were trapped and analyzed using ESR, MALDI-TOF, and ^{19}F NMR spectroscopy.

2. RESULTS

The following study examines the synthesis and characterization of the corresponding dichloride complex and its comparison to the respective dimethyl complex. We start the presentation of the results with the synthesis of the complexes, the X-ray molecular structure of the dichloride complex, and its comparison to the corresponding dimethyl complex.[15a] Furthermore, the polymerization results are described including the effect of various parameters such as temperature, pressure, and cocatalysts. The discussion of the experimental data in addition to the spectroscopic findings using C_{60} as a radical trapping agent has allowed us to propose a plausible mechanism for the reaction.

2.1. Synthesis and Structure of Complexes.

In this study we used the complexes L_2TiCl_2 (**1**) and L_2TiMe_2 (**2**) (L = 1,3-di-*tert*-butylimidazolin-2-imide) as the precatalysts for the polymerization reactions of propylene. As previously reported[13b,15a] both complexes were obtained in almost quantitative yields. Complex **1** is obtained by the reaction of $TiCl_4$ with 2 equiv of *N*-trimethylsilyl-1,3-di-*tert*-butylimidazolin-2-imine, and complex **2** can be obtained by the subsequent methylation of complex **1** with MeLi (eq 1). The ORTEP presentation of the molecular structure of complex **1** is shown in Figure 2. The complex exhibits the expected pseudotetrahedral geometry around the titanium atom with Ti−N−C angles [Ti(1)−N1(1)−C(21) = 173.7(2)° and Ti(1)−N(4)−C(22) = 174.9(2)°] close to linearity and with the Ti−N bond lengths [Ti(1)−N(4) = 1.788(2) Å, Ti(1)−N(1) = 1.7890(19) Å], which are shorter as compared to the molecular structure of complex **2** [Ti−N1 = 1.828(1) Å, Ti−N2 = 1.819(1)) Å]. The nitrogen−carbon bond lengths [(N(1)−C(21) = 1.315(3) and N(4)−C(22) = 1.310(3) Å)] are similar and comparable to those of complex **2**, indicating that both complexes are nearly isostructural.



1 **2** (1)

As aforementioned, the precatalysts **1** and **2** possess more accessible frontier orbitals as compared to the very closely related *ansa*-bridged titanium complexes. For example, the angles between the two iminato ligands in complex **1** and **2** are smaller by 17° and 13°, respectively, as compared to the *ansa*-bridged complex $[Me_2Si(\eta^5\text{-}C_5H_2(SiMe_3)_2]_2TiCl_2$ (**3**) (Figure

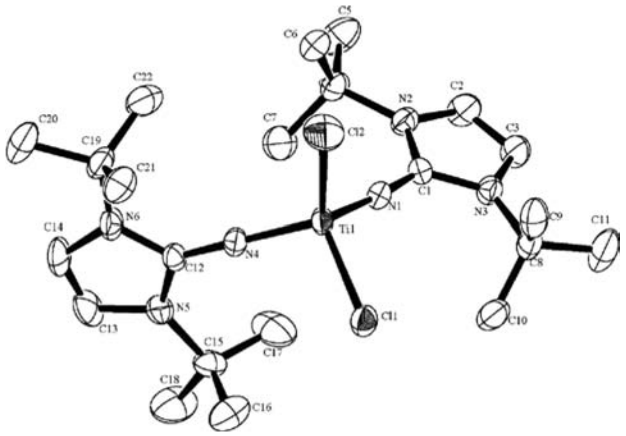


Figure 2. ORTEP representation of the molecular structure of complex **1** with removal of hydrogen atoms for clarity.

3).[21] This reduction in the interligand angle results in a more open coordination sphere, which is expected to induce an increased reactivity in complexes **1** or/and **2** as compared to complex **3**. This structure−reactivity expectation, while maintaining the isolobal relationship to Cp, was our starting point in the use of the imidazolin-2-iminato titanium complexes for the polymerization of propylene.

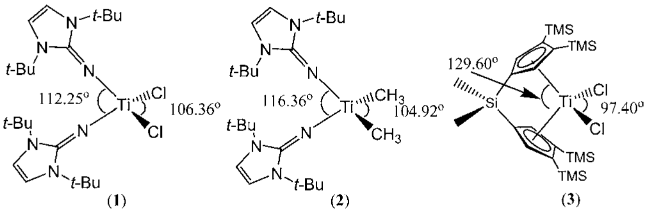


Figure 3. Structural comparison of precatalysts **1** and **2** with the reported complex **3**.

2.2. Propylene Polymerization Studies. We investigated the catalytic activity of complex **1** in comparison with the methylated complex **2** in the polymerization of propylene under identical conditions and found that the latter complex provides better activities under all conditions (however not larger than 10%). Also where different experimental conditions were used (pressure, MAO/catalyst ratio, temperature, etc.), we observed a similarly higher activity for complex **2** than for complex **1**; however the same trends were always observed. As a result of this observed behavior, all further work presented will focus on complex **2**.

2.2.1. Time Dependence on the Activity of Complex ***2***. The time dependence on the catalytic activity of complex **2** was first investigated by repeating the reaction for different periods of time while the concentrations of the catalyst, MAO, and propylene were kept constant (Table 1). Each result presented here is an average of at least three consecutive runs with less than 5% of variance among them.

From Table 1 we can observe that complex **2** remains active even after long periods of time (24 h), yielding as a function of time greater polymer production and higher molecular weights. The lack of linearity in the productivity as a function of time after the first 4 h (80% conversion) is due to the more viscous solution of polymer obtained, resulting in low local concentrations of substrate relative to catalyst inducing mass transport problems. However, a linear increase of the average number molecular weight (M_n) and the amount of obtained polymer as a function of time (Figure 4) suggests a "quasi" living polymerization during the first 4 h of the reaction.

Table 1. Effect of Polymerization Time on the Performance of Complex 2 in the Polymerization of Propylene[a]

time (h)	yield (%)[b]	M_w[c]	M_n[c]	PDI[d]	Ri*10^{-3}[e]	productivity[f]
1	17	242 000	170 600	1.42	42	260
2	30	270 000	184 300	1.46	48	380
3	60	348 000	275 200	1.26	69	810
4	80	438 900	387 800	1.13	75	1100
5	85	420 300	319 700	1.31	60	1180
6	90	424 700	320 900	1.32	51	1200
9	92	472 000	431 600	1.09	36	1260
24	95	513 200	481 000	1.06	14	1340

[a] Catalyst:MAO = 1:918, 5 mg of catalyst, 6 mL of toluene, 30 mL of propylene, polymerization at room temperature. [b] Amount of used propylene. [c] Dalton. [d] PDI = M_w/M_n. [e] Ri = rate of monomer insertion = $(m/M_{w(\text{monomer})})$/min, where m is the mass of the polymer, $M_{w(\text{monomer})}$ is the molecular weight of the monomer (42 g/mol for propylene), and t is the duration of the polymerization. [f] In units of (kg polymer)(mol cat.)$^{-1}$.

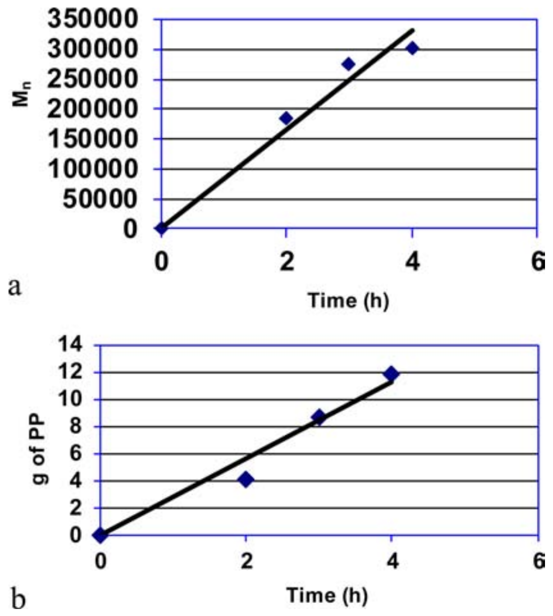


Figure 4. Plot of the M_n as a function of time (a) and polymer weight as a function of time (b) obtained by complex **2** in the polymerization of propylene.

2.2.2. Influence of Temperature and Pressure. The effect of temperature was studied for complex **2** after 4 h to avoid precipitation of polymer and mass transport of the monomer (Table 2). The better efficiency of the catalytic system was found at 25 °C, whereas the lowest activity was produced at 0 °C. Similar trends were observed for the molecular weights of the polymers (besides at 0 °C). A gradual increase in the temperature up to 35 °C resulted in a slight decrease in activity with almost no effect on the molecular weight of the polymer; however, at 55 °C, both the activity and molecular weight were reduced.

Once the ideal reaction time and the working temperature were determined, we examined the optimal operative pressure

Table 2. Influence of Temperature on the Activity of Complex 2 in the Polymerization of Propylene[a]

temp (°C)	yield (%)	M_w	M_n	activity[b]	Ri×10^{-3}
0	30	125 000	86 000	90	25
25	80	438 900	387 800	297	75
30	72	435 000	386 600	262	64
35	70	434 100	383 600	240	60
55	50	395 900	342 400	170	40

[a] Conditions same as those in Table 1; reaction time = 4 h. [b] (kg of PP)*(mol of cat)$^{-1}$(hr)$^{-1}$.

for this study. As such, to determine the effect of propylene pressure on the polymerization efficiency of the catalyst, the polymerization reaction was carried out at various constant pressures while keeping the temperature and catalyst concentration constant; however two different MAO/catalyst ratios (Table 3) were studied. It is clear, as expected, that the reactivity of the complexes is highly affected by the pressure of the monomer; however, at 10 atm, narrower polydispersities were obtained. Moreover, as will be presented, it is evident that the best MAO/catalyst ratio to be used to gain the higher molecular weights is approximately 100:1; however, it was important to study the effect of the cocatalyst ratio as a function of pressure to exclude, and possibly avoid, secondary effects.

Table 3. Influence of Pressure on the Polymerization of Propylene Catalyzed by Complex 2[a]

entry	MAO/catalyst	P (atm)	M_w	M_n	PDI	activity[b]
1	101:1	10	492 210	445 800	1.10	250
2	101:1	5	269 900	184 300	1.46	115
3	101:1	1	13 600	11 300	1.20	6
4	918:1	10	388 800	308 100	1.26	220
5	918:1	5	334 000	252 800	1.32	115
6	918:1	1	11 200	8600	1.30	4

[a] Conditions same as those in Table 1; reaction time = 4 h. [b] (kg of PP)(mol of cat)$^{-1}$(h)$^{-1}$.

2.2.3. Effect of Cocatalysts on the Activity of Complex 2.

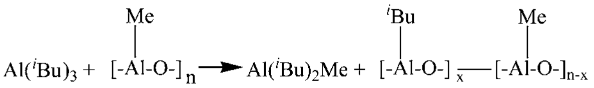
2.2.3.1. MAO as Cocatalyst. MAO was used as the main activator for the polymerizations using complex **2**, and the MAO concentration effects on the polymerization are presented in Table 4. We have performed our cocatalyst studies from very low MAO excess ratios, but very low activity and small amounts of polymer were observed at these ratios; herein we present the changes from an MAO excess ratio of 70 up to 918. Table 4 shows that both the activity and the molecular weight of the polymers increase from an MAO excess of 70 reaching a maximum at an excess of 250, producing polymers possessing a very low polydispersity. Any additional increase in MAO resulted in a somewhat lower activity of complex **2**, and a lower molecular weight, but with the larger MAO excess, a slight increase in the polydispersity of the polymers was obtained. This result indicates the ability to control the molecular weight of the polymers without major critical changes in the activity of complex **2**.

Table 4. Effect of Cocatalyst on the Polymerization of Propylene Promoted by Complex 2[a]

entry	Al/Ti	yield (%)	M_w	M_n	PDI	activity[b]
1	70	70	459 300	408600	1.12	245
2	87	70	493 400	435 300	1.13	255
3	101	75	492 200	445 800	1.10	250
4	173	80	481 900	438 400	1.09	280
5	250	85	560 700	519 900	1.07	300
6	318	80	525 800	487 100	1.07	280
7	459	80	524 800	474 500	1.10	270
8	737	70	378 100	328 600	1.15	255
9	857	70	397 700	320 100	1.24	240
10	918	60	388 800	308 100	1.26	220

[a] Conditions as in Table 1. Reaction time = 4 h. [b] (kg of PP)(mol of cat)$^{-1}$(h)$^{-1}$.

2.2.3.2. Triisobutylaluminum (TIBA) as Cocatalyst. Apart from the commonly used cocatalyst MAO, the complexes were also tested with triisobutylaluminum (TIBA) as a cocatalyst (Table 5). It was observed that complex **2** with TIBA is not active toward the polymerization of propylene (Table 5, entry 2); however, the addition of TIBA to the mixture of complex **2** and MAO resulted in an increase in activity of the polymerization of propylene, indicating that the combined action of TIBA and MAO is responsible for a synergetic catalytic property rather than the expected action as an oxygen and moisture scavenger agent (Table 5, compare entries 4 and 5). When the activity of complex **2** using an excess of MAO (100, 200, or 250) was compared to similar reactions using TIBA in equimolar amounts as MAO, it was observed that the latter reactions consistently resulted in higher activities. Interestingly the molecular weight and the polydispersity of the polymers remained relatively constant with less than 2% deviation. In view of the resulting data, it seems plausible that TIBA reacts with MAO forming a limited MAO−MMAO cocatalyst (eq 2) (MMAO = modified MAO), resulting in



$$\mathrm{Al}(^i\mathrm{Bu})_3 + [\text{-}\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Al}}\text{-O-}]_n \longrightarrow \mathrm{Al}(^i\mathrm{Bu})_2\mathrm{Me} + [\text{-}\overset{\overset{^i\mathrm{Bu}}{|}}{\mathrm{Al}}\text{-O-}]_x\text{—}[\text{-}\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Al}}\text{-O-}]_{n\text{-}x} \qquad (2)$$

better activities. When the reactions were performed using only MMAO (at various excess concentrations), lower activities and molecular weights were always obtained.

Table 5. Effect of TIBA and TIBA−MAO on the Polymerization of Propylene Promoted by Complex 2[a]

entry	Ti/MAO/TIBA	activity[b]
1	1:101:0	250
2	1:0:100	0
3	1:200:0	290
4	1:250:0	300
5	1:101:100	350

[a] Conditions same as those in Table 1. Reaction time = 4 h. [b] (kg of PP) (mol of cat)$^{-1}$(h)$^{-1}$.

2.2.3.3. Triphenylcarbenium (Trityl) Tetra(pentafluorophenyl)borate (TTPB) as Cocatalyst. We have also investigated the effects of complex **2** activated with the cocatalyst triphenylcarbenium (trityl) tetra(pentafluorophenyl)borate (TTPB) along with MAO (Table 6). The interest in such reactions arises from previous work, which described a dramatic increase in the catalytic activities of the benzamidinate dialkyl complexes with this cocatalyst mixture, even rivaling metallocene complexes in some examples.[7d,10j] In contrast, we observed no reactivity of catalyst **2** in the polymerization of propylene using TTPB as the sole cocatalyst. Moreover, it was

Table 6. Activity of Complex 2 in the Polymerization of Propylene Using TTPB and Mixtures of MAO and TTPB as Cocatalysts[a]

2/MAO/TTPB	activity[b]
1:0:0.5	0
1:0:1	0
1:0:2	0
1:50:0	100
1:50:2	5
1:101:0	250
1:101:2	53

[a] Conditions same as those in Table 1. Reaction time = 4 h. [b] (kg of PP)(mol of cat)$^{-1}$(h)$^{-1}$.

evident that any of its mixtures with MAO induced a catalytic inhibition (Table 6). We have shown that TTPB indeed reacts with complex **2**, however, producing an alternative reaction pathway unable to polymerize propylene.

In order to understand the inhibition effect of TTPB, NMR studies were performed on the reaction of TTPB and complex **2**, but the resulting spectra indicated the presence of paramagnetic species, allowing only partial information to be obtained from the ^{19}F NMR analysis. In addition *in situ* ESR spectroscopic measurements were carried out by mixing equivalent amounts of TTPB with complex **2** in toluene. The ESR experiments were carried out at 298 K and resulted in the formation of a Ti(III) moiety as shown in Figure 5. The ESR spectrum together with the hyperfine couplings (Figure 5a) indicates, and matches, the presence of a Ti(III) coordinated to two nitrogen atoms ($a_N(2^{14}N)$ = 3.2G) and one methyl group ($a_H(3H)$ = 2.6G). Furthermore, from the same spectrum we were able to observe a broad signal of another Ti(III) species, presumably obtained by a mixture of agglomerated MAO–Ti(III) compounds as previously reported.[10j] In addition to the Ti(III) signals, the EPR spectrum showed the typical signal for the triphenylmethyl radical (Figure 5b).

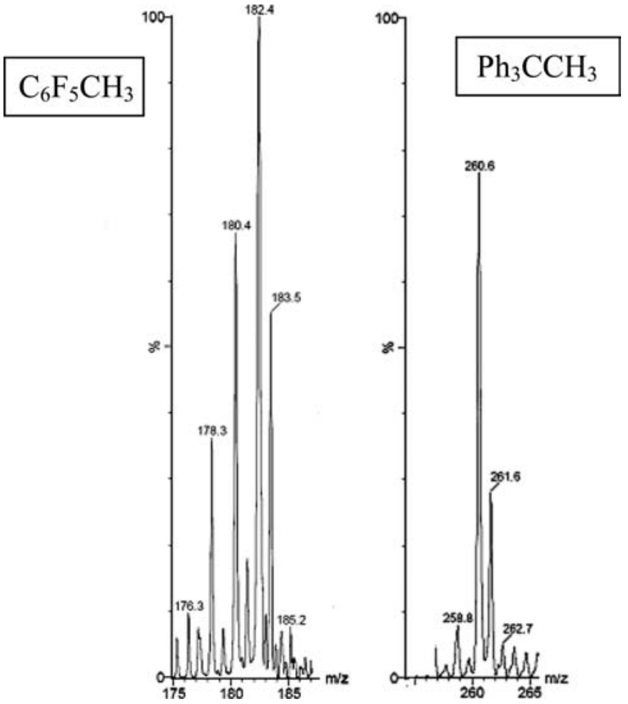


Figure 6. Mass spectra of intermediates in the reaction of complex **2** with TTPB.

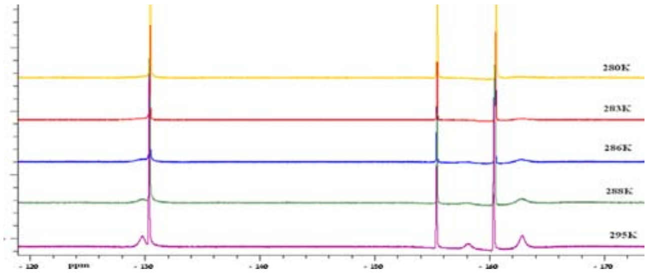


Figure 7. ^{19}F NMR spectra of the catalytic mixture of complex **2** with TTPB as a function of temperature.

Mass spectrometric analysis of this catalytic system showed a cationic radical fragment at 184 D corresponding to MeC_6F_5 and 260 D for $MeCPh_3$ (Figure 6). In addition, the ^{19}F NMR spectrum shows two sets of signals; the first set is composed of three narrow signals not affected by temperature (Figure 7). These signals correspond to free $B(C_6F_5)_3$ and were corroborated by comparison with an analytical sample. The second set of signals is broad, and it showed a dynamic temperature dependence. These signals correspond to a compound, which at low temperature precipitates (the signals disappeared at 280 K) and redissolves after heating to 295 K (Figure 7). The isolated solid is not active in the polymerization, and the signals are similar to those of a $B(C_6F_5)_3$

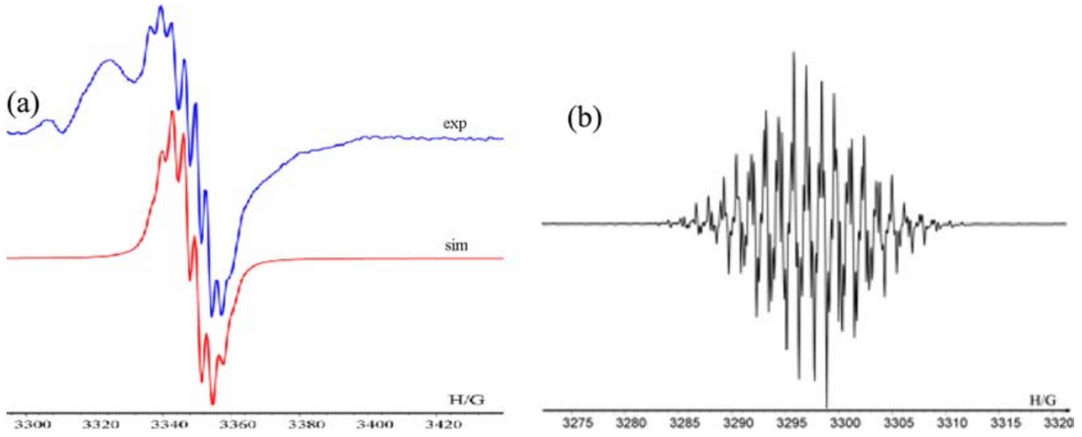
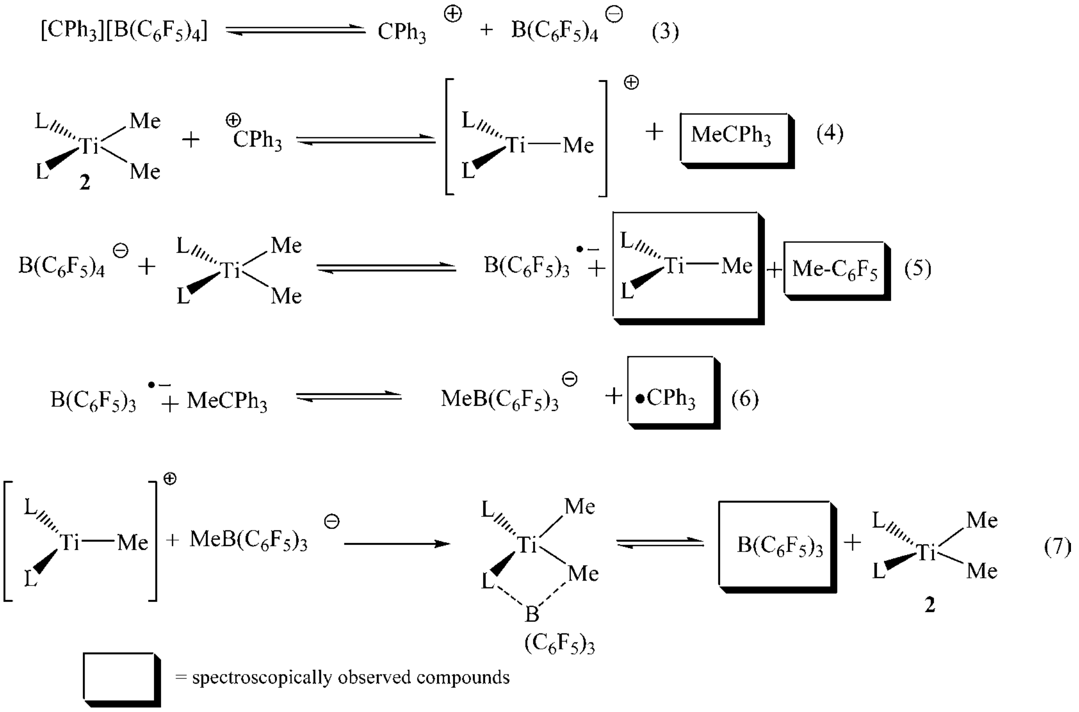


Figure 5. (a) EPR spectrum of complex **2** at 298 K and TTPB, g = 1.988; (b) EPR spectrum of triphenylmethyl radical at 298 K.

Scheme 1. Plausible Mechanism for the Reactivity of Complex 2 with TTPB. L = 1,3-Di-*tert*-butylimidazoline-2-imide



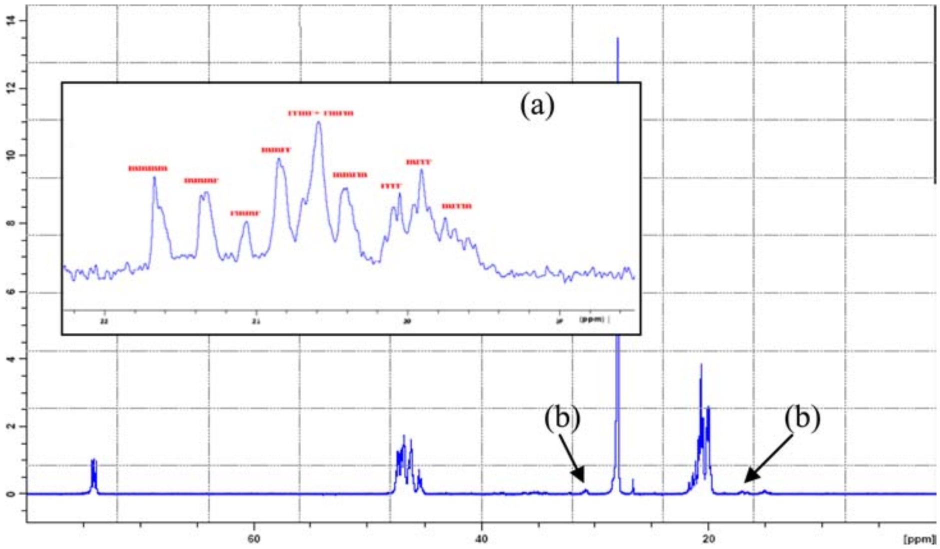


Figure 8. ^{13}C NMR of the polypropylene polymer obtained according to entry 5 in Table 4; (a) methyl pentad area, (b) 2,1-insertions.

moiety coordinated to a nitrogen atom lone pair of electrons, presumably those of the ligand exhibiting these broad signals.[22] The blank reaction of $B(C_6F_5)_3$ with complex **2** yielded the same compound and did not produce any paramagnetic compounds; however other compounds are obtained from the mixture. To date, our attempts to identify this elusive compound by crystallization and other techniques have been unsuccessful. The separation of this solid and its MALDI-TOF study shows a signal at 986 D, which presumably corresponds to the hydrolyzed complex $[L_2Ti(OH)_2(B(C_6F_5)_3Na]$ (L = 1,3-di-*tert*-butylimidazolin-2-imide), under our MALDI conditions.[23]

3. DISCUSSION

As is evident by the presented results, the imidazolin-2-iminato titanium dimethyl complex does not form a trivial polymerization system. Also, this complex and the corresponding dichloride analogue exhibit an extraordinary opportunity to control the molecular weights of the isolated polymers; furthermore we also observe some "quasi living polymerization results", which required further investigation. Moreover, we witness the formation of a Ti(III) species and inhibition by TTPB.

3.1. Inhibition Effect of TTPB. Apart from the most common cocatalyst MAO, we also tested the cocatalyst TTPB, which we have observed as an enhancer for benzamidinate systems. Unfortunately, in this system it seems to act rather as an inhibitor. This inhibition of TTPB can be explained by the following sets of reactions in Scheme 1 (eqs 3−7), taking into account our findings. We propose that in the first step the trityl cation CPh_3^+ initially reacts with the precatalyst to produce the expected monomethyl Ti(IV) cationic species and $MeCPh_3$, which has been detected by mass spectrometry. The anionic $B(C_6F_5)_4^-$ is most likely reacting with the precatalyst as well, forming the radical anion $B(C_6F_5)_3^{\bullet-}$, titanium(III), and the trapped perfluorinated toluene. This radical anion $B(C_6F_5)_3^{\bullet-}$ will react with CH_3CPh_3 to produce the trityl radical and $CH_3B(C_6F_5)_3^-$. The anionic $CH_3B(C_6F_5)_3^-$ will immediately react with the cationic Ti(IV), thereby likely forming a complex in which the boron undergoes coordination to a methyl group and to a nitrogen atom of the ligand, which is in equilibrium with the free borane and the starting Ti(IV) complex. Our attempts to trap the radical $B(C_6F_5)_3^{\bullet-}$ were unsuccessful, presumably due to its very short half-life time (10 min) at low temperatures in THF.[24]

3.2. Polymers and Reaction Mechanism. After the polymerization reaction was conducted using only MAO as a cocatalyst, the polymers were cleaned by washing with a solution of HCl/methanol (1:9), then water, and acetone and drying in vacuum. The polymers were fractionalized in boiling hexane and found mainly as only one soluble fraction (99.6%), which further supports the presence of only one active catalytic species in this process. The resulting polymers are atactic and elastomeric in nature due to their high M_w.[25] The pentad analysis showed that the polymers produced from complex **2** show an almost theoretical Bernoulli distribution of their microstructure (Figure 8a). An unexpected feature of the ^{13}C NMR shows small signals responsible for 2,1 misinsertions (Figure 8b). This result is interesting and peculiar, indicating the lack of "living" features in this catalytic system.

To elucidate this "quasi living" reaction mechanistically and to try to identify the active catalytic species, complex **2** was mixed with MAO in a sealed NMR tube with deuterated toluene, forming a precipitate. The solid was separated from the solution, washed, and dried (about 30% of the initial Ti complex). The solid material exhibits a broad asymmetrical ESR signal shifted upfield (compared to organic radicals) at g = 1.981 (Figure 9). Such asymmetrically structured broad signals with low g-values are typically exhibited by agglomeration of paramagnetic Ti(III) complexes with MAO.[10j,26] Interestingly, this compound was repeatedly reacted at various temperatures with aliquots of propylene, and trace amounts of polymer were formed. On the other hand, the liquid fraction did not show any ESR signal, and addition of propylene gave the same elastomeric polymer and reactivity, indicating that this fraction contains the plausible active cationic Ti(IV) species.

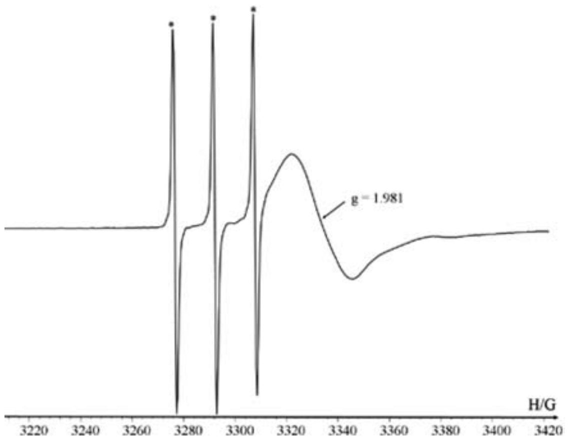


Figure 9. ESR spectrum of **2**, and MAO at 290 K (TEMPO marked by *, g = 2.0058) for Ti(III), g = 1.981.

To find out the source of Ti(III), the same NMR tube reaction was performed with the addition of C_{60} as a radical trapping agent.[10j,27] It is important to note that the performance of the catalytic mixture in the presence of the fullerene shows the same propylene polymerization activity as compared to the polymerization without C_{60}. Since it is expected that a methyl radical will be trapped by C_{60}, visible light ($\lambda > 500$ nm) was used at the ESR cavity to observe the reversible dissociation of the dimeric fullerenyl radical $MeC_{60}{-}C_{60}Me$ (eq 8). The spectrum showed a typical signal for $^{\bullet}C_{60}Me$, which was also supported by MALDI-TOF analysis and the respective fragment at 735 for $^{\bullet}C_{60}Me$, indicating that MAO reduces the titanium center to Ti(III) (Figure 10). It is important to note that the reaction between MAO and C_{60} does not produce the $MeC_{60}^{\bullet}$ radical.

$$MeC_{60}{-}C_{60}Me \rightleftharpoons 2MeC_{60}^{\bullet} \qquad (8)$$

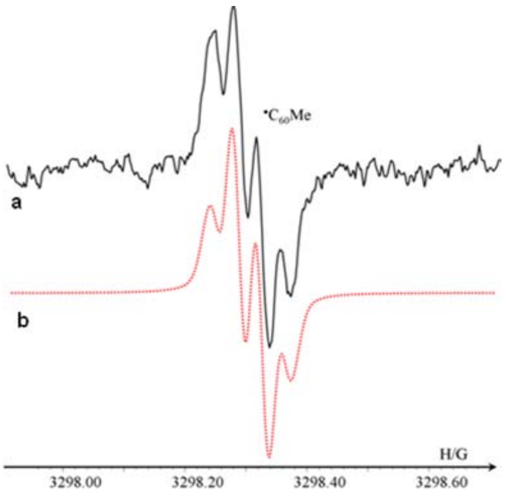
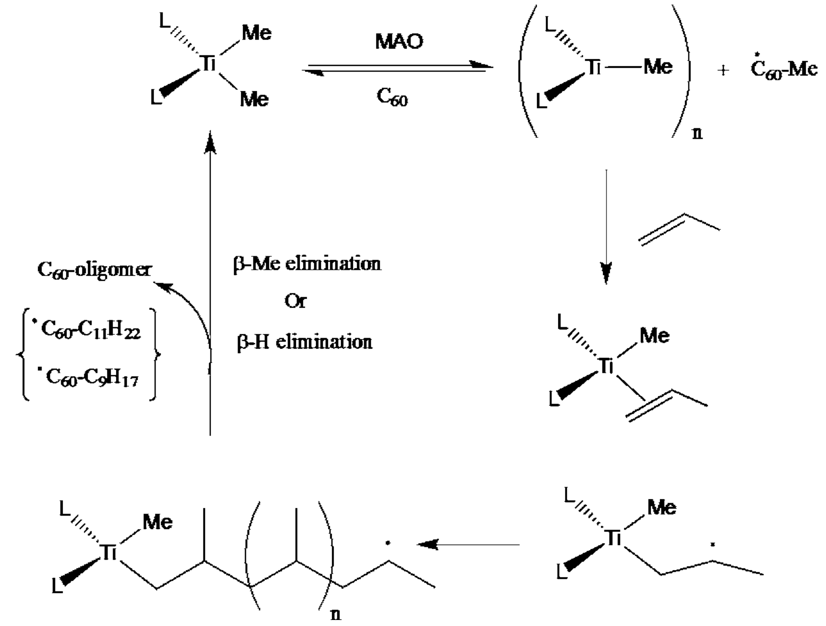


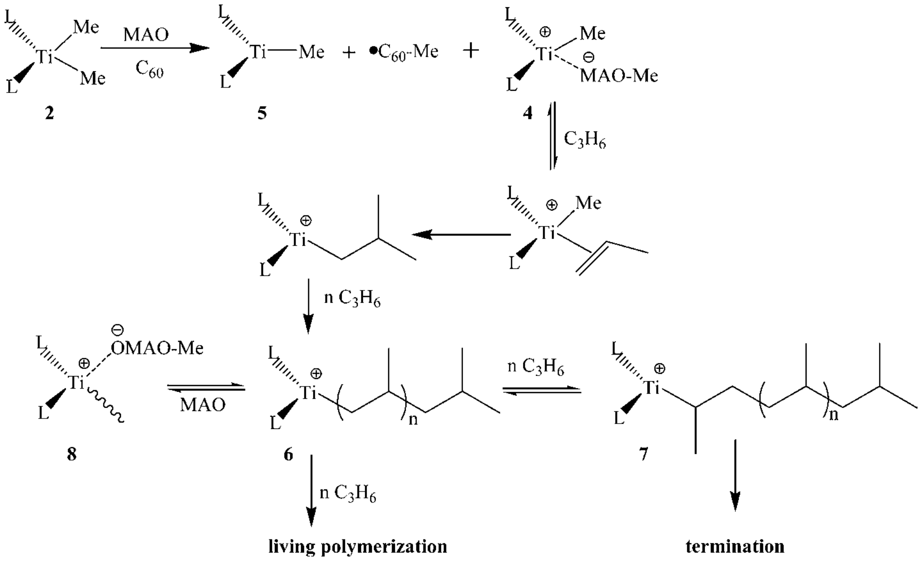
Figure 10. (a) EPR spectrum of $^{\bullet}C_{60}Me$ at high resolution (a_H(3H) = 0.035G); (b) simulated spectrum of $^{\bullet}C_{60}Me$.

A curious result was obtained when aliquot amounts of propylene were added to the NMR tube containing MAO and C_{60}. Aside from the obtained polymer, an increase in the intensity of the $^{\bullet}C_{60}Me$ signal was observed. This result suggests an additional concomitant process operating in concert with the living polymerization. As aforementioned, the Ti(III) is able to react with propylene; however only trace amounts of polymer are produced. Moreover, the additional $^{\bullet}C_{60}Me$ is most likely formed from a Ti(IV), which is again reduced by MAO in the presence of C_{60}. Hence, it seems plausible that the Ti(III) complex is able to react with propylene, inserting a few monomers and then eliminating a Ti(IV) complex and an oligomeric alkyl radical, thereby regenerating the Ti(IV) catalyst. It is important to address at this stage that this process, if plausible, cannot be rapid, as this would induce the formation of a polymer, contrary to the observation of the trace amounts that were produced. By using C_{60} as a radical trapping agent, we were able to observe by MALDI-TOF small amounts of polymeric moieties attached to

Scheme 2. Regeneration of the Ti(IV) Moiety after Its Reduction to Ti(III) via Its Reaction with Propylene and the Increasing Formation of $^{\bullet}C_{60}Me$; L = 1,3-Di-*tert*-butylimidazolin-2-imide



Scheme 3. Proposed Mechanism of the Activation of Complex 2 by MAO; L = 1,3-Di-*tert*-butylimidazolin-2-imide



C_{60} affording fragments at 874 and 869 D. Both signals can be clearly attributed by the difference in the chain termination mechanism via either a β-Me elimination after the insertion of four monomers or a β-H elimination after the insertion of three monomers (appear with a sodium adduct on the MALDI) (Scheme 2). A similar reaction of a Ti(III)-benzamidinate complex with propylene forming the corresponding Ti(IV) complex was already documented in the literature.[10j]

As the Ti(IV) complex is regenerated in the process, it is quite interesting that the reaction produces very low polydispersities (PDI = 1.1). Since we are able to observe the oligomers only under MALDI-TOF conditions and not in the NMR, it is reasonable to regard the recycling of Ti(IV) species as a minor, kinetically disfavored reaction. To further confirm this assumption, the number of moles of polymeric chains as compared to the number of moles of complex **2** were measured. We were puzzled by finding three times more polymeric chains than that of complex **2**, even when 70% are of an active complex. This result clearly indicates that a polymer chain transfer is operative, regenerating an active complex. Hence to prove such a mechanistic pathway involving a "dormant" species, we have reacted the cationic Ti(IV) with an aliquot of propylene for 30 s and then quenched the reaction. Analysis of the polymer by ^{13}C NMR shows that the ratio of 2,1-misinsertions to 1,2-insertions is much higher than in the final polymer, indicating that the chain transfer after the 2,1-misinsertion probably reproduces the active Ti(IV), explaining the somewhat larger polydispersity value of 1.1 instead of 1.0.

Based on the results presented above and by comparison to similar studies we have found in the activation of zirconium benzamidinate complexes,[10j] a possible reaction mechanism is presented in Scheme 3. The first step is the activation step of the catalyst **2** by MAO to form the cationic Ti(IV) species **4** along with the catalytically inactive Ti(III) species **5**, which is responsible for the parallel process as shown in Scheme 2. The catalytically active complex **4** undergoes propylene additions to form complex **6**, the active catalytic species responsible for the living polymerization process. The slow 2,1-misinsertion of propylene to complex **6** will form complex **7**, which will mainly favor elimination of a polymeric chain regenerating the active cationic titanium complex.[28] In general, this process must be very slow, since we observe only minor amounts of 2,1-misinsertions in the final polymer (see Figure 8).

The observation that at higher concentrations of MAO a decrease in activity of the catalyst as well as in the M_n of the polymer is observed can be rationalized by an equilibrium toward the plausible formation of the latent species **8**.

Additionally, it is interesting to compare our results with complex **2** with those of other well-known constrained-geometry complexes **9**[29] and **10**[30] (which produce in all cases atactic polymers), which may be indicative of possible expectations that can be exploited for this new type of complexes (Table 7).

Table 7. Catalytic Activities of CGC Complexes As Compared to Complex 2 in the Polymerization of Propylene

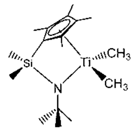
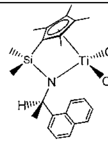
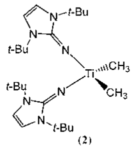
Complex / Parameters	 (9)	 (10)	 (2)
Al:Ti	500:1	3000:1	250:1
Activity	9.6	1269	300
Mw	710500	423000	560700
PDI	N.A.	2.0	1.1

Table 7 shows that the polymerization activity of complex **2** is higher as compared to that of complex **9** but is lower as compared to that of complex **10**. With regard to the molecular weights of the obtained polymers, all the complexes produce comparable materials; however, lower amounts of MAO are needed for complex **2**. Hence, when comparing the metallocenes, the constrained-geometry complexes, and our designed catalysts, we demonstrate the advantage of the smaller cone angle between the two ancillary ligands in facilitating easy access of substrates toward the catalytic site.

4. CONCLUSIONS

The bis(1,3-di-*tert*-butylimidazolin-2-iminato) titanium dichloride (**1**) and dimethyl (**2**) complexes are active in the polymerization of propylene. Both complexes show similar trends; however the dialkyl complex displays higher activities. When the dialkyl complex is activated by MAO, polymers with a narrow molecular weight distribution (polydispersity = 1.10) are obtained. MAO is able to reduce Ti(IV) to Ti(III); however the latter is only responsible for a trace amount of polymer. The "quasi living" polymerization is obtained due to the equilibrium formation of a dormant species after a 2,1-misinsertion of propylene and its concomitant chain termination. The use of the cocatalyst trityl tetrakis(pentafluorophenyl)borate totally inhibits the reaction and also produces the corresponding bis(1,3-di-*tert*-butyl imidazolin-2-iminato) Ti(III) methyl complex, the trityl radical ($^{\bullet}CPh_3$), and $C_6F_5CH_3$. Using a combination of diverse physical methods such as NMR, ESR-C_{60}, and MALDI-TOF, we present a plausible mechanism for the inhibition by use of TTPB and for the polymerization reactions with MAO. Additional bulkier imidazolin-2-iminato ligands are under study for the polymerization of ethylene, propylene, and higher olefins.

5. EXPERIMENTAL SECTION

The syntheses of the complexes **1** and **2** were performed using literature procedures.[15]

The NMR measurements of the complexes and the ligands were conducted in Teflon J. Young valve-sealed NMR tubes after vacuum transfer of the solvent in a high-vacuum line and recorded on Bruker Avance 300, 500, and 600 MHz spectrometers. Chemical shifts for ^1H NMR and ^{13}C NMR are referenced to internal protiosolvent resonances and are reported relative to tetramethylsilane. The NMR for the polymers were performed in deuterated 1,1,2,2-tetrachloroethane at 80 °C, in standard NMR tubes.

5.1. Crystal Structure Determination. Single crystals were immersed in Parathone-N oil and quickly fished with a glass rod and mounted on a Kappa CCD diffractometer under a cold stream of nitrogen at 230 K. Data collection was carried out with monochromatized Mo Kα radiation using ω and π scan to cover the Ewald sphere. Accurate cell parameters were obtained with complete collections of intensities, and these were corrected in the usual way. The structure was solved by direct methods and completed using successive Fourier difference maps. Refinement was performed anisotropically with respect to the non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined using the riding model unit until convergence was reached.

ESR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.4 GHz), digital EPR spectrometer equipped with a Bruker N_2-temperature controller. All spectra were recorded at a microwave power of 6.4 mW, 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 accuracy better than 0.1 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia Software. Molecular weight determinations of the polymers were measured on a Varian system with a PL olexis column and with 1,2,4-trichlorobenzene (HPLC grade, T.G. Baker) as a mobile phase at 160 °C. Relative calibration was done with polystyrene standards (Varian, 2000−1 800 000 Da). MALDI-TOF LD+ and LD− experiments were performed on a Waters MALDI mass spectrometer. The melting crystallization behavior of the polymers was examined using a Perkin-Elmer DSC-7 differential scanning calorimeter. Three runs (heating−cooling−heating) at a rate of 10 deg/min in the range 0−150 °C were performed for each sample of polymer.

5.2. Propylene Polymerization Experiments. The polymerizations were performed in a 100 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was charged with a certain amount of complex cocatalyst and solvent (toluene) inside a glovebox and then connected to a high-vacuum line; the reactor was frozen at liquid nitrogen temperature, and liquid propylene was transferred to the frozen reactor. The temperature was then raised using a fan and kept constant via a thermostat water bath. The pressure in the reactor was measured and followed with a digital manometer. After the reaction stirred for the allotted period of time, it was quenched by opening of the reaction vessel in a well-ventilated hood and addition of 50 mL of 10% HCl in methanol. The polymer was filtered, washed with methanol and acetone, and dried in a vacuum oven at 60 °C. NMR measurements were taken in a solution of TCE at 80 °C.

5.3. Polymerization of Propylene under ESR Monitoring. A Teflon J. Young valve-sealed NMR tube was charged in the presence or absence of fullerene (2 mg/mL solution in toluene) with the corresponding complex, MAO, and a deuterated solvent inside a drybox. The NMR tube was connected to a high-vacuum line, frozen, pumped, thawed, and filled with propylene to 1 atm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details, cif file, and table of bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143. (b) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708. (c) Stille, J. K. *Chem. Rev.* **1958**, *58*, 541.

(2) (a) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (b) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev. (Washington, D.C.)* **1998**, *98*, 2587. (c) Möhring, P. C.; Coville, N. J. *Coord. Chem. Rev.* **2006**, *250*, 18. (d) Razavi, A.; Thewalt, U. *Coord. Chem. Rev.* **2006**, *250*, 155.

(3) For recent reviews, see: (a) Li, H.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15295 and references therein. (b) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friederichs, N. *Chem. Rev.* **2005**, *105*, 4073 and references therein. (c) Kaminsky, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3911. (d) Gladysz, J. A. *Chem. Rev.* **2000**, *100*, 1 ff (special issue on Frontiers in Metal-Catalyzed Polymerization) and references therein. (e) Nayak, P. L. *Popular Plastics & Packaging* **2003**, *48*, 86. (f) Kaminsky, W.; Arndt, M. In *Applied Homogeneous Catalysis with Organometallic Compounds* Cornils, B., Herrmann,W. A., Eds.; VCH: Weinheim, New York, Basel Cambridge, Tokyo, 1996; Vol. *I*, p 220; Vol. *II*, pp 664, 1187. (g) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (h) Brintzinger, H. H.; Fischer, D.; Muelhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(4) (a) Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15288 ff, special feature on polymerization. (b) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (c) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347. (d) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (e) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (f) Amin, S. B.; Marks, T. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 2006. (g) Vanka, K.; Xu, Z.; Seth, M.; Ziegler, T. *Top. Catal.* **2005**, *34*, 143. (h) Bochmann, M. *Organometallics* **2010**, *29*, 4711 and references therein. (i) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450 and references therein.

(5) (a) Miller, S. A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934. (b) Miller, S. A.; Bercaw, J. E. *Organometallics* **2004**, *23*, 1777. (c) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1998**, *110*, 6255. (d) Razavi, A.; Bellia, V.; De Brauwer, Y.; Hortmann, K.; Peters, L.; Sirole, S.; Van Belle, S.; Thewalt, U. *Macromol. Chem. Phys.* **2004**, *205*, 347.

(6) (a) Guo, N.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 2246 and references therein. (b) Li, H.; Li, L.; Schwartz, D. J.; Metz, M. V.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 14756 and references therein. (c) Kim, I.; Ha, C. S. *Polym. Bull.* **2004**, *52*, 133. (d) Tritto, I.; Boggioni, L.; Ferro, D. R. *Coord. Chem. Rev.* **2006**, *250*, 212 and references therein. (e) Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.-W.; Shimizu, F.; Cherian, A. E.; Hustad, P. D.; Rose, J. M.; Coates, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15327 and references therein. (f) Rodriguez-Delgado, A.; Hannant, M. D.; Lancaster, S. J.; Bochmann, M. *Macromol. Chem. Phys.* **2004**, *205*, 334 and references therein.

(7) (a) Bryliakov, K. P.; Talsi, E. P.; Voskoboynikov, A. Z.; Lancaster, S. J.; Bochmann, M. *Organometallics* **2008**, *27*, 6333. (b) Alonso-Moreno, C.; Lancaster, S. J.; Zuccaccia, C.; Macchioni, A.; Bochmann, M. *J. Am. Chem. Soc.* **2007**, *129*, 9282. (c) Roberts, J. A. S.; Chen, M.-C.; Seyam, A. M.; Li, L.; Zuccaccia, C.; Stahl, N. G.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 12713. (d) Ciancaleoni, G.; Fraldi, N.; Budzelaar, P. H. M.; Busico, V.; Macchioni, A. *Dalton Trans.* **2009**, 8824. (e) Stahl, N. G.; Salata, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10898. (f) Sillars, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **2003**, *125*, 9894. (g) Chen, Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. (h) Busico, V.; Cipullo, R.; Cutillo, F.; Vacatello, M.; Van Axel Castelli, V. *Macromolecules* **2003**, *36*, 4258−4261.

(8) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (c) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363. (e) Makio, H.; Fujita, T. *Acc. Chem. Res.* **2009**, *42*, 1532. (f) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(9) (a) Fujita, T.; Makio, H. In *Comprehensive Organometallic Chemistry III*; Robert, H. C., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007, p 691. (b) Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A* **2007**, *267*, 1 and references therein. (c) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691.

(10) (a) Aharonovich, S.; Botoshansky, M.; Balazs, Y. S.; Eisen, M. S. *Organometallics* **2012**, *31*, 3435. (b) Volkis, V.; Aharonovich, S.; Eisen, M. S. *Macromol. Res.* **2010**, *18*, 967. (c) Chen, F.; Kapon, M.; Woollins, J. D.; Eisen, M. S. *Organometallics* **2009**, *28*, 2391. (d) Volkis, V.; Lisovskii, A.; Eisen, M. S. *Stud. Surf. Sci. Catal.* **2006**, *161*, 105. (e) Aharonovich, S.; Volkis, V.; Eisen, M. S. *Macromol. Symp.* **2007**, *260*, 165. (f) Smolensky, E.; Eisen Moris, S. *Dalton Trans.* **2007**, 5623. (g) Gueta-Neyroud, T.; Tumanskii, B.; Kapon, M.; Eisen, M. S. *Macromolecules* **2007**, *40*, 5261. (h) Gueta-Neyroud, T.; Tumanskii, B.; Botoshansky, M.; Eisen, M. S. *J. Organomet. Chem.* **2007**, *692*, 927. (i) Gornshtein, F.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2007**, *26*, 497. (j) Volkis, V.; Tumanskii, B.; Eisen, M. S. *Organometallics* **2006**, *25*, 2722. (k) Volkis, V.; Smolensky, E.; Lisovskii, A.; Eisen, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4505. (l) Smolensky, E.; Kapon, M.; Woollins, J. D.; Eisen, M. S. *Organometallics* **2005**, *24*, 3255.

(11) (a) Collins, S. *Coord. Chem. Rev.* **2011**, *255*, 118. (b) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754. (c) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S.; Yap, G. P. A.; Brown, S. J. *Organometallics* **1998**, *17*, 446. (d) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (e) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355. (f) Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087. (g) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893. (h) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403 and references therein. (i) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 113 and references therein. (j) Hagadorn, J. R.; Arnold, J. *Organometallics* **1994**, *13*, 4670. (k) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307.

(12) (a) Kuhn, N.; Fawzi, R.; Steimann, M.; Wiethoff, J.; Blaeser, D.; Boese, R. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 1779. (b) Kuhn, N.; Fawzi, R.; Steimann, M.; Wiethoff, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 769. (c) Kuhn, N.; Goehner, M.; Grathwohl, M.; Wiethoff, J.; Frenking, G.; Chen, Y. *Z. Anorg. Allg. Chem.* **2003**, *629*, 793.

(13) (a) Tamm, M.; Beer, S.; Herdtweck, E. *Z. Naturforsch., B: Chem. Sci.* **2004**, *59*, 1497. (b) Tamm, M.; Randoll, S.; Bannenberg, T.; Herdtweck, E. *Chem. Commun.* **2004**, 876. (c) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890. (d) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Org. Lett.* **2008**, *10*, 981. (e) Panda, T. K.; Trambitas, A. G.; Bannenberg, T.; Hrib, C. G.;

Randoll, S.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2009**, *48*, 5462. (f) Gloeckner, A.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 4368.

(14) (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635. (b) Golobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(15) (a) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459. (b) Stelzig, S. H.; Tamm, M.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6064. (c) Randoll, S.; Jones, P. G.; Tamm, M. *Organometallics* **2008**, *27*, 3232.

(16) For general organolanthanide and organoactinide reviews, see: (a) Edelmann, F. T. *Coord. Chem. Rev.* **2012**, *256*, 1151. (b) Edelmann, F. T. In *Comprehensive Organometallic Chemistry III*; Robert, H. C., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; p 1. (c) Molander, G. A. *Chemtracts: Org. Chem* **1998**, *11*, 237. (d) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851. (e) Edelmann, F. T.; Gun'ko, Y. K. *Coord. Chem. Rev.* **1997**, *165*, 163. (f) Anwander, R.; Herrman, W. A. *Top. Curr. Chem.* **1996**, *179*, 1. (g) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247. (h) Anwander, R. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH Publishers: New York, 1996; Vol. 2, p 866. (i) Ephritikhine, M. *New J. Chem.* **1992**, *16*, 451. (j) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press, Oxford, U.K., 1995; Chapter 2 and references therein. (k) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

(17) (a) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069. (b) Tatsumi, K; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 3195.

(18) (a) Jeske, C.; Schock, L. E.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (b) Jeske, C.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (c) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. (d) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819.

(19) (a) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (b) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

(20) (a) Dash, A. K.; Gourevich, I.; Wang, J. Q.; Wang, J.; Kapon, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5084.

(21) Douziech, B.; Choukroun, R.; Lorber, C.; Donnadieu, B. *J. Organomet. Chem.* **2002**, *649*, 15.

(22) Holschumacher, D. Diaminocyclopropenylidene und 'frustrierte' Carben/Boran-Lewis-Paare. Ph.D. Thesis, Technischen Universität Braunschweig Fakultät für Lebenswissenschaften, 2010.

(23) See Supporting Information.

(24) Kwaan, R. J.; Harlan, C. J.; Norton, J. R. *Organometallics* **2001**, *20*, 3818.

(25) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

(26) Bryliakov, K. P.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *J. Organomet. Chem.* **2003**, *683*, 23.

(27) Gan, L.; Huang, S.; Zhang, X.; Zhang, A.; Cheng, B.; Cheng, H.; Li, X.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384.

(28) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982.

(29) Resconi, L.; Camurati, I.; Grandini, C.; Rinaldi, M.; Mascellani, N.; Traverso, O. *J. Organomet. Chem.* **2002**, *664*, 5.

(30) Kleinschmidt, R.; Griebenow, Y.; Fink, G. *J. Mol. Catal. A: Chem.* **2000**, *157*, 83.