Titanium and Zirconium Complexes for Polymerization of Propylene and Cyclic Esters

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The new group IV complexes $((CH_3)_3CCOCHCONEt_2)_2Ti(OMe)_2$ (**3**), $((CH_3)_3CCOCHCONMe_2)_2Ti(OMe)_2$ (**4**), $(CH_3COCHCONMe_2)_2Ti(OC(CH_3)_3)_2$ (**5**), and $((CH_3)_3CCOCHCONEt_2)_2ZrCl_2$ (**6**) were synthesized and characterized. The titanium dialkoxide complexes **3**−**5** were produced during the attempts to synthesize the corresponding titanium diamido complexes via an intramolecular metathesis. A mechanism for the intramolecular metathesis is presented. Complexes **3** and **4** exhibit dynamic behavior in solution as a function of temperature. This dynamic behavior is due to a disconnection and recoordination of the β-ketoamidate chelating ligands through the weaker Ti−O bond, resulting in the formation of different octahedral stereoisomers in solution. Complexes **3**−**6**, activated with MAO, were found to be active in the polymerization of propylene, producing elastomeric polypropylene. The elastomeric properties of the polymers obtained using complex **3** as catalyst are due to a dynamic interconversion between two C_2-symmetric enantiomeric structures via an open C_{2v}-symmetric intermediate complex. Additionally, complexes **3**−**6** were found to be active in the polymerization of ε-caprolactone and *rac*-lactide. The activity of the zirconium dichloride complex **6** is higher than the activities of any of the titanium dialkoxide complexes **3**−**5** both in ε-caprolactone and in *rac*-lactide polymerizations.

Introduction

Since the groundbreaking work by Ziegler and Natta in the mid-1950s on the polymerization of high-density polyethylene and polypropylene,[1] and the discovery in the early 1980s by Kaminsky and Sinn that MAO (methylalumoxane) activated group IV metallocenes for the polymerization of both ethylene and α-olefins,[2] an enormous amount of research has been directed toward the development of homogeneous, single-site catalysts.[3] This type of metallocene catalysts can control the molecular weight and polydispersity of the polymers. The tacticity of the polymers is correlated with the symmetry of the precatalysts. Complexes with C_2 symmetry are known to produce isotactic polymers, whereas complexes exhibiting C_{2v} symmetry produce atactic polymers,[4] although in some cases polymers with unique properties, such as stereoblocks (isotactic-atactic) with elastic properties, were obtained.[5]

During the last decade, an effort was made to develop a new generation of nonmetallocene complexes, providing an opportunity to create polymers with novel properties and uses.[6] Complexes containing chelating ligands such as diamides,[7,8] amidinates,[9] and alkoxides[10] have drawn much attention as potential catalysts for polymerization of olefins. Polymerization of α-olefins using chelating acetylacetonate (acac) complexes, which are obtained as a mixture of racemic C_2-symmetric *cis*-octahedral structures, has been already investigated by our group.[11] Among these chelating acac complexes the titanium complex, upon activation with methylalumoxane (MAO), was found to produce an elastomeric polypropylene.[11]

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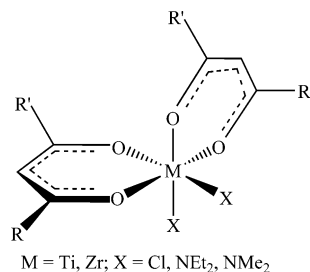
Figure 1. Group IV β-diketonate dichloride or diamido complexes.

The electronic and steric properties of the β-diketonate ligands can be modified by altering the substituents on the main skeleton, creating new potential catalysts for polymerization of α-olefins (Figure 1). This has encouraged us to investigate the reactivity of the substituted acac complexes toward the polymerization of propylene. While attempting to synthesize the desired titanium diamido complexes, we have encountered a unique intramolecular metathesis resulting in novel titanium alkoxide complexes. In addition to α-olefins, alkoxide complexes have been also utilized for ring-opening polymerization (ROP) of cyclic esters (such as lactones and lactides). These catalysts are usually based on aluminum,[12] tin,[13] zinc,[14] magnesium,[15] and iron.[16]

Despite the fact that some outstanding catalysts for the polymerization of cyclic esters have been reported, new well-defined, homogeneous, and nontoxic systems still are highly desirable. In contrast to tin complexes,[17] those of titanium are found to be nontoxic and very promising.[18] The significant number of similarities in the chemistry of tin and titanium have brought up the possibility to use the titanium dialkoxide complexes as potential catalysts in the polymerization of cyclic esters. Surprisingly, although titanium complexes are well known as catalysts for polymerization of olefins, only few reports of titanium dialkoxides as potential catalysts in polymerization of ϵ-caprolactone[19] and lactide[20] have been published.

Here we report the synthesis and characterization of a novel zirconium(IV) dichloride and three new neutral titanium(IV) dialkoxide complexes produced via an intramolecular metathesis from the corresponding titanium diamido complexes. We report the X-ray diffraction studies of two of the titanium dialkoxide complexes. In addition, we describe the catalytic activity of all the new complexes in the polymerization of propylene, ϵ-caprolactone, and *rac*-lactide.

Results and Discussion

Synthesis of the Complexes $((CH_3)_3CCOCHCONEt_2)_2$-$Ti(OMe)_2$ (3), $((CH_3)_3CCOCHCONMe_2)_2Ti(OMe)_2$ (4), $(CH_3COCHCONMe_2)_2Ti(OC(CH_3)_3)_2$ (5), and $((CH_3)_3CCOC$-$HCONEt_2)_2ZrCl_2$ (6). The complexes $((CH_3)_3CCOCHCONEt_2)_2$-$Ti(OMe)_2$ (3) and $((CH_3)_3CCOCHCONMe_2)_2Ti(OMe)_2$ (4) were prepared by the reaction in hexane of 2 equiv of the neutral ligand $(CH_3)_3CCOCH_2CO_2CH_3$ (1) and 1 equiv of the homoleptic tetrakis(diethylamino)titanium or the tetrakis(dimethylamino)titanium complexes, respectively (eq 1). Complex 3 was recrystallized at -20 °C from a toluene−hexane solution to obtain single crystals, which were suitable for X-ray diffraction studies. Reaction of the homoleptic tetrakis(dimethylamino)-

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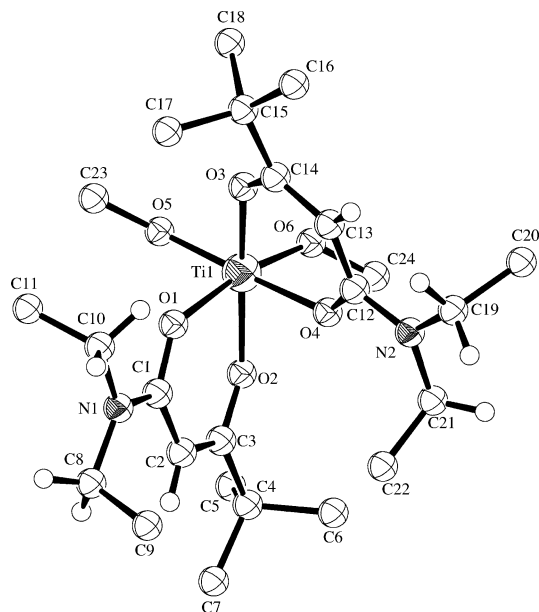
Figure 2. ORTEP plot of the molecular structure of complex ((CH₃)₃CCOCHCONEt₂)₂Ti(OMe)₂ (**3**).

titanium complex with 2 equiv of the neutral ligand CH₃COCH₂-CO₂C(CH₃)₃ (**2**) in hexane afforded the corresponding (CH₃-COCHCONMe₂)₂Ti(OC(CH₃)₃)₂ (**5**) complex (eq 2). Recrystallization of complex **5** at −20 °C from a saturated solution of hexane gave single crystals suitable for X-ray diffraction studies. The complex ((CH₃)₃CCOCHCONEt₂)₂ZrCl₂ (**6**) was prepared by the reaction in toluene of 2 equiv of the lithium salt of ligand **1** and 1 equiv of the zirconium chloride salt (eq 3).
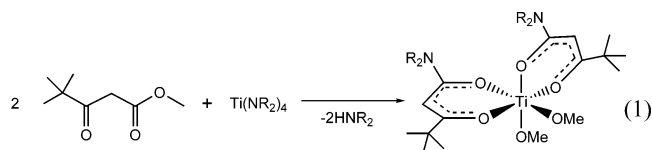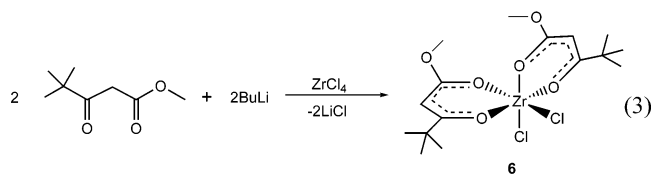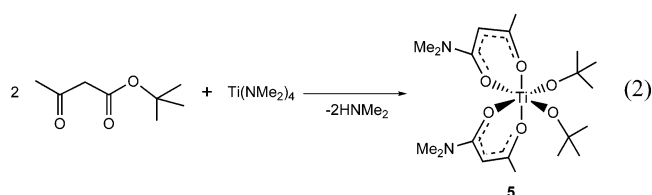
X-ray Structure Characterization of the Complexes ((CH₃)₃-CCOCHCONEt₂)₂Ti(OMe)₂ (3) and (CH₃COCHCONMe₂)₂-Ti(OC(CH₃)₃)₂ (5). The molecular structures of the complexes ((CH₃)₃CCOCHCONEt₂)₂Ti(OMe)₂ (**3**) and (CH₃COCHCON-Me₂)₂Ti(OC(CH₃)₃)₂ (**5**) have been confirmed by X-ray single-crystal diffraction studies. The ORTEP plots of the complexes are shown in Figure 2 and Figure 3, respectively. Crystallographic data and structure refinement details for the complexes and selected bond lengths and angles are listed in Table 1 and Table 2, respectively.
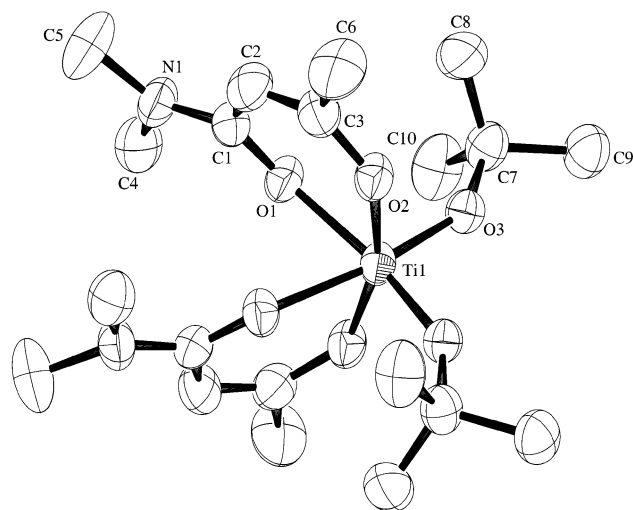
Figure 3. ORTEP plot of the molecular structure of complex (CH₃-COCHCONMe₂)₂Ti(OC(CH₃)₃)₂ (**5**). Ellipsoids are drawn at the 50% probability level.

In the solid state complex **3** was crystallized with one molecule of the solvent (toluene). The single-crystal X-ray diffraction studies of the complex show that the metal is disposed in a slightly distorted octahedral environment with two chelating η^2-β-ketoamidate and two methoxide ligands, exhibiting a C_2-like symmetry. The two methoxide oxygens are positioned *cis* to each other (O(5)−Ti−O(6) = 97.55(15)°), as are the two oxygen atoms of the amido moieties (O(4)−Ti−O(1) = 83.57(13)°). The other two ketonate oxygen atoms of the chelating ligands are located *trans* to each other (O(2)−Ti−O(3) = 165.02(11)°). A close look at the β-ketoamidate ligands shows that the two oxygen atoms of each ligand are not equidistant to the metal center (Ti−O(1) = 2.055(3) Å and Ti−O(4) = 2.052(3) Å as compared to Ti−O(2) = 1.971(3) Å and Ti−O(3) = 1.976(3) Å, correspondingly), due to the larger *trans* effect produced by the methoxide ligands.

The low-temperature X-ray diffraction analysis of complex **5** reveals that in this complex, as in complex **3**, the metal center can be visualized as an octahedral environment with two chelating η^2-β-ketoamidate and two *tert*-butoxide ligands. However, this complex, unlike complex **3**, exhibits a perfect C_2 symmetry. The two *tert*-butoxide oxygen atoms are disposed in a *cis* fashion (O(3)−Ti−O(3)#1 = 99.48(11)°), as are the two oxygen atoms of the amido moieties (O(1)−Ti−O(1)#1 = 78.37(10)°). The other two oxygens are positioned *trans* to each other (O(2)−Ti−O(2)#1 = 164.31(10)°). As in complex **3**, the two oxygen atoms of the amido moieties showed larger bond lengths than the other two oxygens of the β-ketoamidate ligands (Ti−O(1) = Ti−O(1)#1 = 2.0856(17) Å and Ti−O(2) = Ti−O(2)#1 = 1.9743(16) Å, due to the larger *trans* effect produced by the butoxide ligands.

Characterization of the Complex ((CH₃)₃CCOCHCON-Me₂)₂Ti(OMe)₂ (4). The titanium complex **4** was recrystallized several times, but no single crystals were obtained with good quality for X-ray structure determination. The suggested structure for complex **4** is a distorted octahedral complex containing two chelating η^2-β-ketoamidate and two methoxide ligands around the metal center, which is supported by ¹H NOE measurements, showing strong NOE correlation of the acidic −C*H* group of the chelating unit with the methyl hydrogens of the −N−C*H₃* moiety. No NOE correlation was found between the −C*H* and −OC*H₃* groups. Support for the structure can also be acquired by means of ¹H NMR of the complex, showing a

Table 1. Crystal Data and Details of Data Collection for Complexes 3 and 5

	3	**5**
empirical formula	$C_{31}H_{54}N_2O_6Ti$	$C_{20}H_{38}N_2O_6Ti$
fw	598.66	450.42
temperature (K)	293(2)	230.0(1)
wavelength (Å)	0.71073	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $C2/c$
unit cell dimens, a (Å)	9.603(2)	9.6520(6)
b (Å)	9.672(2)	15.4450(9)
c (Å)	19.325(4)	17.1050(13)
α (deg)	92.60(2)	90
β (deg)	100.11(3)	93.967(3)
γ (deg)	90.25(2)	90
V (Å^3)	1765.1(6)	2543.8(3)
Z	2	4
D_{calc} (g/cm^3)	1.126	1.176
μ (mm^{-1})	0.282	0.369
$F(000)$	648	968
cryst size (mm^3)	$0.55 \times 0.25 \times 0.05$	$0.30 \times 0.30 \times 0.18$
θ range for data collection (deg)	2.11 to 25.00	2.39 to 22.88
limiting indices	$-11 \leq h \leq 10$,	$-10 \leq h \leq 10$,
	$-11 \leq k \leq 10$,	$-16 \leq k \leq 15$,
	$-22 \leq l \leq 22$	$-18 \leq l \leq 18$
no. of reflns collected/unique	16 155/5997	2863/1727
	[R(int) = 0.107]	[R(int) = 0.0288]
completeness to $\theta = 25.00$	96.2%	99.1%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	5997/0/379	1727/0/143
goodness-of-fit on F^2	0.726	0.991
final R indices [$I > 2\sigma(I)$]	R1 = 0.0595, wR2 = 0.1119	R1 = 0.0393, wR2 = 0.0960
R indices (all data)	R1 = 0.2005, wR2 = 0.1387	R1 = 0.0565, wR2 = 0.0999
largest diff peak and hole (e·A^{-3})	0.308 and -0.337	0.200 and -0.182

Table 2. Comparison of the Bond Lengths [Å] and Angles [deg] for Complexes 3 and 5

3		**5**	
Ti−O(5)	1.805(4)	Ti−O(3)	1.8002(16)
Ti−O(6)	1.812(3)		
Ti−O(2)	1.971(3)	Ti−O(2)	1.9743(16)
Ti−O(3)	1.976(3)		
Ti−O(4)	2.052(3)	Ti−O(1)	2.0856(17)
Ti−O(1)	2.055(3)		
C(23)−O(5)−Ti	135.2(3)	C(7)−O(3)−Ti	145.97(16)
O(4)−Ti−O(1)	83.57(13)	O(1)−Ti−O(1)#1	78.37(10)
O(5)−Ti−O(6)	97.55(15)	O(3)−Ti−O(3)#1	99.48(11)
O(2)−Ti−O(3)	165.02(11)	O(2)−Ti−O(2)#1	164.31(10)

large resemblance to that of complex **3**. The NMR signals for the −C*H*, −OC*H*₃, and −C(C*H*₃)₃ groups of complex **4** appear in the same field as their equivalents in complex **3** (Figure 4), suggesting a structure similar to that of complex **3**.

Intramolecular Metatheses in Complexes 3, 4, and 5. An interesting phenomenon was observed during the attempted synthesis of the titanium complexes **3**, **4**, and **5**. The expected bis(diethylamino)titanium complex of ligand **1** and bis(dimethylamino)titanium complexes of ligands **1** and **2** were not obtained. Instead, an exchange of the amino and methoxy groups between Ti(NEt₂)₄ or Ti(NMe₂)₄ and ligand **1** occurred, resulting in novel titanium dimethoxide complexes **3** and **4**, respectively. A similar exchange of the amino and *tert*-butoxide groups between Ti(NMe₂)₄ and ligand **2** resulted in a new titanium *tert*-butoxide complex **5**. The exchange mechanism probably involves an opening of one of the chelating ligands through the Ti−O$_{(a)}$ bond (the weakest one) followed by a metathesis between O$_{(b)}$−C$_{(a)}$ and Ti−N bonds to form new O$_{(b)}$−Ti and C$_{(a)}$−N bonds. The aforementioned steps also apply to a second chelating ligand, resulting in the formation of the complexes **3**, **4**, and **5** (Scheme 1).

Dynamic Behavior of Complexes 3 and 4. NMR investigation gives us a look at the dynamic behavior of complexes **3** and **4** in solution and with respect to temperature. The ¹H NMR

spectra of complexes **3** (Figure 4a) and **4** (Figure 4b) showed broad signals for all the assigned groups of both complexes, suggesting an averaging process in solution.

To investigate this further, the dynamic behavior of the complexes was followed by variable-temperature ¹H NMR analysis (Figure 5).

The dynamic behavior of the complexes may be due to one of the following possibilities: (1) a Bailar twist,[21] which proceeds via a nondissociative mechanism, resulting in the opposite enantiomer (Figure 6a), or (2) a disconnection and recoordination of the chelating β-ketoamidate ligands through the weaker Ti−O bond, resulting in the formation of different stereoisomers in solution (Figure 6b).

In order to establish which dynamic process takes place, $\Delta S^{\ddagger}$ values were calculated using Eyring plots. Positive $\Delta S^{\ddagger}$ values were found for both complexes (20.0 cal/mol·K for complex **3** and 13.8 cal/mol·K for complex **4**), indicating ground states that are more ordered than their transition states and implying a dissociative mechanism, hence excluding the possibility for a Bailar twist as the main pathway for the dynamic process.[22] It is thus likely that this dynamic behavior is due to a disconnection and recoordination of the chelating ligands through the weaker Ti−O bond, resulting in the formation of different octahedral stereoisomers in solution.

Interestingly, complexes **5** and **6** did not show any dynamic behavior in solution as a function of temperature (in the temperature range −50 to 60 °C). To our knowledge, the lack of the dynamic process in complex **5** is not due to steric (see Table 2) or electronic reasons. The lack of the dynamic behavior in complex **5** suggests that the dynamic behavior in complexes **3** and **4** is indeed due to a disconnection and recoordination of the chelating ligands forming different octahedral stereoisomers in solution.

(21) Bailar, J. C. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.
(22) Long, R. J.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2006**, *45*, 511.
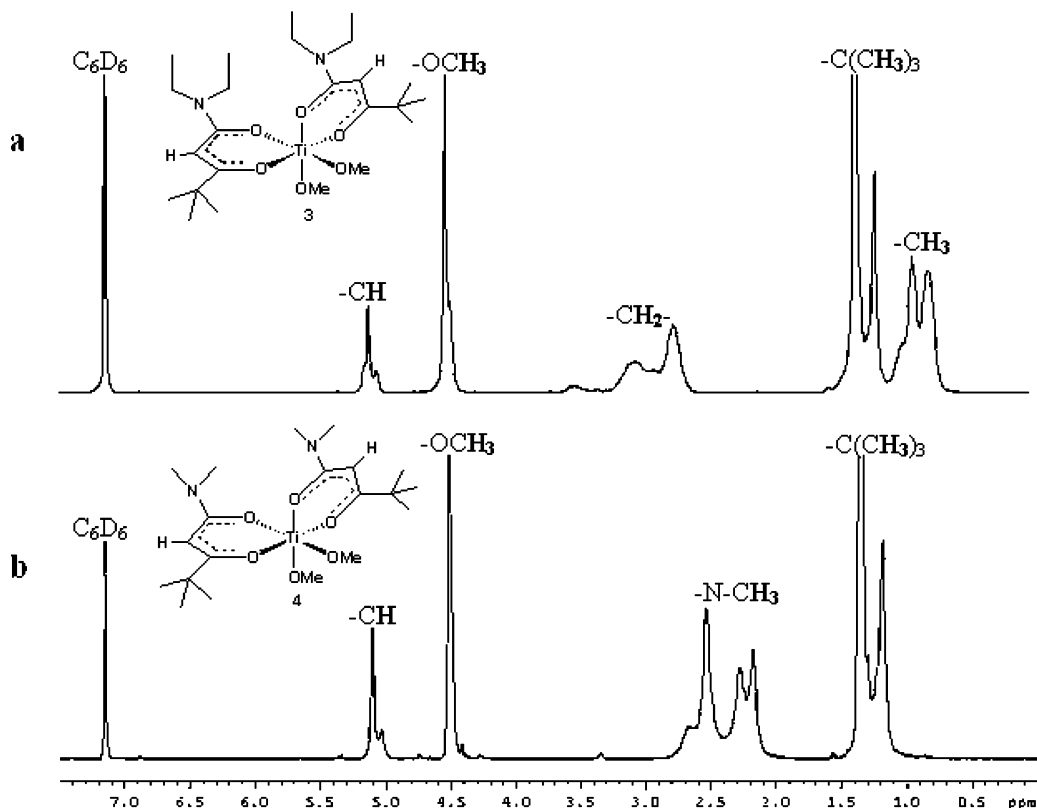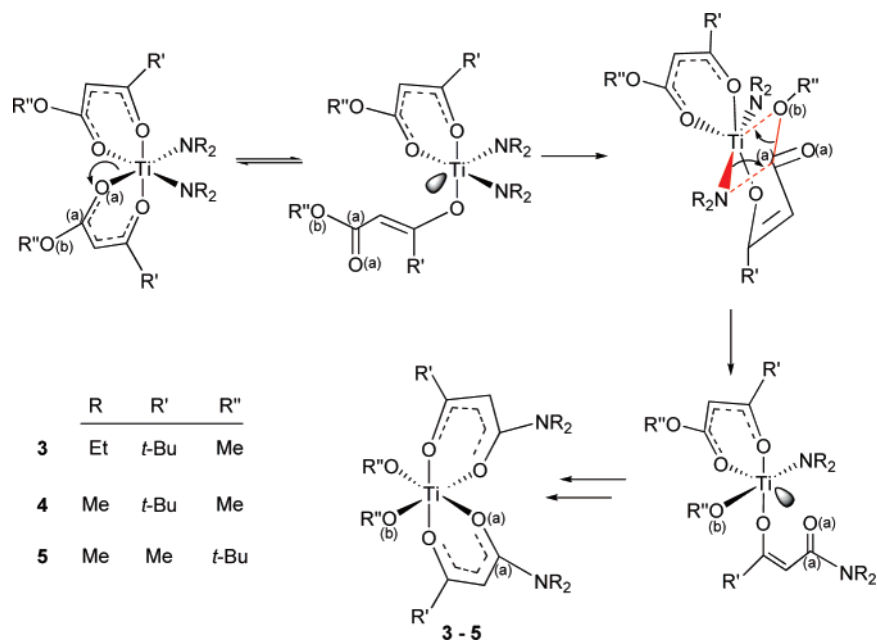
Figure 4. ^{1}H NMR spectra of complex **3** (a) and complex **4** (b) in benzene-d_6 at room temperature.

Scheme 1. Proposed Mechanism for the Intramolecular Metathesis in Complexes 3, 4, and 5

|	R	R'	R"
3	Et	*t*-Bu	Me
4	Me	*t*-Bu	Me
5	Me	Me	*t*-Bu

Propylene Polymerization. The catalytic activity of complexes **3**, **4**, **5**, and **6** activated by MAO in the polymerization of propylene was studied under comparable conditions (Al/M (M = Ti, Zr) molar ratio = 600, polymerization time = 2 h, solvent = toluene). The results are presented in Table 3.

The catalytic activity of complex **3** was found to be more than twice that of complexes **4** and **5** (compare entries 1, 2, and 3 in Table 3), while that of the zirconium complex **6** (entry 4, Table 3) was an order of magnitude lower. The molecular weights of the polymers obtained using titanium complexes **3** and **4** were found to be similar (see entries 1 and 2, Table 3), whereas that obtained by using titanium complex **5** was lower

(entry 3, Table 3). The molecular weight of the polymer obtained by using zirconium complex **6** was the lowest (entry 4, Table 3). All the polymers obtained were found to be elastomers with *mmmm* pentad percentages ranging from 20 to 26%. Fractionation of the polymers, obtained by using titanium catalysts **3**−**5**, shows only one fraction.

Furthermore, the influences of different MAO:catalyst ratios, polymerization times, temperatures, and solvents on the catalytic activity of complex **3** were thoroughly studied, and they are presented in Table 4.

The activity of the complex rises with an increase of the MAO:catalyst ratio, yielding a maximum at 400. A higher MAO
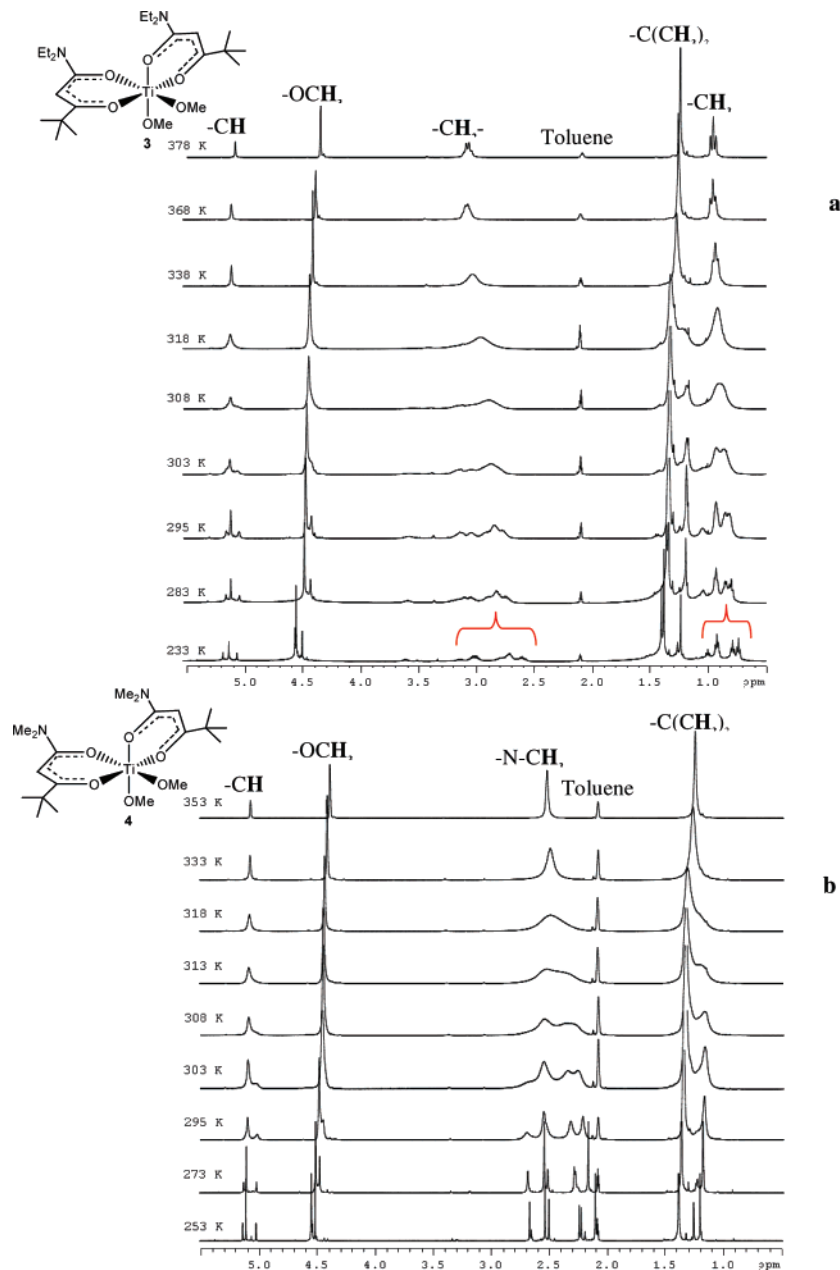
Figure 5. ^{1}H NMR spectra in toluene-d_8 of complexes **3** (a) and **4** (b) measured over a different temperature range.

concentration induced lower activities, achieving a plateau at a ratio of ~1000 (Figure 7). Similar behavior has been observed in various group IV complexes.[4a,9e,f,23] An increase in the MAO:**3** ratio induces a reduction in the molecular weight of the polymers (see entries 1−6, Table 4). This result, along with the finding that no vinylidene or vinyl chain-end groups were detected in the ^{1}H NMR of the polymers, can be attributed to a termination process that operates via an aluminum transfer mechanism, which is larger upon increasing the MAO concentration.

Monitoring the polymerization over time for complex **3** (entries 4, 9, and 10, Table 4) reveals a linear increase of M_n with increasing polymerization time. In a polymerization that proceeds in a living manner an increase of both the polymer weight and M_n is observed, whereas in a nonliving polymerization only an increase of the polymer weight is expected. Therefore, an increase of M_n over time in this case suggests

that a certain percentage of the polymerization proceeds in a living manner. The percentage of living polymerization was calculated according to the formula presented in eq 4 (n_l is the moles of living species and n_{pp} is the moles of polymer chains).

$$\% \text{ of living polymerization} = (n_l 100)/n_{pp} \qquad (4)$$

The number of the moles of living species, n_l, was isolated from eq 5 (where t is the polymerization time, R_i is the rate of monomer insertion, and M_n is the number-average molecular weight; $t = 20$ h was taken for $t \rightarrow \infty$). These calculations showed that at 20 °C about 40% of the polymerization is living.

$$M_n = \text{MW}_{monomer} t R_i/(n_l + (\text{MW}_{monomer} t R_i)/M_{n(t\rightarrow\infty)}) \quad (5)$$

An increase in activity was observed when the reaction temperature was raised from 0 to 20 °C, keeping the MAO:**3** ratio at 600 (compare entries 4 and 7 in Table 4). Further increasing the temperature to 60 °C (entry 8, Table 4) resulted in a decrease in activity. This result can be attributed to a partial

(23) Smolensky, E.; Kapon, M.; Woollins, J. D.; Eisen, M. S. *Organometallics* **2005**, *24*, 3255.
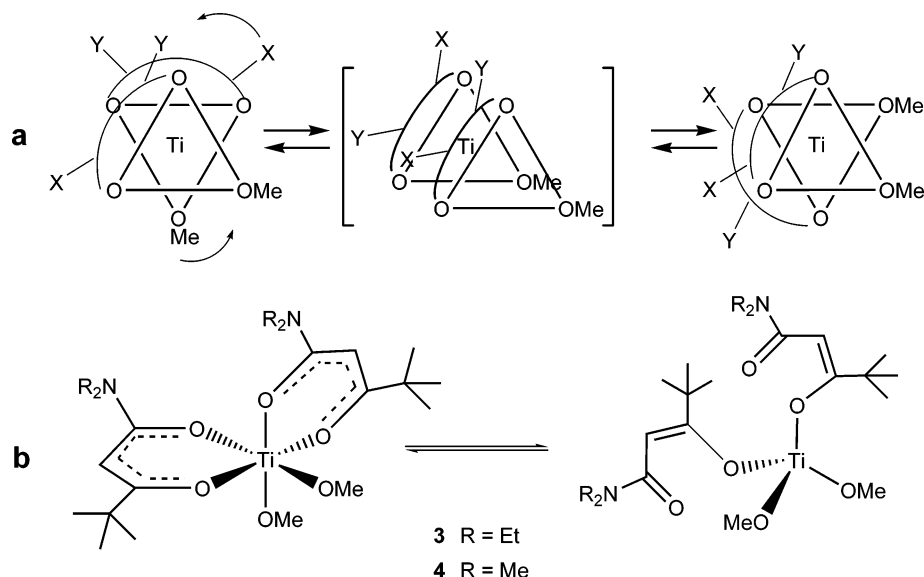
Figure 6. Possible dynamic processes in complexes **3** and **4**.

Table 3. Data for the Polymerization of Propylene Catalyzed by Complexes 3−6 with MAO[a]

entry	catalyst	A^b	% *mmmm*	M_n	M_w	M_w/M_n
1	3	4.61	23.0	47 000	104 000	2.21
2	4	1.97	20.3	41 000	105 000	2.56
3	5	1.78	24.7	28 000	70 000	2.50
4	6	0.09	25.8	14 000	41 000	2.93

[a] All experiments were performed in toluene at MAO:catalyst ratio = 600, 20 °C for 2 h. Catalyst = 5 mg, solvent = 5 mL. [b] Activity in (g PP/mol cat·h) × 10⁴.

decomposition of the catalyst at the higher temperature. In addition, the molecular weight of the polymers decreased upon raising the reaction temperature, presumably due to an increase in the termination rate.

Most of the polymerization reactions were run in toluene as a solvent. However, the influences of different solvents on the catalytic activity of complex **3**, the molecular weight, and the tacticity of the polymers were also tested. Complex **3** was found to be more active in the less polar solvents (entries 10−13, Table 4 and Figure 8).

This result corroborates the stronger coordination of CH_2Cl_2 and toluene, due to their donor abilities, to the metal's free orbital obtained in the formation of the cationic species by the reaction of the complex with MAO. Such coordination stabilizes the cationic center, hence decreasing its accessibility for the insertion of the monomer unit.[24]

The effect of the solvent on the tacticity of the polymers is depicted in Figure 9. The *mmmm* pentad percentage was found to be more pronounced in the more polar solvents, CH_2Cl_2 and toluene, suggesting that the stereoregular discrimination of the two olefinic enantiofaces is larger in those solvents, allowing a stereoregular insertion of the preferred enantioface, leading to higher isotacticities (Figure 9 and Table 4) and lower activities (Figure 8 and Table 4).[24]

The same effect was found in the bis(acetylacetonate) titanium dichloride complex, showing that the more polar solvent (toluene or CH_2Cl_2) is strongly attached to the empty d-orbital (which exists in addition to the cationic orbital of the active site) at the expense of an agostic interaction, positioning the growing polymer chain in a *trans* disposition as compared to the methyl of the monomer and impeding its free rotation (Figure 10), hence inducing a higher isotacticity of the polymer.[24]

The molecular weight of the polymers decreased with increasing solvent polarity (entries 10−13, Table 4 and Figure 11).

To rationalize these results, the relationship between the rates of chain propagation and termination (aluminum transfer) must be taken into account. From the data presented in Table 5 we can conclude that the effect of the solvent on the molecular weight of the polymers is mainly related to the rate of propagation rather than to the rate of termination since there is only a slight change in termination rates as the polarity of the

Table 4. Data for the Polymerization of Propylene Catalyzed by Complex 3 with MAO[a]

| entry	MAO:cat	time (h)	T (°C)	solvent	A^b	% *mmmm*	M_n	M_w	M_w/M_n
1	100	2	20	toluene	3.75	26.0	84 000	173 000	2.06
2	200	2	20	toluene	8.00	25.7	65 000	179 000	2.75
3	400	2	20	toluene	10.74	24.2	55 000	156 000	2.84
4	600	2	20	toluene	4.61	23.0	47 000	104 000	2.21
5	1000	2	20	toluene	3.70	21.7	34 000	92 000	2.70
6	1500	2	20	toluene	3.95	20.7	24 000	52 000	2.17
7	600	2	2	toluene	2.38	19.8	98 000	249 000	2.54
8	600	2	60	toluene	3.83	19.3	24 000	66 000	2.75
9	600	20	20	toluene	1.00	19.5	87 000	203 000	2.33
10	600	6	20	toluene	2.74	22.1	65 000	146 000	2.25
11	600	6	20	CH_2Cl_2	1.37	10.1	27 000	50 000	1.85
12	600	6	20	propylene	3.77	8.7	56 000	193 000	3.45
13	600	6	20	hexane	4.98	20.6	75 000	187 000	2.49

[a] Catalyst = 5 mg, solvent = 5 mL. [b] Activity in (g PP/mol cat·h) × 10⁴.

Figure 7. Activity obtained in the polymerization of propylene by complex **3** activated by MAO as a function of the MAO:**3** ratio.
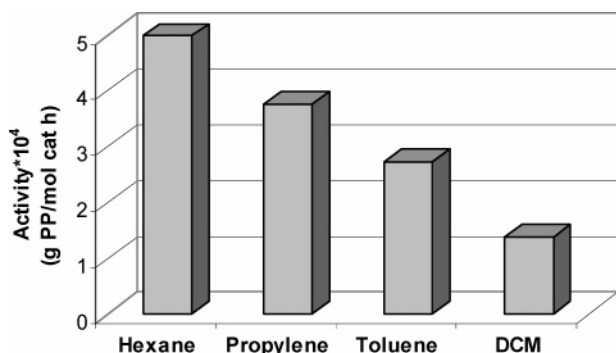
Figure 8. Effect of the solvent on the catalytic activity of complex **3** (DCM = dichloromethane).
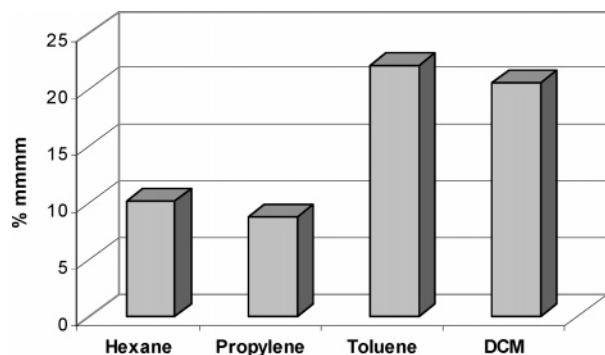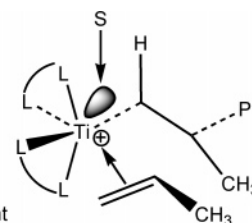

Figure 9. Effect of the solvent on the tacticity of the polymers obtained in the polymerization of propylene by complex **3** activated by MAO (DCM = dichloromethane).

solvent is changed. A stronger coordination of the more polar solvent impedes fast monomer insertions, resulting in lower molecular weight.

Fractionation of the obtained elastomeric polymers showed that only one fraction of the polymer was obtained, suggesting a single-site catalyst, which was also corroborated by the low polydispersities ($M_w/M_n \approx 2$) of the polymers (besides entry 12 in Table 4). It seems conceivable that the formation of the elastomeric polymers is obtained by a dynamic interconversion between two *cis*-octahedral C_2-symmetric enantiomeric structures via an open C_{2v}-symmetric intermediate complex, which is formed by an opening of at least one of the chelating ligands. The open intermediate complex is expected to produce atactic blocks, while the closed complex should produce isotactic ones (Figure 12).[23] This result is similar to the findings in which the formation of the isotactic fraction was attributed to a bis-(benzamidinate) titanium methyl complex with C_2 symmetry,

(24) Volkis, V.; Smolensky, E.; Lisovskii, A.; Eisen, M. S. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 4505.

Figure 10. Coordination of the polar solvents (toluene and CH$_2$-Cl$_2$) to the cationic center of the active species.
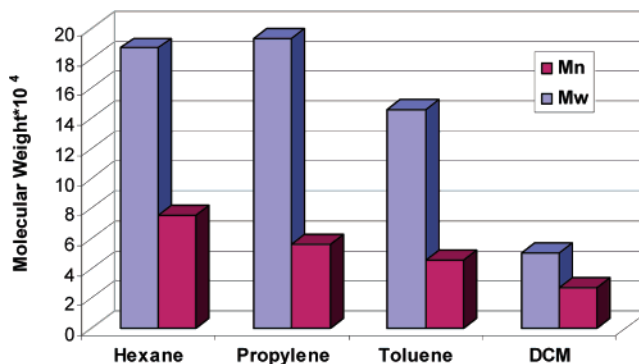
Figure 11. Effect of the solvent on the molecular weight of the polymers obtained in the polymerization of propylene by complex **3** activated by MAO (DCM = dichloromethane).

Table 5. Effects of Different Solvents on the Chain Propagation and Termination Rates for Complex 3[a]

	hexane	propylene	toluene	DCM[d]
$R_i \times 10^{-3}$ [b]	11.71	8.85	6.43	3.21
$R_t \times 10^{-6}$ [c]	6.56	6.64	5.00	5.00

[a] All experiments were performed at MAO:catalyst ratio = 600, 20 °C for 6 h. [b] Rate of monomer insertion (molecules/h). [c] Rate of chain termination (mol of polymer/h). [d] DCM = dichloromethane.

whereas the formation of the elastomeric polymer was attributed to a monomeric mono(benzamidinate) titanium cationic alkyl complex.[25]

The microstructures for some of the polymers obtained in propylene polymerization catalyzed by complex **3** are presented in Table 6.

The average length of isotactic sequences, n_{iso}, which can be calculated according to the formula $n_{iso} = 4 + 2([mmmm]/[mmmr])$,[26] was found to be 8 and was not affected by changing the reaction time or the reaction temperature. The average length of the atactic sequences, n_a, was calculated according to the formula presented in eq 6 [where n is the number of sequences (both isotactic and atactic) and M_n is the number-average molecular weight].

$$(n_{iso})_n(n_a)_n = M_n/MW_{monomer} \qquad (6)$$

These calculations showed that the average length of the atactic sequences, as the average length of the isotactic sequences, also does not change significantly with the change of the reaction time or temperature, having a value that varies from 27 to 34. However, the *number* of both the isotactic and the atactic sequences, n, increased with the increase in the reaction time (at 20 °C the calculated values for both the isotactic

(25) Volkis, V.; Lisovskii, A.; Tumanskii, B.; Shuster, M.; Eisen, M. S. *Organometallics* **2006**, *25*, 2656.
(26) (a) Mansel, S.; Pérez, E.; Benavente, R.; Pereña, J. M.; Bello, A.; Röll, W.; Kirsten, R.; Beck, S.; Brintzinger, H.-H. *Macromol. Chem. Phys.* **1999**, *200*, 1292. (b) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779.
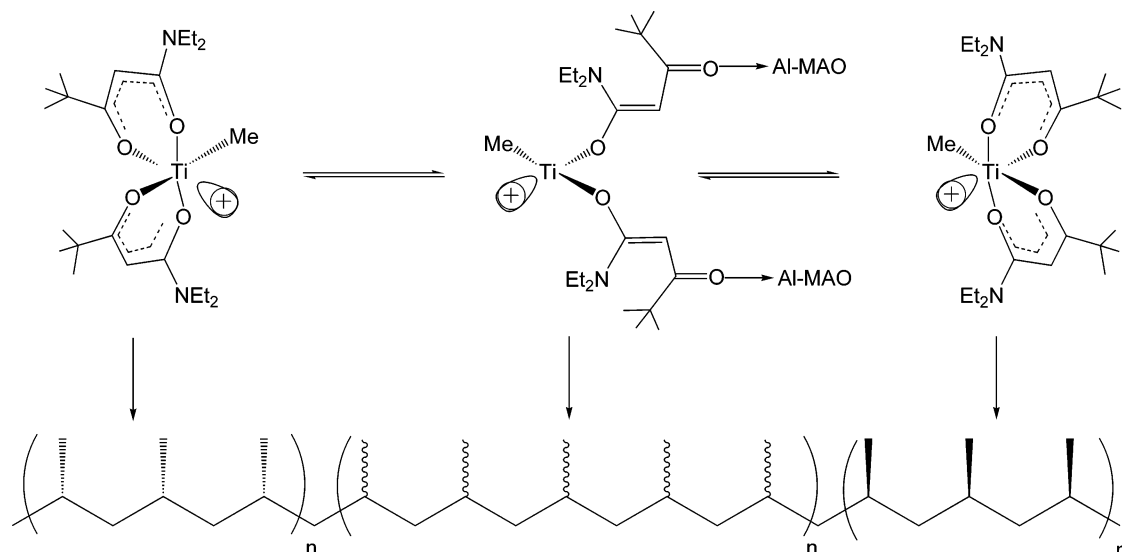
Figure 12. The two possible *cis*-octahedral enantiomeric structures operative during the polymerization of propylene by the system **3**/MAO.

Table 6. Pentad Distributions (in %) for Selected Polymers Obtained in Propylene Polymerization Catalyzed by Complex 3

entry[a]	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm] + [rrmr]	[mrmr]	[rrrr]	[rrrm]	[mrrm]
1	26.0	12.0	3.8	13.9	14.3	5.9	6.8	8.9	8.4
3	24.2	11.5	3.7	14.0	14.9	6.2	7.1	9.8	8.6
5	21.7	11.6	4.1	14.1	15.5	7.0	6.5	10.0	9.5
7	19.8	11.2	4.0	14.1	16.1	7.4	7.1	10.6	9.7
9	19.5	12.9	6.3	14.4	14.2	8.2	7.0	8.6	8.9

[a] Entry number refers to Table 4.

Table 7. Data for Solvent-Free Polymerization of ε-Caprolactone Catalyzed by Complexes 3−6[a]

entry	catalyst	monomer:cat	time (h)	conversion (%)	A[b]	M_n	M_w	MWD
1	**3**	1200	18	23.1	0.18	20 300	26 100	1.29
2	**3**	600	25	79.5	0.22	23 600	41 400	1.75
3	**3**	600	18	66.7	0.25	15 900	29 200	1.83
4	**3**	600	6	22.0	0.25	2200	2900	1.32
5	**3**	600	4	14.2	0.25	2600	3300	1.28
6	**3**	600	2	7.6	0.25	1000	1200	1.16
7	**3**	600	1	2.2	0.20	550	600	1.07
8	**4**	1200	18	62.2	0.47	44 600	88 500	1.99
9	**4**	600	18	56.3	0.21	35 900	59 700	1.67
10	**4**	600	6	16.4	0.19	7500	8700	1.16
11	**5**	1200	18	57.6	0.44	87 700	133 800	1.56
12	**5**	600	18	94.0	0.36	66 900	106 400	1.59
13	**5**	600	6	36.0	0.41	12300	15 100	1.23
14	**6**	1200	6	88.8	1.97	78 900	131 500	1.67
15	**6**	600	6	98.7	1.13	62 400	102 200	1.64

[a] All experiments were performed at 120 °C. [b] Activity in (g PCL/mol cat·h) × 10^4.

and the atactic sequences are 32, 36, and 56 for 2, 6, and 20 h, respectively) and decreased upon raising the reaction temperature (for $t = 2$ h the calculated values for both the isotactic and the atactic sequences are 58, 32, and 14 at 0, 20, and 60 °C, respectively). These results indicate that the *ratio* between the chelating ligands' opening and closing rates remains almost constant and is not affected by changing the reaction time or the reaction temperature.

ε-Caprolactone and *rac*-Lactide Polymerization. Complexes **3−6** were found to be active catalysts also in the polymerization of ε-caprolactone (ε-CL) (Table 7) and *rac*-lactide (*rac*-LA) (Table 8). A comparison of the catalytic activities of complexes **3−6** under similar reaction conditions shows that the activity of the zirconium dichloride complex **6** is higher than the activities of any of the titanium dialkoxide

complexes **3−5** both in ε-CL (compare entries 4, 10, 13, and 15 in Table 7) and in *rac*-LA polymerizations.

For ε-CL polymerization, a comparison of the molecular weight of polycaprolactone catalyzed by complex **5** with that of polymers obtained using titanium complexes **3** and **4** (compare entries 4, 10, and 13; entries 3, 9, and 12; entries 1, 8, and 11 in Table 7) and other known titanium alkoxide complexes reveals that complex **5** yielded polycaprolactone with the highest molecular weight.[27]

(27) (a) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437. (b) Takashima, Y.; Nakayama, Y.; Watanabe, K.; Itono, T.; Ueyama, N.; Nakamura, A.; Yasuda, H.; Harada, A.; Okuda, J. *Macromolecules* **2002**, *35*, 7538. (c) Okuda, J.; Rushkin, I. L. *Macromolecules* **1993**, *26*, 5530.

Table 8. Data for Solvent-Free Polymerization of *rac*-Lactide Catalyzed by Complexes 3–6[a]

entry	catalyst	monomer:cat	time (h)	conversion (%)	A^b	M_n	M_w	MWD
1	**3**	600	6	23.3	3.36	7600	8700	1.14
2	**3**	600	12	63.5	4.58	8800	9900	1.12
3	**4**	600	6	13.0	1.87	15 400	17 800	1.15
4	**4**	600	12	15.5	1.12	12 700	19 500	1.53
5	**5**	600	6	8.3	1.20	13 300	22 900	1.72
6	**5**	600	12	13.3	0.96	14 500	23 700	1.64
7	**6**	600	6	39.4	5.68	45 100	80 600	1.79
8	**6**	600	12	72.9	5.25	47 700	77 300	1.62

[a] All experiments were performed at 120 °C. [b] Activity in (g PLA/mol cat·h) $\times 10^3$.

When the polymerization of ϵ-CL was catalyzed by complexes **3–5** in an ϵ-CL:catalyst ratio of 600 and the reaction was quenched after different reaction times, increases in M_n and yields were observed (compare entries 2–7, entries 9/10, and 12/13, respectively, in Table 7), indicating that, again, a certain part of the polymerization is living.

When the monomer:catalyst ratio was increased from 600 to 1200, a decrease in the conversion was observed for complexes **3**, **5**, and **6** (entries 1 and 3, 11 and 12, 14 and 15, respectively, in Table 7), indicating that some deactivation of the corresponding catalysts takes place.

To shed light on the mechanism of the polymerization reaction with complex **3** as catalyst, we performed the reaction using a low catalyst:monomer ratio (1:20). Analysis of the polymer by NMR revealed a methoxy group (−OMe) chain-end (3.64 ppm), suggesting a ring-opening polymerization via a coordination–insertion mechanism.

For *rac*-LA polymerization, a comparison of the conversion and reactivity of the titanium complexes **3–5** reveals that the titanium complex **3** exhibits the larger conversion and reactivity (compare entries 1, 3, and 5 and entries 2, 4, and 6, respectively, in Table 8). The molecular weights of the polymers obtained using titanium complexes **3–5** are comparable to those found in the literature.[20a,d]

When the polymerization of *rac*-LA was catalyzed by complexes **3–6** in a *rac*-LA:catalyst ratio of 600 and the reaction was quenched after different amounts of time, similar molecular weights and polydispersities were obtained, whereas the conversion increased (Table 8), indicating that the polymerization does not proceed in a living manner, but is rather entropy driven, as the polymer chains break down at some stage of the polymerization process and do not grow longer.

Conclusions

The bis-β-ketoamidate dialkoxide complexes of titanium and the dichloride complex of zirconium have been synthesized and characterized. The titanium dialkoxide complexes were obtained during attempts to synthesize the corresponding diamido complexes via an intramolecular metathesis. The solid-state structures for two of the titanium complexes (**3** and **5**) were obtained. Titanium complexes **3** and **4** showed dynamic behavior in solution attributed to a disconnection and recoordination of the chelating β-ketoamidate ligands through the weaker Ti−O bond, resulting in the formation of different octahedral stereoisomers in solution. Complexes **3–6**, activated with MAO, were found to be active in the polymerization of propylene, producing elastomeric polypropylene. The elastomeric properties of the polymers obtained using complex **3** as catalyst are due to a dynamic interconversion between two C_2-symmetric enantiomeric structures via an open C_{2v}-symmetric intermediate complex. Moreover, complexes **3–6** were found to be active in the polymerization of ϵ-caprolactone and *rac*-lactide.

Experimental Section

General Remarks. All manipulations of air-sensitive materials were carried out with the vigorous 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 O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were freshly distilled under nitrogen from Na−K alloy (hexane) or from Na (toluene). All solvents for vacuum line manipulations were stored in vacuum over Na−K alloy in resealable bulbs. Deuterated solvents (C_6D_6 and toluene-d_8) were further distilled by vacuum transfer to resealable bulbs. Neutral ligands (CH_3)$_3$CCOCH$_2$CO$_2$CH$_3$ (**1**, 99%, Aldrich) and CH_3COCH$_2$CO$_2$C(CH_3)$_3$ (**2**, 98%, Aldrich) were distilled under vacuum from molecular sieves and degassed. Ti-(NMe$_2$)$_4$ (Aldrich) was degassed prior to use. Ti(NEt$_2$)$_4$ and Zr-(NEt$_2$)$_4$ were prepared from HNEt$_2$ and TiCl$_4$ or HNEt$_2$ and ZrCl$_4$, respectively, according to a known procedure.[28] Diethylamine (HNEt$_2$, Aldrich) was degassed and freshly vacuum-distilled. ZrCl$_4$ (Aldrich) was sublimed under vacuum prior to use. TiCl$_4$ and *n*-BuLi (Aldrich) were used as received. ϵ-Caprolactone (99%, Aldrich) was distilled under vacuum from CaH$_2$. *rac*-Lactide (Aldrich) was degassed prior to use. NMR spectra were recorded on Bruker Avance 300 and Bruker Avance 500 spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR are referenced to internal solvent resonances and reported relative to tetramethylsilane. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young). The polypropylene NMR experiments were conducted in deuterated 1,1,2,2-tetrachloroethane at 85 °C. The molecular weights of polypropylene were determined by the GPC method on a Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene as a mobile phase at 150 °C. The molecular weights of polycaprolactone and polylactide were determined by the GPC method on a Waters GPC Breeze system using tetrahydrofuran as a solvent at 30 °C.

Low-temperature X-ray diffraction experiments were carried out on a Nonius-KappaCCD diffractometer with graphite-monochromatized Mo Kα radiation. The crystals were placed in dry and degassed Parathon-N (DuPont) oil in a glovebox. Single crystals were mounted on the diffractometer under a stream of cold nitrogen at 230 K. Cell refinements and data collection and reduction were carried out with the Nonius software package.[29] The structure solution was carried out by the SHELXS-97[30] and SHELXL-97[31] software packages. The ORTEP program incorporated in the TEXRAY structure analysis package was used for molecular graphics.[32]

(28) Bradelly, D. C.; Thomas, I. M. *J. Chem. Soc.* **1959**, 340.

(29) *KappaCCD Collect* Program for data collection and *HKL Scalepack* and *Denzo* (Otwinowski and Minor, 1997) software package for data reduction and cell refinement; Enraf-Nonius, Delft, The Netherlands, 1997.

(30) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(31) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

(32) *ORTEP*, *TEXRAY* Structure Analysis Package; Molecular Structure Corp.: The Woodlands, TX, 1999.

Synthesis of ((CH₃)₃CCOCHCONEt₂)₂Ti(OMe)₂ (3). Ti(NEt₂)₄ (0.66 g, 1.97 mmol) was added via a syringe under an argon flow to a well-stirred solution of 0.62 g (3.95 mmol) of ligand **1** in 30 mL of hexane. The resulting mixture was stirred for 60 h at room temperature. After filtration of the solution through a frit and evaporation of the solvent and diethylamine under reduced pressure, the reddish-brown, oily product was washed with hexane to remove traces of the ligand and Ti(NEt₂)₄. The obtained oil was then precipitated in a mixture of toluene and hexane (1:10) to give a red powder, which was filtered and dried under vacuum, yielding 0.87 g (87%) of complex **3**. Pale yellow-green crystals of the complex were obtained by recrystallization from a mixture of toluene and hexane (1:10) at −15 °C.

Anal. Calcd for $C_{24}H_{46}N_2O_6Ti$ (506.50): C, 56.91; H, 9.15; N, 5.53. Found: C, 55.88; H, 9.04; N, 5.98. ^1H NMR (toluene-d_8, 300 MHz, 378 K): δ 0.96 (t, 6H, $^3J_{HH}$ = 7 Hz, −CH_3), 1.25 (s, 9H, −CCH_3), 3.07 (q, 4H, $^3J_{HH}$ = 7 Hz, −CH_2−), 4.35 (s, 3H, −OCH_3), 5.08 (s, 1H, −CH). ^{13}C NMR (toluene-d_8, 75 MHz, 363 K): δ 13.7 (−CH₃), 28.6 (−C(CH₃)₃), 39.4 (−C(CH₃)₃), 42.1 (−CH₂−), 62.8 (−OCH₃), 81.8 (−CH), 170.0 (−C−N(C₂H₅)₂), 190.2 (−C−C(CH₃)₃).

Synthesis of ((CH₃)₃CCOCHCONMe₂)₂Ti(OMe)₂ (4). Ti-(NMe₂)₄ (0.50 g, 2.23 mmol) was added via a syringe under an argon flow to a well-stirred solution of 0.70 g (4.44 mmol) of ligand **1** in 30 mL of hexane. The resulting mixture was stirred for 60 h at room temperature. After filtration of the solution through a frit and evaporation of the solvent, the reddish, oily product was washed with hexane to give a yellowish-pink powder, which was filtered and dried under vacuum, yielding 0.90 g (90%) of complex **4**.

Anal. Calcd for $C_{20}H_{38}N_2O_6Ti$ (450.39): C, 53.33; H, 8.50; N, 6.22. Found: C, 53.51; H, 8.20; N, 6.31. ^1H NMR (toluene-d_8, 300 MHz, 363 K): δ 1.24 (s, 9H, −C(CH_3)₃), 2.55 (s, 6H, −N(CH_3)₂), 4.36 (s, 3H, −OCH_3), 5.06 (s, 1H, −CH). ^{13}C NMR (toluene-d_8, 75 MHz, 363 K): δ 28.7 (−C(CH₃)₃), 36.0 (−N(CH₃)₂), 39.4 (−C(CH₃)₃), 62.9 (−OCH₃), 81.5 (−CH), 171.2 (−C−N(CH₃)₂), 190.7 (−C−C(CH₃)₃).

Synthesis of (CH₃COCHCONMe₂)₂Ti(OC(CH₃)₃)₂ (5). Ti-(NMe₂)₄ (0.50 g, 2.23 mmol) was added via a syringe under an argon flow to a well-stirred solution of 0.70 g (4.44 mmol) of ligand **2** in 30 mL of hexane. The resulting mixture was stirred for 60 h at room temperature. The mixture was then filtered through a frit and evaporated under reduced pressure. The obtained yellowish-brown oil was washed with hexane to give complex **5** in 89% (0.89 g) yield. Pale yellow crystals of the complex were obtained by recrystallization from hexane at −20 °C.

Anal. Calcd for $C_{20}H_{38}N_2O_6Ti$ (450.39): C, 53.33; H, 8.50; N, 6.22. Found: C, 50.74; H, 7.82; N, 5.71. ^1H NMR (C₆D₆, 500 MHz, 298 K): δ 1.60 (s, 9H, −C(CH_3)₃), 2.13 (s, 6H, −N(CH_3)₂), 2.36 (s, 3H, −CH_3), 4.79 (s, 1H, −CH). ^{13}C NMR (C₆D₆, 125 MHz, 298 K): δ 15.1 (−CH₃), 28.9 (−C(CH₃)₃), 38.8 (−N(CH₃)₂), 76.9 (−C(CH₃)₃), 87.7 (−CH), 160.4 (−C−CH₃), 168.8 (−C−N(CH₃)₂).

Synthesis of ((CH₃)₃CCOCHCONEt₂)₂ZrCl₂ (6). To a stirred solution of 0.66 g (4.20 mmol) of ligand **1** in 30 mL of hexane was added dropwise 2.62 mL of a 1.6 M solution of butyllithium in hexanes at −78 °C. The reaction mixture was allowed to reach room temperature and stirred for 16 h. The solvent was then evaporated. ZrCl₄ (0.49 g, 2.10 mmol) was added to a stirred

solution of the obtained lithium salt of ligand **1** in 50 mL of toluene at room temperature. The reaction mixture was refluxed for 96 h and then allowed to cool to room temperature. After removal of LiCl by filtration and evaporation of the solvent, 0.61 g (61%) of a pale yellow powder was obtained.

Anal. Calcd for $C_{16}H_{26}Cl_2O_6Zr$ (476.50): C, 40.33; H, 5.50; Cl, 14.88. Found: C, 39.78; H, 5.51; Cl, 15.19. ^1H NMR (C₆D₆, 500 MHz, 295 K): δ 1.00 (s, 9H, −C(CH_3)₃), 3.15 (s, 3H, −CH_3), 5.30 (s, 1H, −CH). ^{13}C NMR (C₆D₆, 125 MHz, 295 K): δ 27.4 (−C(CH₃)₃), 39.1 (−C(CH₃)₃), 52.9 (−CH₃), 88.5 (−CH), 176.1 (−C−C(CH₃)₃), 195.2 (−C−OCH₃).

Propylene Polymerization. The polymerization experiments were carried out in a 100 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was charged inside a glovebox with 5 mg of the desired catalyst and the corresponding amount of MAO. After the introduction of the solvent (e.g., 5 mL of the solvent) via a syringe under an argon flow, the reactor was frozen in liquid nitrogen. Liquid propylene (40 mL) was then vacuum transferred into the frozen reactor, the valve was closed, and the temperature was quickly (5 min) raised to 25 °C. During this heating time, no stirring was performed. At room temperature, the stirrer was operated, and the reaction was stirred for 2 h at a pressure of 10.2 atm. The reaction mixture was then quenched by the exhaustion of the unreacted propylene, followed by washing with H₂O−acac (5: 1) solution (acac = acetylacetonate). The polymer produced was then collected, washed with acetone, and dried in vacuo.

Fractionation of Polypropylene. The polymer samples were fractionated by extraction with refluxing hexane. The polymers (∼1 g) were packed into a cellulose thimble placed in a Soxhlet extractor. The latter was attached to a round-bottom flask (250 mL) filled with 100 mL of hexane. After extaction for ∼40 h, the solvent was evaporated. For every polypropylene sample one fraction (hexane-soluble) was obtained.

Polymerization of ϵ-Caprolactone and *rac*-Lactide. The polymerizations were conducted in a solvent-free environment. In a glovebox, 5 mg of the desired catalyst and the corresponding amount of ϵ-caprolactone or *rac*-lactide were introduced into a dry reaction vessel equipped with a magnetic stirrer bar. The vessel was placed in an oil bath thermostatically heated to 120 °C for the required time. All the polymerizations were quenched by opening the reaction vessels in a hood and dissolving the polymers in CH₂-Cl₂. The polymers were then precipitated in cold methanol and dried to a constant weight. The molecular weight values obtained by the GPC method were calibrated versus polystyrene standards and corrected for lactide and caprolactone.

Supporting Information Available: Eyring plots for complexes **3** and **4**, derivation of eq 5, CIF files giving complete X-ray experimental details and tables of bond lengths, angles, and positional parameters for complexes **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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