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β-Diketiminate complexes of Group 4: active complexes for the isomerization of α-olefins and the polymerization of propylene towards elastomeric polypropylene

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Abstract

The β-diketiminate lithium ligand [{N(SiMe$_3$)C(Ph)}$_2$CH][Li] reacted with Group 4 metal salts (Ti and Zr) to yield the complexes [{N(SiMe$_3$)C(Ph)}$_2$CH]$_2$TiCl$_2$ (**5**) and [{N(SiMe$_3$)C(Ph)}$_2$CH][N(SiMe$_3$)C(Ph)NC(Ph)CH(SiMe$_3$)]ZrCl$_2$ (**6**). The crystal structure of **6** shows that one of the two ketamidinate ligands undergoes an isomerization to the corresponding substituted benzamidinate. A mechanism for the catalyzed isomerization of the β-diketiminate ligand is presented. Complex **5** was found to be active in the polymerization of propylene, producing remarkably high-molecular weight ($>100{,}000$ g mol^{-1}) elastomeric polymer, whereas the zirconium complex was found inactive. Complex **5**, and surprisingly complex **6**, were found to be active catalysts, in the presence of MAO (methylalumoxane), for the isomerization of aliphatic olefins (1-octene, allylbenzene). Each complex catalyzed the olefins by different mechanisms. Kinetic studies for the isomerization of allylbenzene by complex **5** show that the reaction rate follows a first order in both catalyst and olefin concentrations with $\Delta H^{\ddagger} = 14.7(4)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33(1)$ e.u. These findings support the epimerization mechanism of the last inserted monomer that is proposed for as the primary cause for the elastomeric properties of polypropylene produced by this complex. In addition, we show how complementary isomerization studies of α-olefins shed light on the polymerization mechanism.

Keywords: Diketiminates; Polymerization; Isomerization; Elastomeric polypropylene; Titanium; Zirconium; X-ray structure

1. Introduction

Since the pioneering work in 1950s by Ziegler and Natta on the polymerization of ethylene to high-density polyethylene and propylene to stereoregular polypropylene, a great impetus has been concentrated in both academic and industrial research activities focused on understanding the relationships between the properties of the obtained polymers and catalyst structure, activity, and selectivities [1]. These studies opened a new era with the discovery that MAO (methylalumoxane) activated Group 4 metallocenes, producing new Ziegler–Natta type of homogeneous "single-site" catalysts for the polymerization of α-olefins [2,3]. These catalysts have been found to provide high activities, high stereoregularities, narrow polydispersities of the polymers, and control over the polymeric architecture [2–4]. Metallocene catalysts generally belong to Group 3 or 4, although some of these systems (constrained geometry) contain one cyclopentadienyl and one pendant ligand [5]. The ligand structures both electronically and sterically affect the properties of the metallocenes and thus, predictably determined the stereospecificity of these catalysts providing the basis for the development of new and improved catalytic systems. The tacticity of the polymers fluctuate predictably with the symmetry of the pre-catalysts. Complexes with C_2 or C_1 symmetry are expected to produce isotactic polyolefins, whereas complexes with C_{2v} symmetry are known to induce the formation of atactic polymers [6]. In general, these catalytic systems, as represented by **I**, contain the

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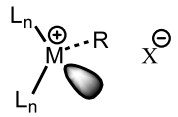
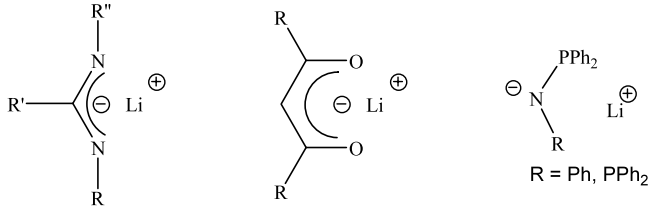
many required motifs for an active polymerization catalyst. Those comprise an appropriate spectator ancillary ligation (Ln), an electron deficient and coordinatively unsaturated metal center (M), and an effective weakly coordinating counteranion/cocatalyst (X^-) at the appropriate reaction conditions.



R = alkyl group

During the last decade, tremendous efforts were made at the synthesis of non-cyclopentadienyl complexes as potential catalysts for the polymerization of olefins [7]. A large range of carbon- [8], oxygen- [9], and nitrogen-based ligands [10,11] has been described. Great interest was aimed at chelating di(amido) ligands [12,13], chelating alkoxo [14] and boratabenzene [15], chelating salicilaldiminato [15,16] and acetylacetonate [17,18], and chelating amidinates [19] compounds.

Group 4 complexes containing the chelating ancillary ligations are normally obtained as a mixture of racemic *cis*-octahedral C_2 symmetry structures when those ligations bound the metal in a η_2 fashion. Among these chelating ligands, a special interest that has attracted our interest lies in bulky heteroallylic compounds as alternative to the classical cyclopentadienyl moiety. The steric and electronic properties of ligands such as benzamidinates (**1**), β-diketonates (**2**), or dynamic phosphinoamines (**3**) can be easily modified by the choice of substituents on the main framework [17,18,20].



1 **2** **3**

The complexes with C_2 symmetry are expected to produce highly isotactic polypropylene. However, we have found that the epimerization of the growing polypropylene chain, at the last inserted monomer unit, is responsible for a considerable amount of stereodefects [20,21] resulting in polymers from atactic to highly isotactic through elastomers, which can be modulated by monomer concentration. The occurrence of epimerization can be corroborated, in theory, by the isomerization of higher α-olefins, having low polymerization rates. With the polymerization subdued, epimerization becomes dominant, resulting in isomerization of the α-olefin.

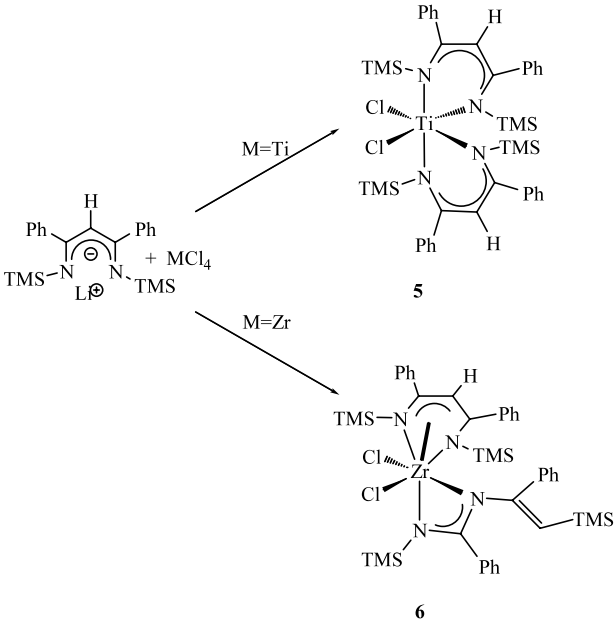
Here we report the synthesis of some Group 4 octahedral ketimidinate complexes [22]. The X-ray diffraction studies of the zirconium complex with a mixed benzamidine–ketimidinate ligation produced presumably via a retro-Brook rearrangement are disclosed [23]. The performance of the complexes in the polymerization and isomerization of olefins was studied. The chelating ring size effect as compared to other benzamidinates or acetylacetonato complexes is disclosed. The different effects of monomer pressure, temperature, and cocatalyst concentration in the polymerization process as well as the properties of the obtained polymers are discussed.

2. Results and discussion

2.1. Synthesis and characterization of complexes

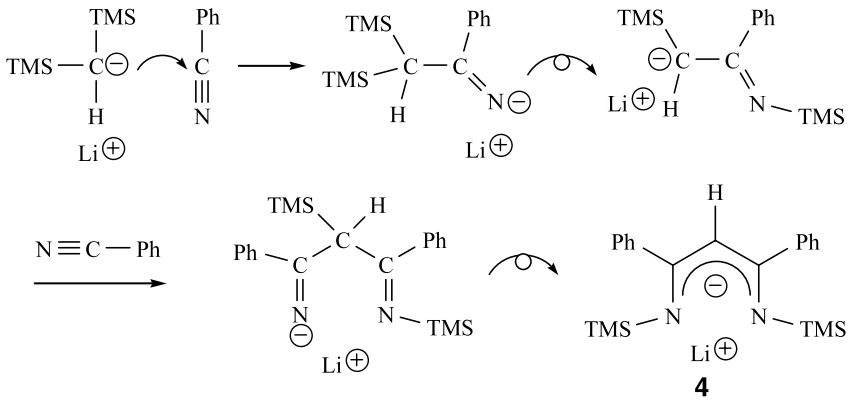
The β-diketiminate lithium salt (**4**) was synthesized following the procedure reported by Lappert and coworkers [24]. The reaction involves mechanistically two consecutive nucleophilic attacks on a nitrile molecule, each one followed by a sigmatropic shift of a trimethylsilyl (TMS) moiety (Scheme 1). The lithium salt was recrystallized from ether–hexane and obtained in good yields (94%).

Reactions of the metal salts, $TiCl_4$ and $ZrCl_4$, with two equivalents of the β-diketiminate lithium salt (**4**) in ether at low temperatures afforded the corresponding dichloro complexes **5** (90%) and **6** (64%) as either a reddish-brown powder or yellow crystalline solids, respectively (Eq. (1)).



(1)

The titanium complex was found to be highly soluble even in non-polar solvents, and was recrystallized several times, but no single crystals were obtained with

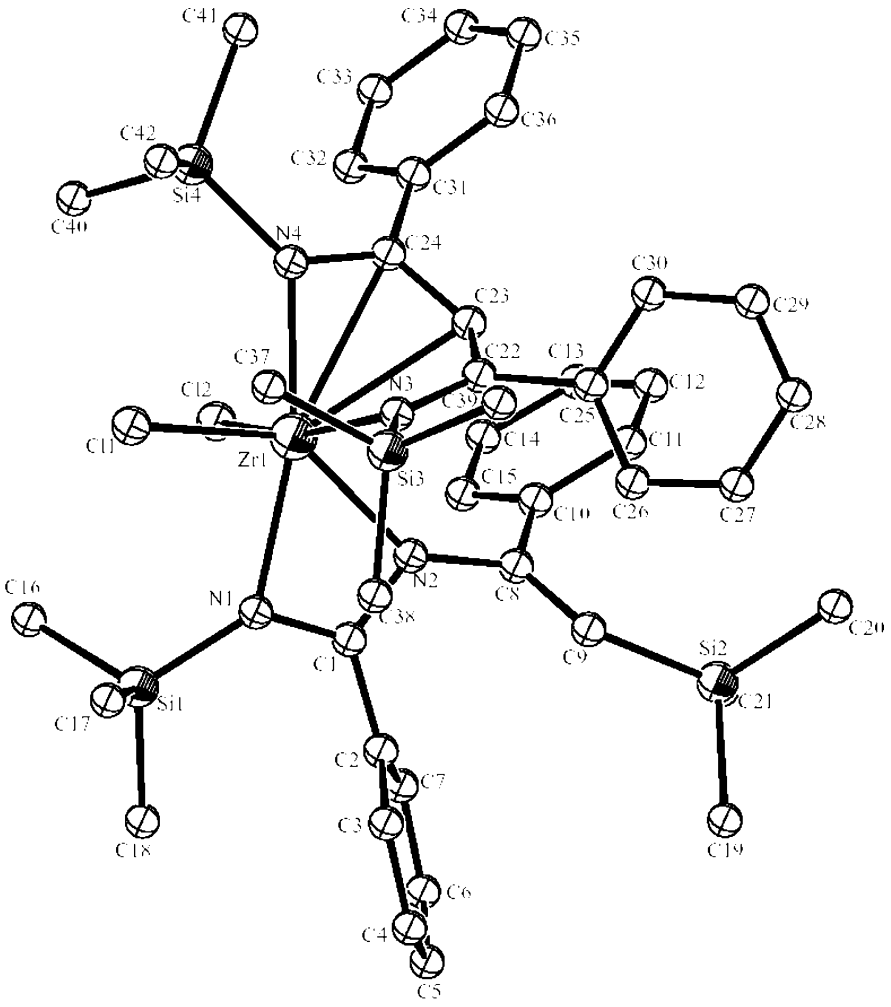


Scheme 1. Proposed mechanism for the formation of the lithium β-ketimidinate (**4**) complex.

good quality for X-ray structure determination. The suggested structure for the Ti complex **5** is of a distorted octahedral complex with intermediate η^2 coordination, which is supported by the ^{1}H-NMR showing two signals for the four TMS groups (the TMS groups are diastereotopic). A support of the structure can be acquired by means of ^{13}C-NMR showing also two signals for the four TMS groups at 0.3 and 2.3 ppm. The C2-hydrogen and the corresponding carbon of the ancillary ligation appear as a single signal in both ^{1}H- (5.28 ppm) and ^{13}C (123.7 ppm)-NMR spectroscopy since they are equivalent.

The zirconium complex **6** was successfully crystallized from a 10:1 toluene:hexane solution mixture to obtain single crystals suitable for X-ray measurements. Diffraction studies reveal that the metal center can be visualized with a tetrahedral environment with one η^2-benzamidinate, one η^5-β-diketiminate, and two chloride ligations (Figs. 1 and 2). A close look at the ancillary β-ketimidinate ligation shows that the two nitrogen atoms are not equidistant to the metal center (Zr–N(3) = 2.555(4) Å and Zr–N(4) = 2.208(4) Å). Two of the three carbons of the β-ketimidinate moiety are equidistant to the metal center (Zr–C(23) = 2.646(4) Å and Zr–C(24) = 2.649(4) Å), whereas the additional carbon is remote from the metal center (Zr–C(22) = 2.735(4) Å). Regarding the electronic interactions of the ancillary ligation with the metal center it can be described as an azaallyl interaction in addition to a lone pair of electrons from the second nitrogen atom. This interaction can be corroborated when comparing the bond lengths through the main core of the ketimidinate moiety. Thus, the bond length N(4)–C(24) = 1.343(5) Å is longer than N(3)–C(22) = 1.317(5) Å, and the bond length C(24)–C(23) = 1.393(6) Å is longer than C(23)–C(22) = 1.442(6) Å indicating the asymmetry of the ancillary ligation when attached to the metal center. A similar type of azaallyl–lone pair of electrons interaction was observed at the molecular structure of the dimer of the ligand lithium salt [25]; in addition, a similar type of interaction between a β-diketiminate and a uranium dichloride complex was observed by Lappert and coworkers [24]. The most interesting aspect relates to the formation of the benzamidinate ligation through the isomerization of the β-ketimidinate, which takes place only when attached to the zirconium metal. Interestingly, a similar isomerization of a ketimidinate ligation forming the benzamidinate moiety has been reported for a mixed valence uranium complex [26].

The four-membered ring $ZrCN_2$ at the benzamidinate moiety is coplanar (mean deviation from the plane defined by Zr–N(1)–C(1)–N(2) = 0.0079 Å and sum of angles around C(1) = 360(10)°). The disposition of the benzamidinate is symmetrical around the metal as observed by the corresponding bond lengths Zr–N(1) = 2.269(3) Å, Zr–N(2) = 2.242(3) Å, C(1)–N(1) = 1.335(5) Å and C(1)–N(2) = 1.346(5) Å. By comparison to other benzamidinate complexes, the Zr–N distances are somewhat longer than in the dimeric compound $[C_6H_5C(NSiMe_3)_2ZrCl_3]_2$ (2.14 and 2.19 Å) [27], while similar as in the monomeric complexes $[C_6H_5C(NSiMe_3)_2ZrCl_2]$ (2.20 and 2.24 Å) [28a–28c] and $[C_6H_5C(NSiMe_3)_2ZrMe_2]$ (2.24 and 2.31 Å) [28a–28c]. Comparing the benzamidinate ligation with other lanthanide/actinide and early transition metal complexes reveals a small difference between the N(1)–C(1)–N(2) angle in **6**, 113.2(3)°, and those of analogous complexes of Nd, 121.4° [29], in Ti(III), 116.5° [30], in Y, 119.8° [31], in Ti(IV), 112.9° [32], in U(IV), 115.7° [33], in U(V), 115.2° [34], and in U(III), 116.4° [25], and those of 122.6° [35] and 115.0° [36] in the mixed benzamidinate–cyclopentadienyl Zr and Hf complexes, respectively. This differences can be attributed to the slightly more ionic nature of the bonding character of the lanthanide/actinide and Ti(III) than with Ti(IV) and mixed cyclopentadienyl–benzamidinate Zr(IV) systems. The opposite effect has been observed for *N*-phenyl-substituted amidinates with late transition complexes [37]. The bond lengths Zr–Cl(1) = 2.4475(12) Å and Zr–Cl(2) = 2.4557(12) Å are significantly elongated with respect to Group 4 benzamidinate complexes [28b,31] and shorter than similar actinide complexes [25,32]. The C=C double bond in the



(a)

Fig. 1. ORTEP diagram (50% ellipsoid) for complex **6**. Complete molecular structure (a) and partial molecular structure after deleting phenyl and methyl rings for bonding clarity (b).

amidinate ligand C(8)–C(9) = 1.331(6) Å indicates a lack of conjugation with the amidine moiety. Crystal data and structure refinement are present in the experiment section. Selected bond distances and angles for complex **6** are presented in Table 1. An ORTEP drawing of complex **6** is given in Fig. 1.

The $\eta^5 \rightarrow \eta^3$ isomerization of one of the ketimidinate ligations has been suggested to be a consequence of steric hindrance [24]. Therefore, temperature-dependent NMR studies of complexes **4**, **5**, and **6** were studied at temperatures ranging from −25 to 90 °C to determine if this isomerization is dynamically operative or operative regardless the complex. It is worth noting that no signal changes were observed, in the ^{1}H- and ^{13}C-NMR, for any of the complexes between the ranges of measured temperatures indicating the stability of the three complexes. Hence, in the synthesis of complex **6** the pure β-ketamidinate ligation **4** was utilized, implicating that the isomerization of the β-diketiminate ligand to the benzamidinate form was catalyzed by the zirconium complex. This isomerization presumably occurs via a retro-Brook rearrangement [23]. A plausible mechanism for this Zr-mediated isomerization is suggested in Scheme 2. The proposed mechanism is shown starting from the amidinate ligand, since it is easier to follow the process from this direction. The process involves changes in the binding of the ligand to the metal center, from metal–nitrogen to metal–carbon bond, followed by rearrangement of the TMS group from a nitrogen atom to another one. Additional metal–nitrogen bond change and nucleophilic attack of the carbanion on a coordinated nitrile followed by a second TMS rearrangement generate the formation of the final product. Based on the temperature-dependent NMR studies, this isomerization process is irreversible.

2.2. Propylene polymerization

The catalytic activity of complex **5** activated by MAO in the polymerization of propylene was studied at

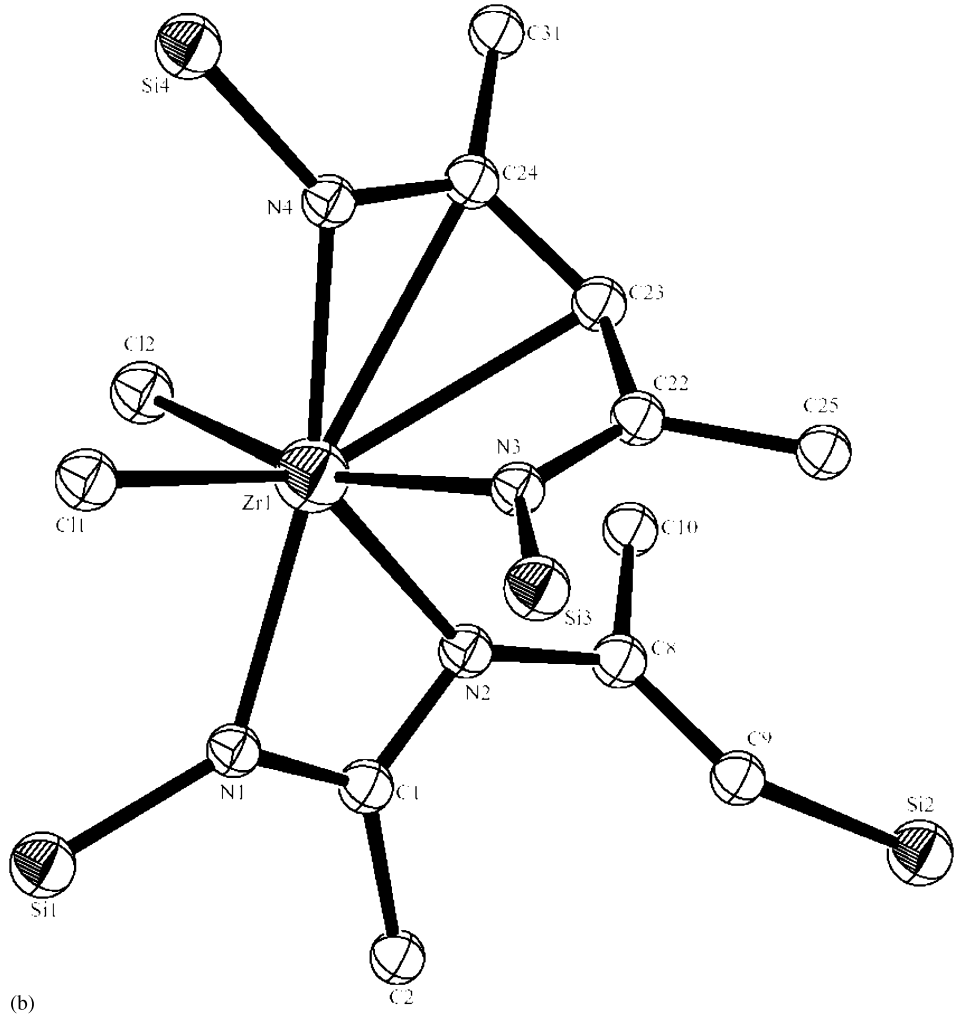


Fig. 1 (*Continued*)

different temperatures and MAO:catalyst ratios. The results are presented in Table 2. The polymerizations were carried out under rigorously anaerobic/anhydrous vacuum line conditions, and after the appropriate times the reactions were quenched with methanol–HCl solutions prior to collection of the polymers, followed by washing with acetone and drying. Microstructures of the polymers were characterized by ^{13}C-NMR spectroscopy

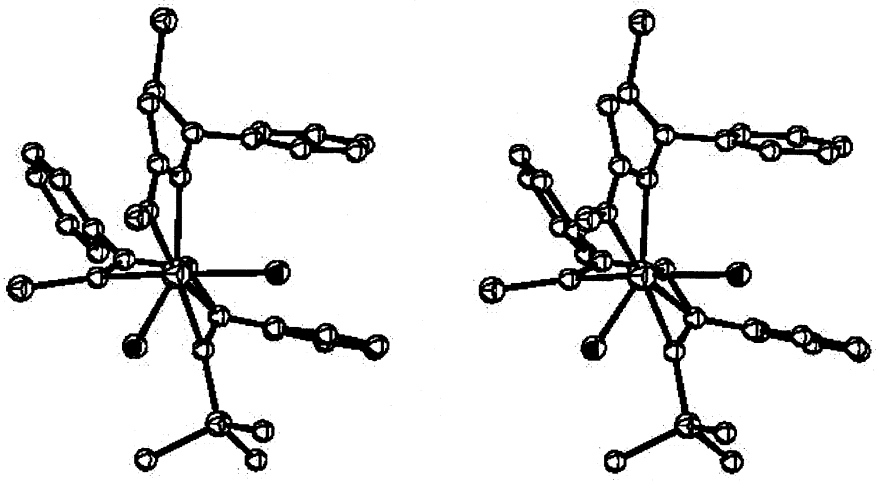


Fig. 2. Stereoview of complex **6**.

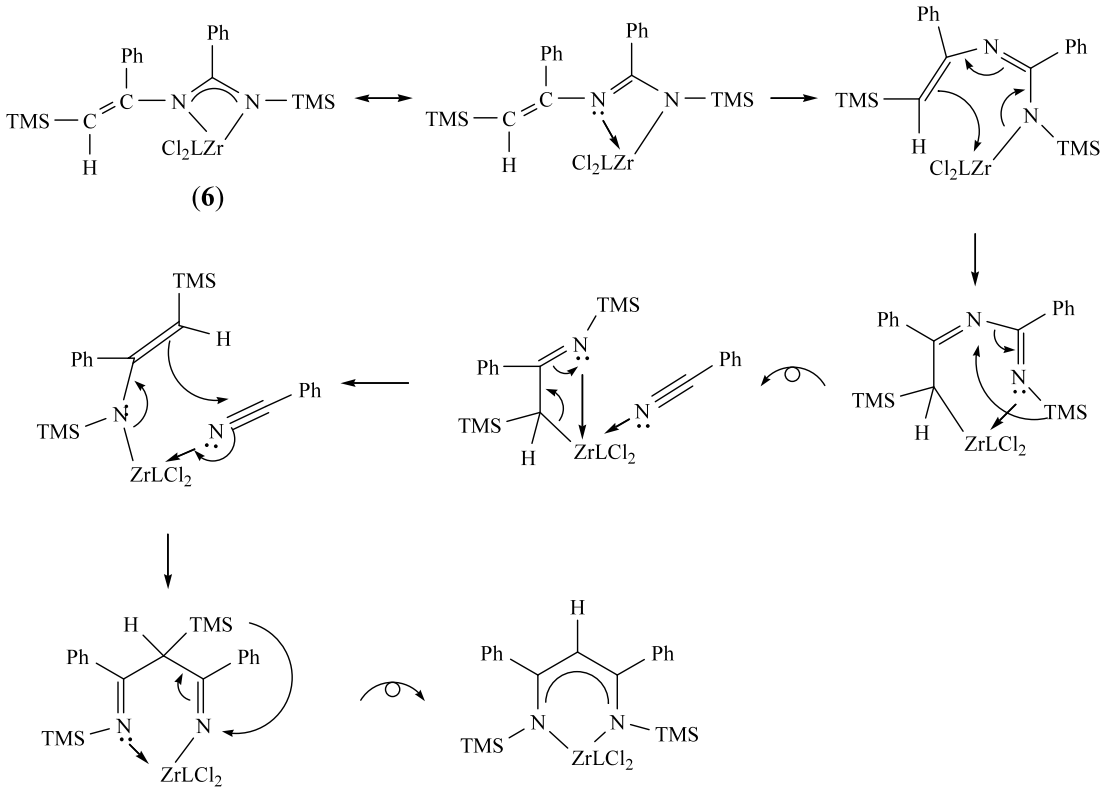
Table 1
Bond lengths (Å) and angles (°) for complex **6**

Bond length (Å)	
Zr(1)–N(4)	2.208(3)
Zr(1)–N(2)	2.242(3)
Zr(1)–N(3)	2.256(4)
Zr(1)–N(1)	2.269(3)
Zr(1)–Cl(1)	2.4475(12)
Zr(1)–Cl(2)	2.4557(12)
Zr(1)–C(23)	2.653(4)
Zr(1)–C(24)	2.649(4)
Zr(1)–C(1)	2.696(4)
Zr(1)–C(22)	2.737(4)
Si(4)–N(4)	1.766(3)
Si(3)–N(3)	1.788(4)
Si(1)–N(1)	1.772(3)
Si(2)–C(9)	1.877(4)
N(1)–C(1)	1.335(5)
N(2)–C(1)	1.346(5)
N(2)–C(8)	1.442(5)
N(3)–C(22)	1.319(5)
N(4)–C(24)	1.344(5)
C(8)–C(9)	1.331(6)
C(8)–C(10)	1.480(6)
Bond angles (°)	
N(4)–Zr(1)–N(2)	133.47(12)
N(4)–Zr(1)–N(3)	82.07(12)
N(2)–Zr(1)–N(3)	88.67(12)
N(4)–Zr(1)–N(1)	166.68(12)
N(2)–Zr(1)–N(1)	59.51(12)
N(3)–Zr(1)–N(1)	103.07(12)
N(4)–Zr(1)–Cl(1)	85.25(9)
N(2)–Zr(1)–Cl(1)	140.89(9)
N(3)–Zr(1)–Cl(1)	92.52(9)
N(1)–Zr(1)–Cl(1)	82.28(9)
N(4)–Zr(1)–Cl(2)	86.38(9)
N(2)–Zr(1)–Cl(2)	90.28(9)
N(3)–Zr(1)–Cl(2)	162.99(9)
N(1)–Zr(1)–Cl(2)	90.96(10)
Cl(1)–Zr(1)–Cl(2)	98.94(5)
N(4)–Zr(1)–C(23)	57.94(12)
N(2)–Zr(1)–C(23)	78.42(12)
N(3)–Zr(1)–C(23)	58.36(13)
N(1)–Zr(1)–C(23)	135.19(12)
Cl(1)–Zr(1)–C(23)	133.82(9)
Cl(2)–Zr(1)–C(23)	104.83(10)
N(4)–Zr(1)–C(24)	30.43(12)
N(2)–Zr(1)–C(24)	103.07(12)
N(3)–Zr(1)–C(24)	76.70(13)
N(1)–Zr(1)–C(24)	162.47(12)
Cl(1)–Zr(1)–C(24)	115.23(9)
Cl(2)–Zr(1)–C(24)	87.02(10)
C(23)–Zr(1)–C(24)	30.48(12)
N(4)–Zr(1)–C(1)	163.26(12)
N(2)–Zr(1)–C(1)	29.88(11)
N(3)–Zr(1)–C(1)	96.26(12)
N(1)–Zr(1)–C(1)	29.64(11)
Cl(1)–Zr(1)–C(1)	111.49(9)
Cl(2)–Zr(1)–C(1)	91.21(9)
C(23)–Zr(1)–C(1)	107.01(12)
C(24)–Zr(1)–C(1)	132.94(12)
N(4)–Zr(1)–C(22)	73.75(12)
N(2)–Zr(1)–C(22)	76.60(12)
N(3)–Zr(1)–C(22)	28.62(12)
N(1)–Zr(1)–C(22)	116.49(12)
Cl(1)–Zr(1)–C(22)	118.25(10)
Cl(2)–Zr(1)–C(22)	135.25(10)
C(23)–Zr(1)–C(22)	31.00(13)
C(24)–Zr(1)–C(22)	55.99(13)
C(1)–Zr(1)–C(22)	96.81(12)

and molecular weights were measured by GPC at 135 °C in 1,2,4-trichlorobenzene.

Various interesting tendencies are evident in the polymerization data (Table 2). The activity of the complex rises with an increase of the MAO:catalyst ratio yielding a maximum at 800. A higher MAO concentration induced lower activities (entries 1–4). The molecular weights of the polymers as a function of MAO concentration were found to rise, also passing through a maximum which was obtained at the MAO:-catalyst ratio of 600. A reduction in the molecular weight of the polymers was observed when the MAO concentration was further increased. This behavior is opposite to that observed when cyclopentadienyl early transition metal complexes are used [1–3]. These results can be accounted for in terms of the known dependence on the cocatalyst concentration towards the relative proportion of the various possible eliminations, alkyl transfer pathways, and deactivation processes [38]. The polymers obtained were found to be elastomers with mmmm pentad percentages ranging from 27 to 44%. An increase in activity and molecular weight was observed when the reaction temperature was raised from 0 to 20 °C keeping the MAO:catalyst ratio at 400 (compare entries 1 and 7); at a higher MAO:catalyst ratio (800) the activity increases whereas the molecular weight decreases. This result indicates an increased insertion rate as a function of temperature, with changes at the termination rate based on MAO concentrations. This change in temperature from 0 to 20 °C also results in a decrease in %mmmm. This result can be attributed to an increase of either the epimerization rate or 2,1-misinsertions contributing to the decrease in isotacticity. When the temperature was further raised to 60 °C at an MAO:catalyst ratio of 400 (compare entries 1 and 5) the result is a sharp increase in molecular weight, a small increase in activity, and a slight decrease in %mmmm. The temperature effect when the MAO:catalyst ratio was 600 (compare entries 2 and 6) results in a slight decrease in activity and a sharp decrease in isotacticity and molecular weight of the polymers. This result is due presumably to an increase in the termination rate at this MAO concentration and temperature, causing lower molecular weights. The relatively small difference in activity at both MAO concentrations (400 and 600), at both temperatures (20 and 60 °C), and the large difference in %mmmm decrease values (27 → 25 and 32 → 20) suggests that in all cases a similar cationic complex is active at the polymerization. The relationship between catalyst and cocatalyst varies at different MAO concentrations based on temperatures, forming at the higher MAO concentration values a complex more predispose to misinsertions or epimerizations.

The GPC analysis of the polymers shows that there is only one polymeric fraction arguing for single-site catalysis. Similar corroboration was observed by the



Scheme 2. Proposed mechanism for the zirconium-catalyzed isomerization of β-ketimidinates.

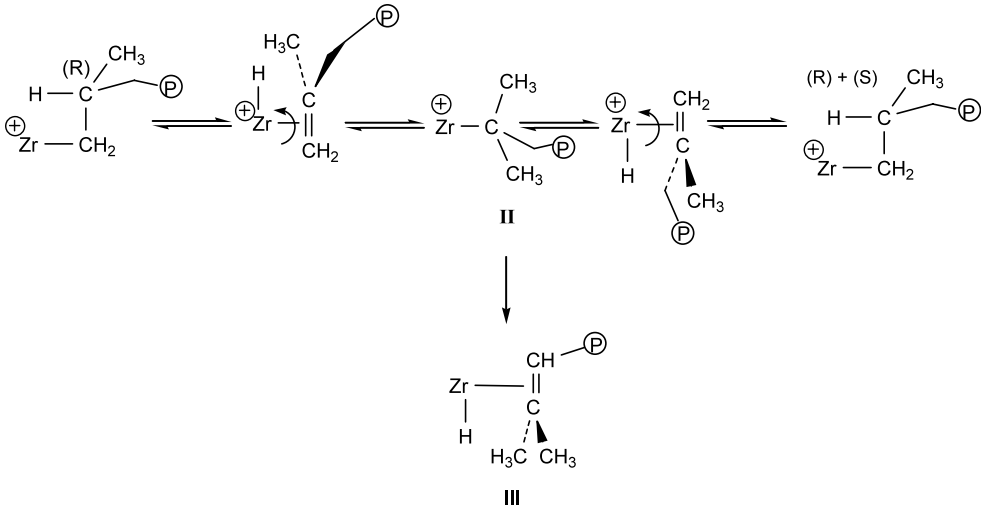
low polydispersities ($M_w/M_n \approx 2$) of the obtained polymers (besides entries 2 and 9 in Table 1). The elastomeric polypropylenes were obtained with high molecular weights ($\sim 10^5$ g mol^{-1}). Previously reported elastomeric polypropylene molecular weights range from 200,000 g mol^{-1} at 50 °C reported by Resconi et al. [39] to almost 1,000,000 g mol^{-1} at −18 °C reported by Waymouth and coworkers [40]. Elastomeric polypropylene obtained in our group using either benzamidinate or acetylacetonate catalysts ranges in molecular weights from 10,000 g mol^{-1} at ambient temperatures to almost 400,000 g mol^{-1} at 0 °C. Consequently, this complex complement the availability of other octahedral complexes to obtain elastomeric polypropylene with high molecular weights obtained with large activities at room temperatures.

Most of the reactions were run with toluene as the solvent. When the polymerization was conducted in dichloromethane, for comparison, lower activities were encountered (compare entries 3 and 9). This result relates to the increased polarity of the solvent, causing a greater charge separation between the putative catio-

Table 2
Activity and molecular weight data for the polymerization of propylene by complex **5**

Entry	Al:M ratio	T (°C)	Activity [a] ($\times 10^{-4}$)	%mmmm	M_w	M_n	M_w/M_n	Solvent	Reference
1	400	20	11.5	27	308200	165700	1.86	Toluene	This work
2	600	20	16.0	32	650200	176600	3.68	Toluene	This work
3	800	20	19.0	34	171150	66500	2.57	Toluene	This work
4	1000	20	8.3	27	182050	76000	2.39	Toluene	This work
5	400	60	13.0	25	759900	326700	2.32	Toluene	This work
6	600	60	15.0	20	193450	86250	2.24	Toluene	This work
7	400	0	4.2	44	293450	133500	2.19	Toluene	This work
8	800	0	2.0	41	251750	109450	2.30	Toluene	This work
9	800	20	1.8	< 6	328400	93500	3.51	CH_2Cl_2	This work
10 [b]	1000	20	19.0	21	93700	51300	1.83	Toluene	[20d]
11 [c]	430	20	1.9	15	167200	129350	1.29	Toluene	[17]

[a] In units of g of polymer (mol of cat)$^{-1}$ h^{-1}.
[b] Bis(benzamidinate)titanium dimethyl.
[c] Bis(acetylacetonato)titanium dichloride.



Scheme 3. Epimerization mechanism for the last inserted monomer in the polymerization of propylene.

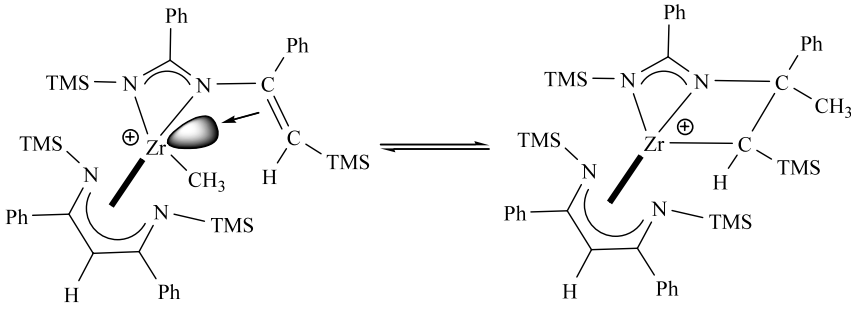
nic complex and the MAO anion, rendering the catalyst open to deactivations. Due to the charge separation and the coordinative unsaturation of the complex large amount of insertions are operative, responsible for the high molecular weight, although with a lack in stereoregularities.

Since fractionation of the obtained polymers did not produced atactic polymer fractions, it seems conceivable that the formation of the elastomeric polypropylene is obtained via an epimerization of the last inserted unit. This assumption was substantiated by examining the complex's activity in the isomerization of higher α-olefins (vide infra). It is important to point out that in ^{1}H-NMR of the polymers no terminal allylic or isobutenyl end groups were observed, making it impossible to identify the most predominant termination pathway.

When complex **6** was reacted with propylene and MAO in toluene, no polymer was obtained at any of the reaction conditions. A plausible explanation for complex **6**'s inactivity in the polymerization of propylene rises from examination of its structure. Reaction of the Zr complex with MAO creates a cationic species with a free coordination site. The double bond at the ancillary ligand is posed in close proximity to the empty orbital, either before (Fig. 2) or after rearrangement of the amidine ligation, impeding the insertion of an olefinic monomer. A second variant possibility is the insertion of the methyl into the ligand double bond forming a stable complex and rendering the complex inactive for polymerization (Eq. (2)).

2.3. Isomerization of α-olefins

As described above, a plausible mechanism for the elastomeric formation of polypropylene is accredited to an epimerization reaction of the last inserted unit as presented in Scheme 3 [21]. In the epimerization process, the configuration of the last inserted unit is epimerized via a β-hydrogen elimination and consecutive reinsertion. The key intermediate is complex **II**, which forms the two epimeric available complexes, to continue the polymerization reaction. A close look at complex **II** reveals also that besides the elimination of hydrogen from either one of the CH_3 groups, an additional β-hydrogen elimination from the growing chain may take



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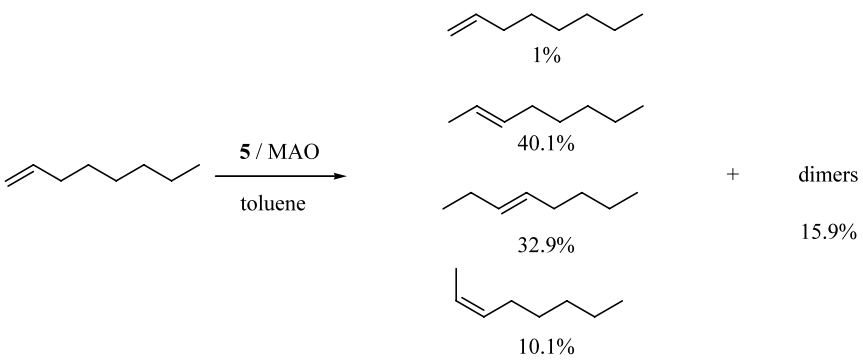


(3)

place. This process will induce the isomerization reaction forming complex **III**.

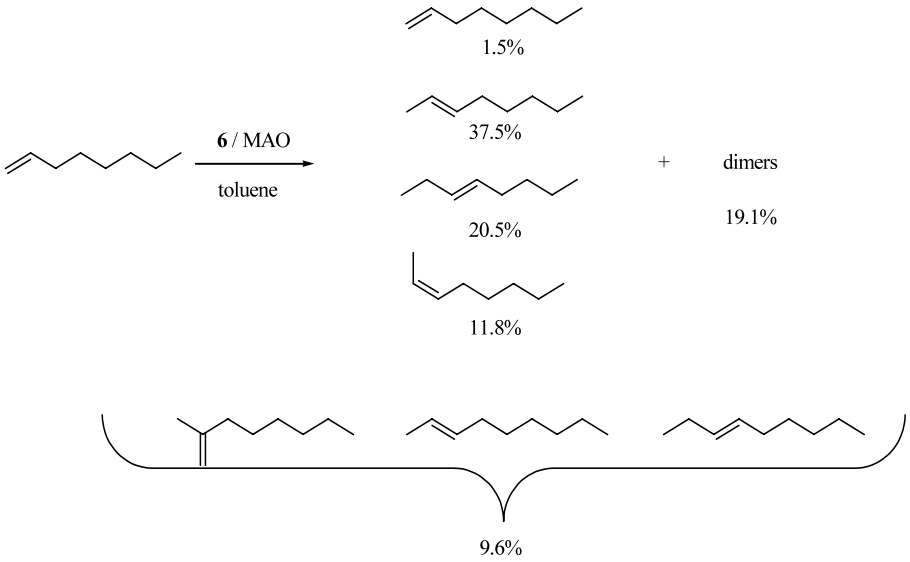
To account for the epimerization reaction, the catalytic activities of complexes **5** and **6** were studied with the substrates 1-octene and allylbenzene, using MAO as the cocatalyst. In addition to gaining knowledge of the mechanism responsible for the formation of elastomeric polypropylene, the isomerization reaction, if catalyzed by complex **6**, will shed light on the structure(s) formed, which are inactive for the polymerization process.

The isomerization reactions were carried out in toluene, keeping at all times the MAO:catalyst ratio of 100. The products were identified by GC/MS and by comparing to known compounds. The product ratio and conversions were determined by GC spectroscopy using internal standards.

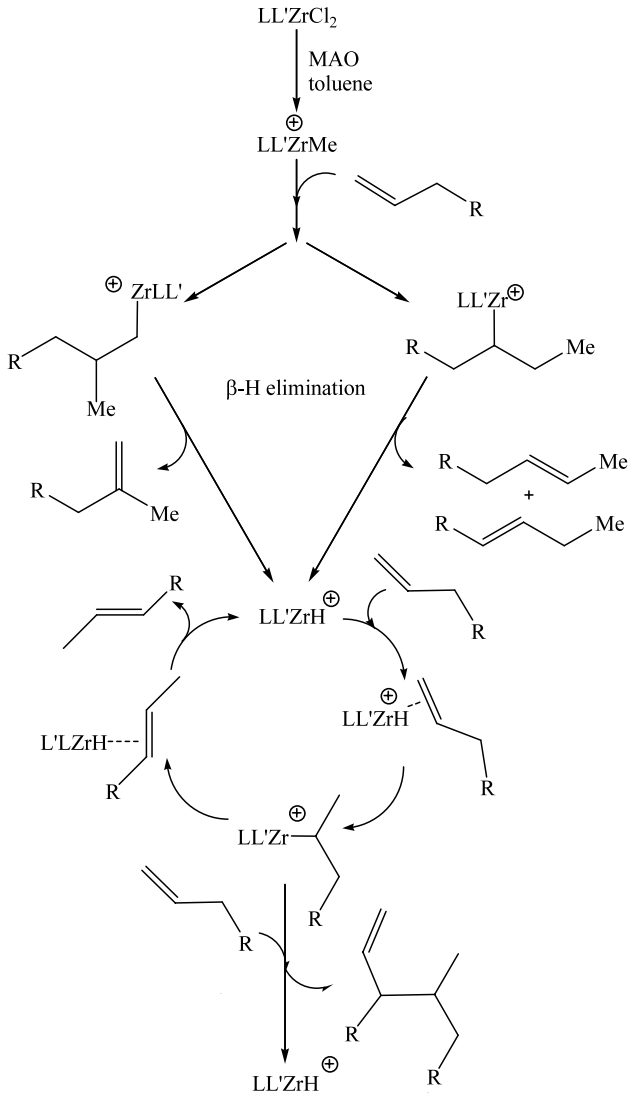
1-Octene was isomerized (conversion = 99%) with complex **5** producing three major products (*E*)-2-octene, (*Z*)-2-octene and (*E*)-3-octene, and small amounts of a mixture of dimers. No compounds with molecular weights of C_9H_{18} (nonenes) were identified (Eq. (3)).

For complex **6**, surprisingly 1-octene was isomerized (conversion = 98.5%) to a similar mixture of octenes and dimers as obtained with complex **5**, although stoichiometric amounts of (C_9H_{18}) nonenes were also detected (Eq. (4)).

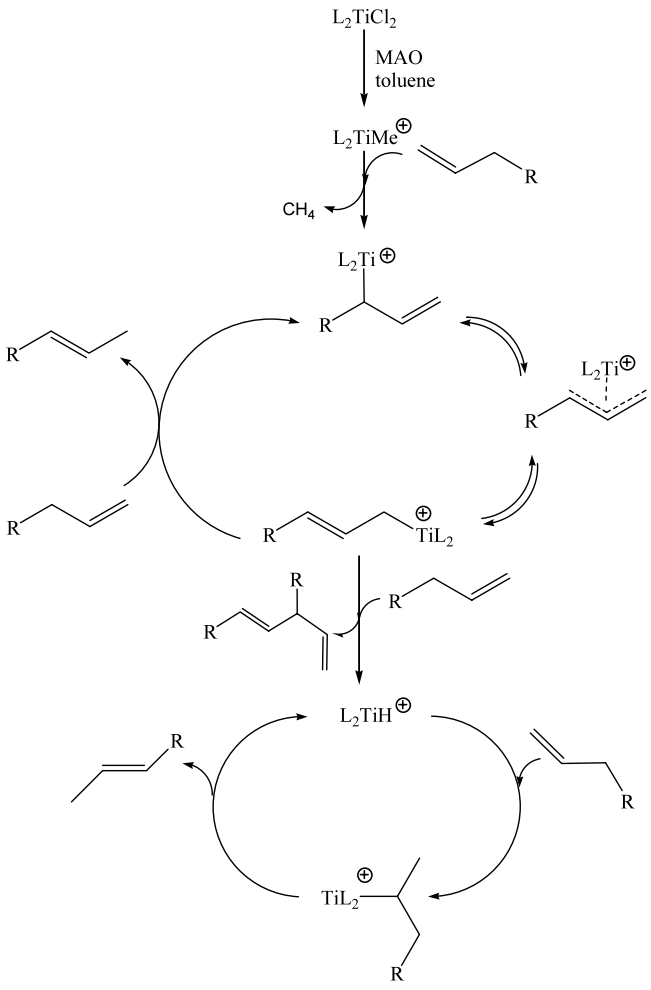
With allylbenzene as a substrate, complex **5** yielded *trans*-β-methylstyrene exclusively (yield: > 99.5%) while for complex **6** *trans*-methylstyrene was obtained (yield: 93.4%) in addition to 1-phenyl-1-butene (4.1%) (Eq. (5)). Interestingly, no *cis*-β-methylstyrene was observed indicating the lack of isomerization between the *cis* and *trans*-β-methylstyrenes as contrary to the results obtained for late transition metal complexes in which the isomerized products are in equilibrium [41]. The fact that complex **6** produces products with an additional



(4)



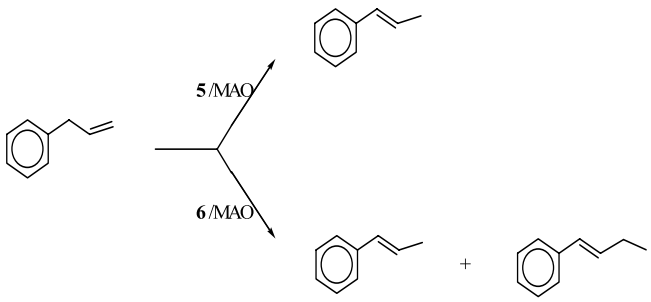
Scheme 4. Proposed mechanism for the isomerization of α-olefins promoted by the catalytic system **6**–MAO.



Scheme 5. Proposed mechanism for the isomerization of α-olefins promoted by the catalytic system **5**–MAO.

methyl group for the two different substrates (1-octene and allylbenzene), while with complex **5** no traces of these products were found, suggests that the two complexes react via different mechanisms [42].

The methyl addition products formed stoichiometrically by the zirconium complex **6** can only be expected if the cationic methyl complex obtained between compound **6** and MAO inserts into the olefin followed by a β-H elimination. Additional insertions of the obtained hydride and concomitant β-H eliminations will be responsible for the production of the rest of the monomeric isomerized compounds. Dimers will be formed by the cleavage of the isomerized olefin from the metal complex by an allylic hydrogen of an additional monomer resulting in the starting organometallic hydride and various dimers. A plausible mechanism for the isomerization of α-olefins promoted by the catalytic system complex **6**–MAO is described in Scheme 4.



(5)

For the titanium complex **5**, the most plausible mechanism involves an allylic C–H activation pathway forming in addition to CH_4 the isomerization products without forming those compounds with an extra methyl group (Scheme 5). The dimers are formed by the cleavage of the allylic complex with an additional olefin forming as well the corresponding hydride, which will continue the isomerization reaction. In the isomerization

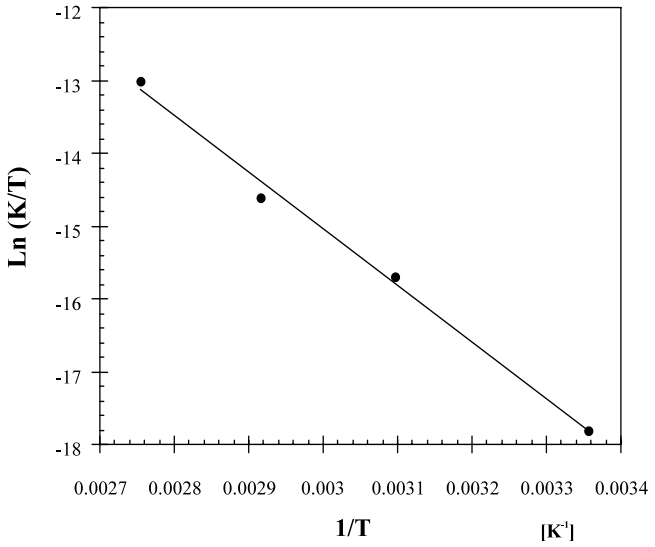


Fig. 3. Eyring plot for the isomerization of allylbenzene to *trans*-methylstyrene with complex **5**. The line represents the least-squares fit to the data.

of allylbenzene by complexes **5** and **6**, through both proposed mechanisms, the absence of the corresponding *cis*-β-methylstyrene product suggests that in the last step, in either of the mechanisms, the releasing of the product from the metal complex is irreversible.

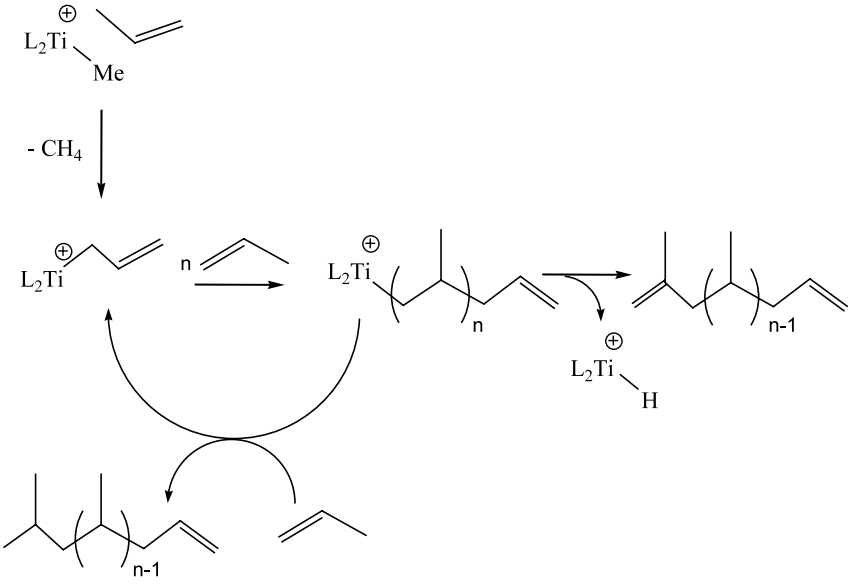
Kinetic measurements were conducted in order to learn about the substrate, catalyst, and temperature influence on the rate of isomerization. The substrate chosen for these experiments was allylbenzene, since the isomerization product was essentially *trans*-β-methylstyrene and its formation was easily followed by ^{1}H-NMR. The disappearance of the benzylic methylene resonance (at $\delta = 3.20$ ppm) and the appearance of the methyl resonance of the product (at $\delta = 1.65$ ppm) were followed and normalized. The kinetic experiments were carried out using the pre-catalyst **5** with MAO as cocatalyst at a constant ratio of 1:100.

When the catalyst and MAO concentrations were kept constant, a plot of k_{obs} as a function of substrate concentration shows a linear behavior over a 10-fold concentration range. This linear result indicates a first-order dependence in substrate concentration. In a similar fashion, when the substrate concentration was maintained constant and the pre-catalyst/MAO concentration was varied over a 10-fold range, a plot of the reaction rate vs. pre-catalyst concentration also shows a first-order dependence. Based on these results, the rate law expression for the isomerization of allylbenzene promoted by the pre-catalyst **5** activated by MAO can be formulated as presented in Eq. (6).

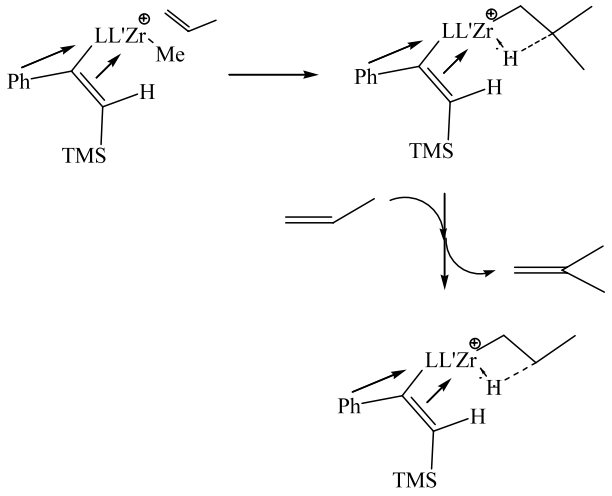
$$v = k[\text{complex } \mathbf{5}]^1[\text{allylbenzene}]^1 \quad (6)$$

The derived enthalpy of activation, energy of activation, and a large negative entropy of activation (derived from an Eyring analysis) (Fig. 3) are $\Delta H^{\ddagger} = 14.7(4)$ kcal mol^{-1}, $E_a = 14.1(4)$ K cal mol^{-1}, and $\Delta S^{\ddagger} = -33(1)$ e.u., respectively. These parameters suggest a highly ordered transition state with considerable bond making to compensate for bond breaking. These results corroborate for rapid methane elimination and argue for the irreversible cleavage of the *trans*-isomer as the rate-determining step. The large negative entropy supports a four-center transition state as the approach of the complex and the olefin at the limiting step.

It is worth noting that the isomerization results obtained shed light on the polymerization mechanism for the titanium complex and the inactivity of the zirconium complex. Since in the isomerization of 1-octene and allylbenzene, promoted by the titanium



Scheme 6. Plausible mechanisms for the polymerization of propylene promoted by complex **5**.



Scheme 7. Proposed interactions of α-olefins with the cationic complex **6** impeding the insertion of additional monomers (to see the interactions of the double bond or the phenyl ring with the metal center, please see Fig. 2).

complex **5**, nonenes and phenylbutenes were not observed suggesting an allylic activation, it seems plausible that for propylene a similar commencement pathway is operative. Thus, the cationic titanium methyl complex may react with propylene forming a cationic allylic complex, to which additional insertions will produce the elastomeric polymer. Cleavage of the chain by the same allylic route will yield polymers with isopropyl and allylic terminal groups. If the growing polymer chain is cleaved via a β-hydrogen elimination, then only for the first catalytic cycle, a molecule of polymer with both ends containing double bonds will be produced and the obtained titanium hydride will continue the polymerization (Scheme 6).

For the zirconium complex, in the isomerization of both 1-octene and allylbenzene, stoichiometric amounts of products containing one more methyl were obtained suggesting that in the polymerization of propylene the first methyl insertion should take place. The cationic center may contain various interactions with the β-phenyl ring or with the double bond of the amidinate ligation (Fig. 2), the latter only if a rearrangement of the ligand is operative. Therefore, the lack of additional insertions of propylene is possibly an indication of the difference of energy between a chelate formation, by the olefin and a β-hydrogen of the olefin after the methyl insertion, and the olefin after the methyl insertion and the ligand double bond (or phenyl) interaction. Thus, it seems plausible that the first insertion is operative followed by a β-hydrogen elimination of isobutylene which may reinsert propylene but unable to add an additional propylene molecule due to the interaction within the ligand (Scheme 7).

3. Conclusions

The bis-β-diketiminate dichloride complexes of titanium and zirconium have been synthesized and characterized. For the latter, the solid-state characterization was studied exhibiting a benzamidinate ligand and a non-symmetrical β-diketiminate ligation coordinated as an azaallyl in conjunction with a donation of a lone pair of electrons from the second nitrogen atom of the β-diketiminate molecule. The benzamidinate ligand is a result of an isomerization of the one of the ketimidinate ligations at the metal center. The complexes were found to react with MAO forming presumably cationic complexes. The titanium complex was found to be active for the polymerization of propylene yielding elastomeric polymers with high molecular weights, whereas the zirconium complex was inactive. In the isomerization of 1-octene and allylbenzene, both complexes were found to be active. The titanium complex forms isomerization products and dimers without forming nonenes or phenyl butanes, suggesting that the most plausible operative isomerization mechanism is the allylic pathway. For the zirconium complex, stoichiometric amounts of nonenes and phenyl butanes were obtained from the first insertion of the starting methyl complex on the corresponding olefin followed by a β-hydrogen elimination, indicating a different mechanism and corroborating the formation of the corresponding methyl complex upon reaction with MAO.

4. Experimental

4.1. General procedure

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 glove box 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. Ether solvents were distilled under nitrogen from sodium benzophenone and hydrocarbon solvents (toluene, benzene, and hexane) from Na–K alloy. Dichloromethane was distilled from P_2O_5 under nitrogen. All solvents for vacuum line manipulations were stored in vacuum over Na–K alloy in resealable bulbs. 1-Octene and allylbenzene (Aldrich) were degassed before use. The β-diketiminate ligand was prepared according to literature procedure [24]. NMR spectra were recorded on a Bruker AM 200 and Bruker AM 400 spectrometers. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young). Chemical shifts are referenced to internal

solvent resonances and are reported relative to tetramethylsilane. Molecular weights of polypropylene were determined by GPC recorded on Waters 150 CV instrument at 135 °C in 1,2,4-trichlorobenzene. GC analysis was conducted on a Varian CP-3800 instrument. GC/MS analysis was conducted on an ITS40 Finnigan instrument.

4.2. [{N(SiMe$_3$)C(Ph)}$_2$CH]$_2$TiCl$_2$ (5)

$TiCl_4$ (0.5 ml, 4.6 mmol) was added to a solution of the lithium β-diketiminate (1.4 g, 3.8 mmol) in Et_2O (30 ml) at −78 °C. The mixture was stirred for 1 h at −78 °C and then allowed to warm to room temperature and stirred for additional 12 h. After filtration and evaporation of the solvent, the reddish-brown oily product was washed with hexane to give a fine powder, which was filtered and dried under vacuum to yield 1.46 g (90%). The complex was co-precipitated with one molecule of LiCl. Analysis for $C_{42}H_{58}Cl_3LiN_4Si_4Ti$ requires: C, 56.52; H, 6.55; Cl, 11.92; N, 6.28. Found: C, 55.56; H, 6.39; N, 6.38; Cl, 11.01%.

Spectroscopic data for (**5**): ^{1}H-NMR (200 MHz, toluene-d_8): δ 6.90–7.70 (m, 10H, phenyl), 5.28 (s, 1H, CH), 0.22, −0.13 (s, 9H, Me_3Si); ^{13}C{H}-NMR (50.32 MHz, toluene-d_8): δ 157.2, 141.1 and 134.8 (C_6H_5), 123.6 (CH), 2.31, 0.35 ($(CH_3)_3Si$).

4.3. [{N(SiMe$_3$)C(Ph)}$_2$CH][N(TMS)C(Ph)NC(Ph)CH(TMS)]ZrCl$_2$ (6)

$ZrCl_4$ (0.58 g, 4.6 mmol) and Li{N(SiMe$_3$)C(Ph)}$_2$CH (1.66 g, 3.8 mmol) were stirred at 25 °C for 15 h in a Schlenk vessel containing Et_2O (50 ml). The solution was filtered through a frit No. 4 and the solvent evaporated under reduced pressure to obtain an oily yellow product. The oil was washed with hexane to obtain a yellow powder that was crystallized from a 10:1 mixture of toluene and hexane yielding 1.4 g (64%). Analysis for $C_{42}H_{58}Cl_2N_4Si_4Zr$ requires: C, 56.46; H, 6.54; Cl, 7.94; N, 6.27. Found: C, 49.45; H, 6.54; Cl, 9.50; N, 5.04%.

Spectroscopic data for (**6**): ^{1}H-NMR (200 MHz, toluene-d_8): δ 6.80–7.70 (m, 20H, phenyl), 5.83 (s, 1H, C*H*), 5.18 (s, 1H, =C*H*), 0.35 (s, 18H, (C*H*$_3$)$_3$Si), 0.09 (s, 9H, (C*H*$_3$)$_3$Si), −0.20 (s, 9H, (C*H*$_3$)$_3$Si); ^{13}C-NMR (50.32 MHz, toluene-d_8): δ 130.9, 129.7, 126.2 (Ph), 124.6 (*C*H), 98.0 (=*C*HSi), 3.81, 3.68, 0.52 (3 × (C*H*$_3$)$_3$Si).

4.4. X-ray crystallography

The crystal structure data for complex **6** was collected on a Nonius Kappa CCD diffractometer. Experimental data collection (22,467 reflections) was collected at 220 K. Data reduction was performed with DENZO SMN [43]. Structure determination and refinement was done using the set of MAXUS 1.4 programs [44]. Figures were prepared by TEXSan.

Crystal data for complex **6**: $C_{42}H_{58}Cl_2N_4Si_4Zr$, M_w = 893.40, Mo–K$_\alpha$ radiation ($\lambda = 0.7107$ Å), monoclinic, $P21/c$, $a = 21.076(4)$ Å, $b = 1.466(4)$ Å, $c = 13.567(3)$ Å, $\beta = 105.19(2)°$, $U = 4819.7(2)$ Å^3, $Z = 4$, $D_{calc} = 1.231$ g cm^{-1}, $\mu = 0.470$ mm^{-1}, crystal size = 0.30 × 0.20 × 0.07 mm^3, 8416 unique reflections ($R_{int} = 0.088$), R_1 = 0.0533, $wR_2 = 01123$ [$I > 2\sigma(I)$].

4.5. Propylene polymerization

Polymerization reactions were conducted under dry anaerobic conditions on a Schlenk line. The general procedure was as follows: an amount of 5 mg catalyst and the desired amount of MAO were weighted into a glass reactor inside the glove box. The required MAO weight was calculated in reference to the molecular weight of one unit (58 g mol^{-1}). The reactor was connected to the Schlenk line and the desired amount of the solvent was added by a syringe. The solution was degassed to enable the addition of the monomer. Propylene was compressed into the reactor at low temperature until liquefied and the reactor remained closed during the rest of the reaction. After monomer addition, the required temperature was stabilized by means of oil, water, or ice bath and the reaction mixture was stirred for the duration of the reaction.

After a predetermined period of 1 h the reaction was quenched by venting the excess of propylene in a hood, exposure to air, and washing with HCl/methanol (1:1) solution. The polymer produced was then collected, washed with acetone and hexane, and dried under vacuum. For NMR and molecular weight analysis the polymers were redissolved in hot 1,2,4-trichlorobenzene, filtered hot, precipitated with cold acetone, and dried again. The rest of the solution was checked for atactic polypropylene fractions by extraction with the reaction solvent, separation of the organic phase, and drying under vacuum.

4.6. General procedure for the catalytic isomerization of α-olefins

In a typical procedure inside the glove box, the specific amount of an olefin (50 μl) was pipetted from a stock solution into a J-Young NMR tube containing 5 mg of the specific catalyst and a specific amount of MAO (keeping the catalyst:MAO:olefin ratio as 1:100:16) in 0.5 ml of toluene-d_8. The sealed tube was kept in an oil bath at 25 °C for 1 h. The organic products were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, GC/MS spectroscopy, and by comparing with known compounds [45].

4.7. Kinetic study of the isomerization of allylbenzene

In a typical experiment, an NMR sample was prepared as described in the typical NMR scale catalytic reactions section but maintained at −78 °C until kinetic measurements were started. The sealed tube was heated at NMR and at suitable time intervals NMR data were acquired using four scans with a long pulse delay to avoid saturation of the signal. The kinetic studies were usually monitored by the intensity changes in the substrate resonances and in the product resonances over three or more half-lives. The substrate concentration (C) was measured from the area (A_s) of the ^{1}H-normalized signal of the solvent (A_b). All the data collected could convincingly fit ($R > 0.98$) by least-squares to Eq. (7) where C_0 ($C_0 = A_{s0}/A_{b0}$) is the initial concentration of substrate and C (A_s/A_b) the substrate concentration at time t.

$$mt = \log\left(\frac{C}{C_0}\right) \tag{7}$$

The ratio of catalyst to substrate was accurately measured by using stock solutions of the catalyst and micropipetting the clean substrate. Turnover frequencies (N_t, h^{-1}) were calculated from the least-squares slope (m) of the resulting plots. Typical initial olefin concentrations were in the range 0.07–0.67 M and typical catalyst concentrations were in the range 2.2–22 mM.

4.8. Isomerization of 1-octene

4.8.1. GC/MS data for octenes

m/e: 111 [M−1$^+$], 97 [M$^+$−CH_3], 83 [M$^+$−CH_2CH_3], 69 [M$^+$−$CH_2CH_2CH_3$], 55 [M$^+$−$CH_2CH_2CH_2CH_3$], 41 [M$^+$−$CH_2CH_2CH_2CH_2CH_3$].

4.8.2. GC/MS data for nonenes

m/e: 124 [M$^+$], 110 [M$^+$−CH_3], 97 [M$^+$−CH_2CH_3], 83 [M$^+$−$CH_2CH_2CH_3$], 69 [M$^+$−$CH_2CH_2CH_2CH_3$], 55 [M$^+$−$CH_2CH_2CH_2CH_2CH_3$], 41 [M$^+$−$CH_2CH_2CH_2CH_2CH_2CH_3$].

4.8.3. GC/MS data for dimers with molecular weight of 224 g mol^{-1}

m/e: 224 [M−2$^+$], 138 [M$^+$−$CH_2CH_2CH_2CH_2CH_3$], 125 [M$^+$−$CH_2CH_2CH_2CH_2CH_2CH_3$], 111 [M$^+$−$CH_3CHCH_2CH_2CH_2CH_2CH_2CH_3$], 97, 83, 69, 55, 41.

All isomers with the same molecular weight show the same MS except for differences in intensities.

4.9. Isomerization of allylbenzene

4.9.1. GC/MS data

m/e: 117 [M−1$^+$], 103 [M$^+$−CH_3].

4.9.2. GC/MS data for 1-phenyl-1-butene

m/e: 132 [M$^+$], 117 [M$^+$−CH_3], 103 [M$^+$−CH_2CH_3], 77 [M$^+$−$CHCHCH_2CH_3$].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205539 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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