

Group 4 Octahedral Benzamidinate Complexes: Syntheses, Structures, and Catalytic Activities in the Polymerization of Propylene Modulated by Pressure

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Abstract: The synthesis and structural X-ray diffraction studies for some benzamidinate ligations and several group 4 benzamidinate complexes are presented. The use of the *cis*-octahedral C_2 -symmetry compounds was studied to shed light on the conceptual applicability of these complexes as potential catalysts for the stereoregular polymerization of propylene. We demonstrate that the stereoregular polymerization of propylene catalyzed by early-transition metal octahedral benzamidinate complexes, activated with either MAO or $B(C_6F_5)_3$ as cocatalysts, can be modulated by *pressure* (from atactic to isotactic through elastomers). The different effects in the polymerization process such as the nature of solvent or cocatalyst, temperature, pressure, molar ratio catalyst:cocatalyst, and the relationship between the symmetry of the complex and the polymer microstructure have been investigated. When the complex $[4-CH_3-C_6H_4C(NTMS)_2]_2ZrMe_2$ (**9**) was activated with MAO, it was found to be a good catalyst for the polymerization of propylene, at atmospheric pressure, producing an oily polymer resembling an atactic polypropylene. Being activated with $B(C_6F_5)_3$, complex **9** produces a highly isotactic (mmmm = 98%) product. Likewise, when the polymerization of propylene was performed with complex **9** and MAO at high pressure (liquid propylene), a highly stereoregular polymer was also obtained. Larger activities and stereoregularities were achieved by performing the reaction in CH_2Cl_2 as compared to toluene. Contrary to complex **9**, at atmospheric pressure the complex $[4-CH_3-C_6H_4C(NTMS)_2]_2TiMe_2$ (**10**) is not active either in CH_2Cl_2 or in toluene. At high pressure, complex **10** produces elastomeric polypropylene. Activities of the isolobal complexes $[C_6H_4C(NTMS)_2]_2ZrMe_2$ (**11**) and $[C_6H_4C(NTMS)_2]_2TiMe_2$ (**12**) were found to be larger than those of complexes **9** and **10**, respectively. Contrary to the structures of the elastomeric polypropylenes described in the literature, the obtained elastomers are characterized by frequent alternation of the isotactic domains with stereodefects. The stereoregular errors are formed by the intramolecular epimerization of the growing chain at the last inserted unit. The epimerization reaction was corroborated through the isomerization of alkenes.

Introduction

Metal-mediated olefin polymerization catalysts have experienced a vast growth since the pioneering work of Ziegler and Natta, which showed that systems such as $TiCl_4/AlClEt_2$ catalyze the polymerization of ethylene to high-density polyethylene and propylene to stereoregular polypropylene.¹ Successful application of the Ziegler–Natta catalysts has stimulated intense academic and industrial research activity focused on understanding the relationships between the structure, activity, selectivity of the catalysts, and the properties of the obtained polymers.

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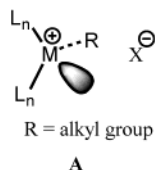
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These studies resulted in the discovery of metallocenes as a new Ziegler–Natta type of homogeneous “single-site” catalysts for the polymerization of α -olefins.^{2,3} These metallocenes being activated with either methylalumoxane (MAO) or perfluorinated boron cocatalysts provide high activities, high stereoregularities, narrow polydispersities of the polymers, and control over the

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polymeric architecture.²⁻⁴ In addition, comonomer incorporation and long chain branching can be modulated to a significant extent by suitable adjustment of both catalyst and cocatalyst structures' design.⁵

In general, these catalytic systems, as represented by A, contain many required motifs for an active polymerization catalyst, including a suitable spectator ancillary ligation (L_n), an electron-deficient and coordinatively unsaturated metal center (M), an effective weakly coordinative counteranion/cocatalyst (X⁻), and the appropriate temperature, solvent, and pressure conditions.



The majority of the catalysts belong to groups 3 and 4 metallocene derivatives, although some are known to contain one cyclopentadienyl ring and one pendant ligand.⁶ The tacticity of the polymers varies predictably with the structure of the metallocenes. Hence, C₂- or C₁-symmetry complexes are expected to produce isotactic poly- α -olefins, whereas C_{2v} induces the formation of atactic polymers.⁷ Because in the polymerization of α -olefins the ligation around the metal center is crucial in determining the activity and stereospecificity of the catalysts, affecting both electronic and steric properties, a growing interest in the development of noncyclopentadienyl ligations has been stimulated.⁸

A tremendous effort has been made in designing new complexes with different ancillary ligations of the metals of groups 3–13 as suitable precursors for the polymerization of α -olefins.⁸ The wide variety of carbon-,⁹ oxygen-,¹⁰ and nitrogen-based ligands^{11,12} has been described. Most attention has been directed to chelating di(amido) ligands,¹³ some of whose group 4 transition metal complexes induce the living polymerization of α -olefins.¹⁴ Recently, chelating alkoxy,¹⁵ boratabenzene,¹⁶ chelating salicylaldiminato,^{15,17} acetylacetonate,¹⁸ phosphinoamines,¹⁹ and chelating amidinate²⁰ compounds have received attention as ancillary ligands in the synthesis of potential Ziegler–Natta catalysts.

Within the amidinate-based ligands, a variety of benzamidine group 4-containing complexes have been described. These

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systems are in principle devoted mainly to the use of N,N' -bis-(trimethylsilyl)benzamidinate ligation. The benzamidinate ligands can be considered as a steric equivalent of Cp or Cp* (Cp = C₅H₅; Cp* = C₅Me₅), although they are unique in their electronic properties.^{20,21} The anionic moiety [R-C(NSiMe₃)₂]⁻ is a four-electron donor, promoting a higher electrophilicity at the metal center, as compared to the six electrons of the cyclopentadienyl ligands. The possibility to simply modify both steric bulk and electronic properties of the benzamidinate-based ligands, through changes in either the organic substituents at the nitrogen atom and/or different functional groups at the aromatic ring, makes these ligands very attractive for synthesis of various organometallic complexes and their corresponding utilization as catalytic precursors in the polymerization of α -olefins.

Previously, others and we have investigated the polymerization of α -olefins catalyzed by several group 4 chelating benzamidinate complexes.²² The bis(benzamidinate) dichloride/dialkyl group 4 complexes are normally obtained as a mixture of racemic C₂-symmetry *cis*-octahedral structures, and, when activated with methylalumoxane (MAO), these complexes were found to be active catalytic precursors for the polymerization of ethylene, propylene, the oligomerization of 1,5-hexadiene, and the isomerization of internal and terminal olefins.^{7a,22} For propylene, performing the polymerization at atmospheric pressure produced polypropylene as an oil, despite the expected isotactic polymer.²³ These results raise conceptual questions regarding the applicability of *cis*-octahedral C₂-symmetry complexes to the stereospecific polymerization of α -olefins.

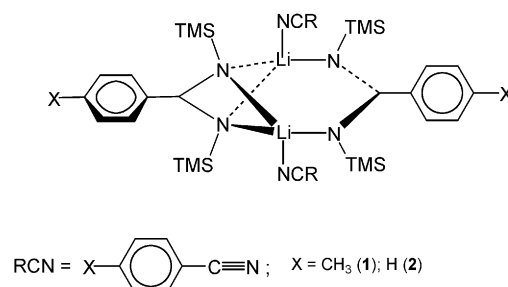
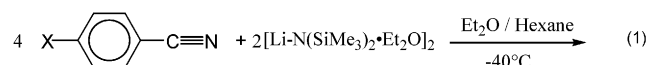
Here, we present the synthesis and structural X-ray diffraction studies on several group 4 benzamidinate complexes. We introduce the application of these complexes as new catalytic precursors for the highly stereoregular polymerization of propylene, which can be modulated by *pressure*. To our knowledge, this is the first example of stereoregular polymerization of α -olefins catalyzed by early-transition metal octahedral complexes, modulated by pressure (from atactic to isotactic through elastomers). We present a thorough study disclosing the different effects, such as pressure, temperature, and nature of solvents in the polymerization process and in the properties of the polymers

obtained. Moreover, we introduce a new type of elastomeric polypropylene that is facile to design and to tailor. The mechanism for the formation of the various types of polypropylene (atactic, isotactic, and elastomeric) at the different conditions is discussed.

Results and Discussion

The goal of this investigation was to examine the scope, relationship between symmetry of the complex and polymer microstructure, stereoregularity, metal sensitivity, monomer concentration, substituent effect at the ancillary ligation, temperature, solvent, cocatalyst, polymerization time, and to propose a plausible mechanism for the polymerization of propylene promoted by racemic mixtures of *cis*-octahedral complexes. This study represents an extension of the unique reactivities of this type of complex in the polymerization of propylene, when activated by either MAO or perfluoroaryl borane cocatalysts. In the following presentation of the results, we focus on the synthesis of the ligands and group 4 metal complexes, and on the different parameters affecting the polymerization of propylene toward the formation of either atactic, isotactic, or elastomeric polymers. We report the X-ray single-crystal diffraction studies for the benzamidinate ligands and the corresponding group 4 complexes. In addition, we present evidence, through the isomerization of alkenes, for the epimerization of the last inserted monomer as the major mechanistic pathway, responsible for the formation of polypropylene with elastomeric properties. We start the presentation of the results with various synthetic pathways of different ancillary benzamidinate ligations followed by the synthesis and characterization of the corresponding group 4 complexes.

Synthesis of Benzamidinate Ligands. The preparation of the lithium benzamidinate was carried out through the reaction between benzonitrile (or *p*-tolunitrile) and the lithium salt LiN(SiMe₃)₂.²⁴

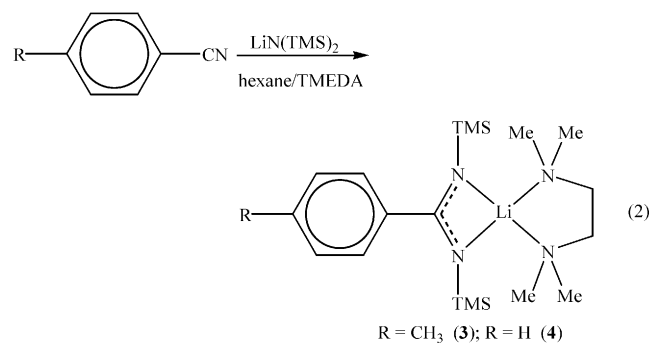


In the absence of a strong coordinating polar solvent, the dimeric structures **1** or **2** are the major products obtained (eq 1), in addition to some trimeric species, although when the reaction is carried out in the presence of TMEDA (tetramethylethylenediamine), as the coordinated solvent, the monomeric

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complexes $[\text{R-PhC}(\text{NSiMe}_3)_2\text{Li}(\text{TMEDA})]$ ($\text{R} = \text{CH}_3$ (**3**); H (**4**)) are obtained as the sole products (eq 2).



The low-temperature X-ray analysis of **2** (Figure 1, Tables 1 and 10) shows a dimeric benzamidinate structure with two distorted-tetrahedral lithium cations. Each lithium atom is π -bonded by one bidentate benzamidinate moiety, σ -bonded to the second benzamidinate nitrogen atom, and σ -bonded to a nitrogen of a benzonitrile molecule. The core units are comprised by a four-membered ring Li-N-C-N and a six-membered ring Li-N-C-N-Li-N . The planes formed by the two η^3 -diazallyl motifs make a dihedral angle of almost 90° , forming a distorted C_{2v} -symmetry complex. The four C–N bond lengths in both amidinates are close to the average of the C=N [1.30 Å] and C–N [1.36 Å] bond lengths, as compared to similar protonated N-substituted phenyl ligands.²⁵ This result suggests that the anion in complex **2** is best described as a system containing two diazaallyl moieties, one of which acts as a double bridge of two lithium atoms.

The molecular structure of complex **4** (Figure 2, Tables 2, 10) shows a slightly distorted tetrahedral monomeric lithium atom (angle between the two planes containing the metal = 93.3 (4) $^\circ$) attached in an almost symmetrical mode to both amidine and TMEDA moieties [$\text{Li-N}(5) = 2.033$ (6), $\text{Li-N}(13) = 2.019$ (6), $\text{Li-N}(18) = 2.120$ (6), $\text{Li-N}(23) = 2.116$ (7) Å]. The similar electronic delocalization throughout the amidine moiety is observed by the similar C–N distances [$\text{N}(5)\text{--C}(6) = 1.331$ (4), $\text{C}(6)\text{--N}(13) = 1.325$ (4) Å]. Interestingly, there is almost no electronic interaction between the aromatic phenyl ring and the diazaallyl section as exhibited by the torsional angle (94.2°).

Synthesis of Zr and Ti Bis(benzamidinate) Complexes. The reaction of MCl_4 ($\text{M} = \text{Zr}, \text{Ti}$) with 2 equiv of the appropriate ligands **3** and **4** takes place at room temperature in toluene to give pale yellow (Zr) and brown-red (Ti) solutions, from which analytically pure compounds **5–8** were isolated. For the zirconium complexes, high yields (88–89%) are achieved, whereas for the corresponding titanium complexes, lower yields are obtained (60–70%). The solid X-ray characterization of complexes **7**^{21b,22d,i} and **8**²⁶ has been already reported. It is noteworthy that complexes **7** and **8** can be also attained by the reaction of the MCl_4 ($\text{M} = \text{Zr}, \text{Ti}$) and 1 equiv of the corresponding benzamidinate lithium dimer **2**, whereas com-

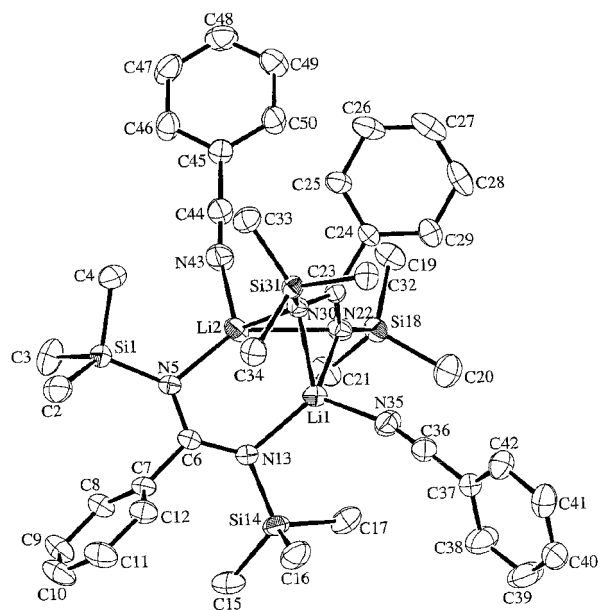


Figure 1. ORTEP diagram (50% probability ellipsoid) of complex **2**.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complex **2**

Li(1)–N(13)	2.055(4)
Li(1)–N(35)	2.086(4)
Li(1)–N(22)	2.104(4)
Li(1)–N(30)	2.126(4)
Li(1)–C(23)	2.392(4)
Li(1)–Li(2)	2.465(5)
Li(2)–N(5)	1.995(4)
Li(2)–N(30)	2.069(4)
Li(2)–N(43)	2.088(4)
Li(2)–N(22)	2.364(4)
Li(2)–C(23)	2.408(4)
N(13)–Li(1)–N(35)	118.53(18)
N(13)–Li(1)–N(22)	122.39(19)
N(35)–Li(1)–N(22)	111.28(18)
N(13)–Li(1)–N(30)	121.56(18)
N(35)–Li(1)–N(30)	106.25(17)
N(22)–Li(1)–N(30)	64.88(11)
N(5)–Li(2)–N(30)	116.67(18)
N(5)–Li(2)–N(43)	120.7(2)
N(30)–Li(2)–N(43)	110.84(17)
N(5)–Li(2)–N(22)	140.8(2)
N(30)–Li(2)–N(22)	61.16(11)
N(43)–Li(2)–N(22)	92.61(15)

plexes **5** and **6** can be prepared in lower yields, when they are formed using the corresponding dimer **1**. Alkylation of complexes **5–8** with 2 equiv of $\text{MeLi}\cdot\text{LiBr}$ in ether yields yellow dimethyl complexes of zirconium (**9** and **11**) or wine-red dimethyl complexes of titanium (**10** and **12**) in quantitative yields (98–99%) (eq 3).

The crystalline structures of complexes **11**^{21b,22d} and **12**²⁷ have been reported in the literature. The crystallographic data for complexes **9** and **10** are given in Table 10. Selected bond lengths and angles are listed in Tables 3 and 4, and their molecular structures are shown in Figures 3 and 4, respectively. The low-temperature X-ray analysis of complex **9** shows that the central Zr atom is octahedral-bonded to two benzamidinate ligands and two terminal methyl groups. The octahedral complex is formed

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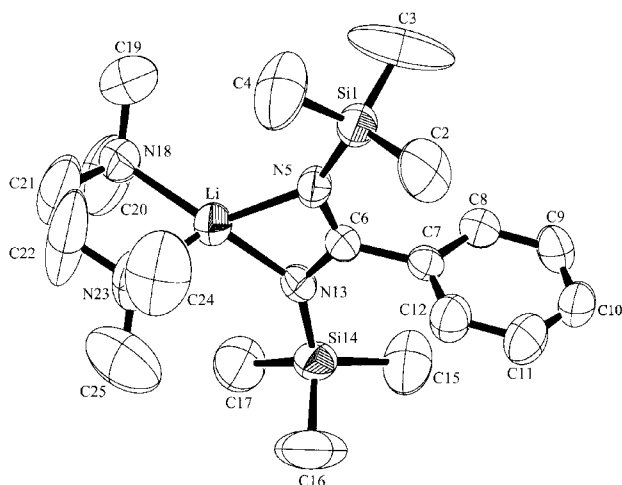
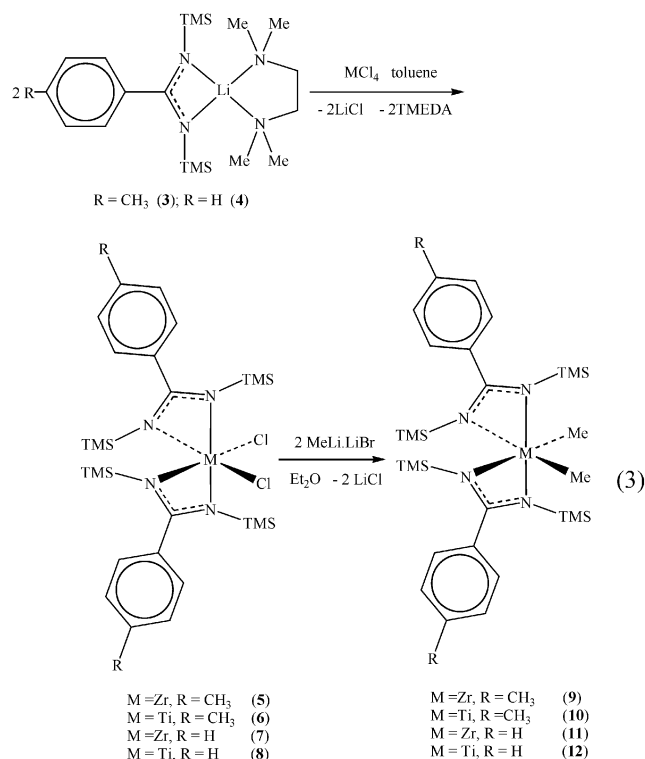


Figure 2. ORTEP diagram (50% probability ellipsoid) of complex 4.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complex 4

Li–N(13)	2.019(6)
Li–N(5)	2.033(6)
Li–N(23)	2.116(7)
Li–N(18)	2.120(6)
N(5)–C(6)	1.331(5)
C(6)–N(13)	1.325(4)
N(13)–Li–N(5)	69.14(19)
N(13)–Li–N(23)	119.6(3)
N(5)–Li–N(23)	122.5(3)
N(13)–Li–N(18)	136.1(3)
N(5)–Li–N(18)	128.6(3)
N(23)–Li–N(18)	86.4(2)

in such a way that one carbon atom from the methyl groups (C(1)) and one nitrogen atom from the chelating benzamidinate



unit (N(4)) are in the axial positions, similarly as in complex 10, producing a C₂-symmetric complex. The two four-membered

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Complex 9

Zr(1)–N(1)	2.227(4)
Zr(1)–C(1)	2.246(5)
Zr(1)–N(4)	2.295(4)
Zr(1)–C(11)	2.672(5)
Zr(1)–N(3)	2.234(4)
Zr(1)–C(2)	2.248(6)
Zr(1)–N(2)	2.320(4)
Zr(1)–C(3)	2.578(5)
N(1)–Zr(1)–N(3)	91.1(2)
N(1)–Zr(1)–N(4)	122.3(2)
N(1)–Zr(1)–N(2)	59.34(14)
N(4)–Zr(1)–N(2)	172.23(14)
N(3)–Zr(1)–C(1)	97.4(3)
N(1)–Zr(1)–C(1)	144.5(2)
N(1)–Zr(1)–C(2)	91.3(2)
N(3)–Zr(1)–C(2)	143.2(2)
C(1)–Zr(1)–N(4)	143.2(2)
C(1)–Zr(1)–C(2)	101.8(3)
N(3)–Zr(1)–N(4)	59.3(2)
C(2)–Zr(1)–N(4)	89.0(2)
N(3)–Zr(1)–N(2)	113.93(14)
C(2)–Zr(1)–N(2)	98.7(2)

Table 4. Selected Bond Lengths [Å] and Angles [deg] for Complex 10

Ti–N(14)	2.124(2)
Ti–C(19)	2.120(4)
Ti–N(5)	2.137(2)
Ti–C(6)	2.515(3)
N(5)–C(6)	1.321(3)
C(6)–N(14)	1.321(3)
N(14)–Ti–N(14)#1	94.88(12)
N(14)–Ti–C(19)#1	91.75(17)
N(14)–Ti–C(19)	153.16(13)
C(19)#1–Ti–C(19)	94.0(3)
N(14)–Ti–N(5)#1	108.32(8)
N(14)#1–Ti–N(5)#1	63.17(8)
C(19)#1–Ti–N(5)#1	90.06(12)
C(19)–Ti–N(5)#1	97.89(13)
N(14)–Ti–N(5)	63.17(8)
N(5)#1–Ti–N(5)	168.37(12)

rings ZrCN₂ are almost symmetric: the C–N and Zr–N bond lengths are respectively equal (N(2)–C(11) = 1.345 (6), N(1)–C(11) = 1.325 (6), N(3)–C(3) = 1.336 (6), N(4)–C(3) = 1.322 (6), Zr–N(1) = 2.227 (4), Zr–N(2) = 2.320 (4), Zr–N(3) = 2.234 (4), Zr–N(4) = 2.295 (4) Å). By comparison to other benzamidinate complexes, the Zr–N(1) to Zr–N(4) distances are somewhat longer than those in the dimeric compound [C₆H₅C(NSiMe₃)₂ZrCl₃]₂ (2.14 and 2.19 Å),²⁸ while they are similar to those in the monomeric complexes [C₆H₅C(NSiMe₃)₂–ZrCl₂] (2.20 and 2.24 Å)^{21b,22d,i} and [C₆H₅C(NSiMe₃)₂–ZrMe₂] (2.24 and 2.31 Å).^{21b,22d} The benzamidinate moieties are located almost in one plane with the ZrCN₂ units, with the corresponding angles Zr–C(3)–C(4) and Zr–C(11)–C(12) of 168.7 (3) and 170.6 (4)°, respectively.

The X-ray study of the dimethyl titanium bis(benzamidinate) complex (10) shows that the Ti atom is octahedrally distorted surrounded by two chelating benzamidinate ligands and two terminal methyl groups. The methyl carbon atom (C(19)) and the nitrogen atom (N(14)) are in the axial positions [C(19)–Ti–N(14) = 153.16 (13)°], while the second methyl group and the remaining nitrogen atoms occupy the equatorial position [C(19)–Ti–N(14)# = 91.75 (17), C(19)–Ti–N(5) = 90.06

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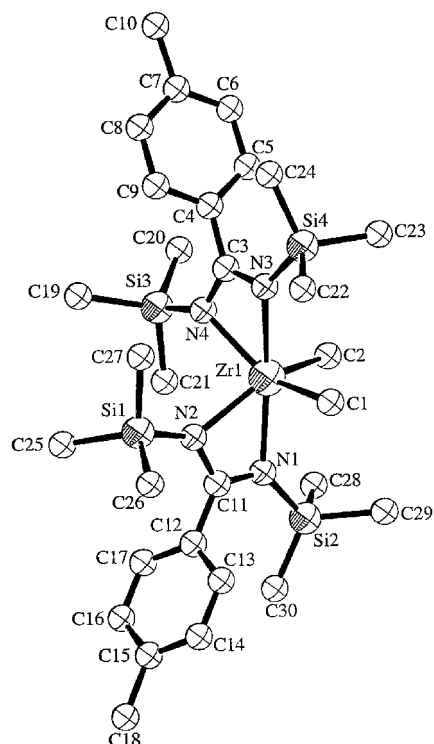


Figure 3. ORTEP diagram (50% probability ellipsoid) of complex **9**.

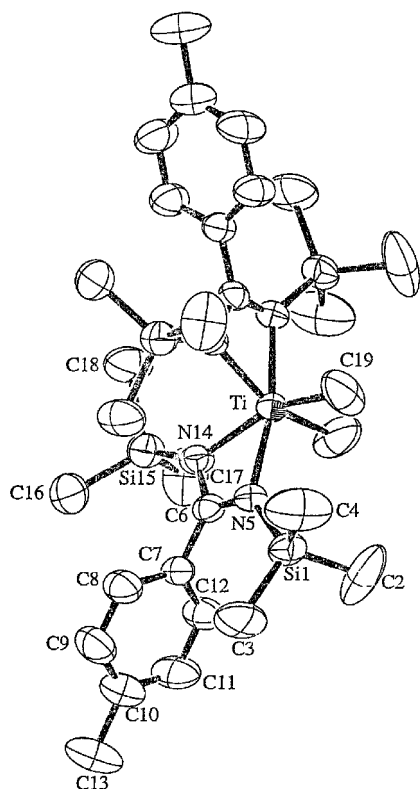


Figure 4. ORTEP diagram (50% probability ellipsoid) of complex **10**.

(12), $N(5)-Ti-N(14) = 63.17(8)^\circ$]. As a result, the C–N bond lengths of the two chelate units are equidistant (C–N = 1.321 (3) Å), similar to those in the corresponding unsubstituted benzamidinate complex.^{21b}

During the selection of the best crystal of complex **10** for the X-ray analysis, solitary crystals with a more pronounced

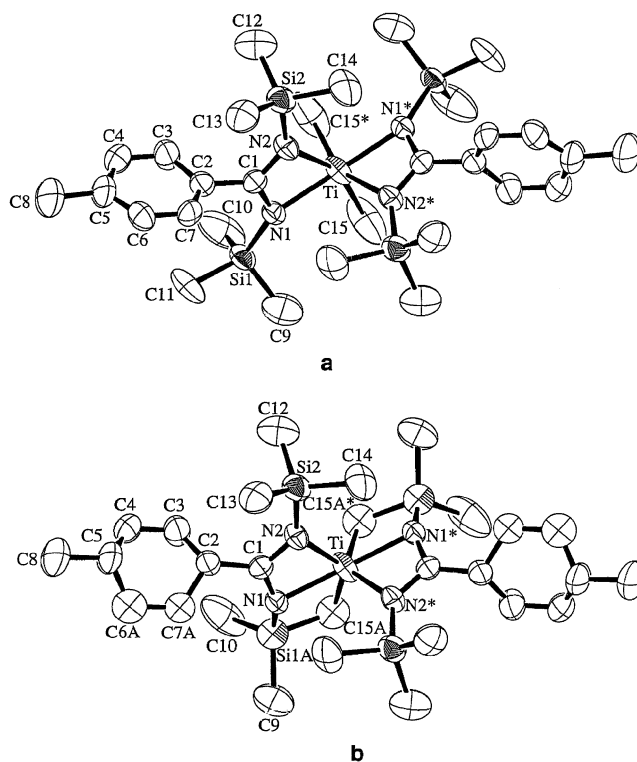


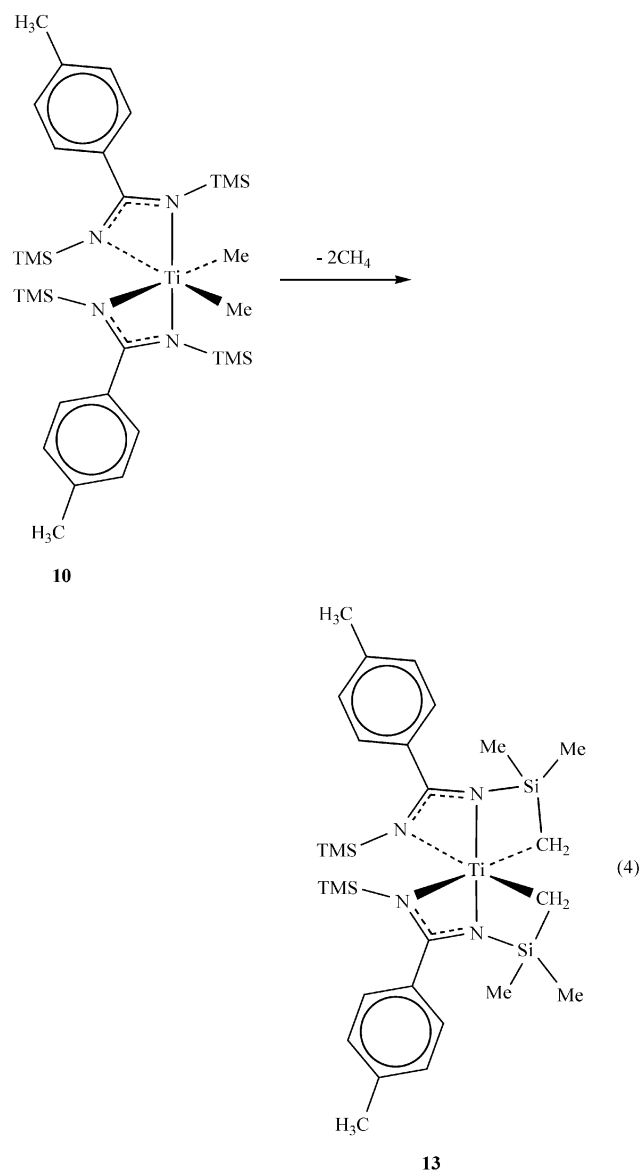
Figure 5. ORTEP diagram (50% probability ellipsoid) of complexes **10*** (a) and **13** (b).

Table 5. Selected Bond Lengths [Å] and Angles [deg] for Complexes **10*/13**

Ti–N(1)	2.106(4)
Ti–N(2)	2.117(5)
Ti–C(15)	2.139(11)
Ti–C(15A)	2.150(4)
N(1)#1–Ti–N(1)	167.3(2)
N(1)#1–Ti–N(2)	107.35(17)
N(1)–Ti–N(2)	63.50(16)
N(2)–Ti–N(2)#1	96.2(2)
N(1)–Ti–C(15)#1	98.5(3)
N(2)–Ti–C(15)#1	88.9(6)
N(1)–Ti–C(15)	89.8(3)
N(2)–Ti–C(15)	153.2(3)
C(15)#1–Ti–C(15)	98.3(12)
N(1)–Ti–C(15A)#1	120.3(10)
N(1)–Ti–C(15A)	70.8(10)
N(2)–Ti–C(15A)	131.1(10)
N(2)#1–Ti–C(15A)	113.5(10)
C(15A)#1–Ti–C(15A)	75(2)

reddish color were observed. The X-ray analysis of this latter complex “**10***” (Figure 5a) gave almost the same crystal data (unit cell parameters, Table 10) as compared to those of **10**, but with different bond lengths and angles, due to the partial (22%) cocrystallization of the additional complex **13** (Table 5). Complex **13** is formed by the elimination of two methane molecules, which are produced from the symmetric C–H activation of the methyl group in the TMS moieties with the metal–methyl bonds (eq 4) (Figure 5b). The C–H activation of the TMS groups in complex **13** induces the elongation of the Ti–C bond length [Ti–C(15A) = 2.15 (4) Å] and the shortening of the Si–N bond length [Si(1A)–N(1) = 1.562 (10) Å], as compared to the corresponding bond distances in complex **10** [Ti–C(19) = 2.120 (4), Si(1)–N(5) = 1.750 (2) Å]. The

activation of C–H moieties in titanium alkyl complexes containing TMS-amido groups has been reported in the literature.²⁹



Synthesis of Hf Bis(benzamidinate) Complex. An attempt to achieve the corresponding hafnium bis(benzamidinate) dichloride complex was intended following a similar protocol, as described for the other lighter isolobal group 4 elements (eq 3), between the lithium salt of the ligand and $\text{HfCl}_4 \cdot 2\text{THF}$, resulting in an oily yellow mixture of products containing TMEDA. Dissolving the oily compound in toluene and removing under vacuum all of the liquids afford the production of a glassy yellow solid. The ^1H and ^{13}C NMR of this solid indicate the formation of the expected complex $[(4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2)_2\text{-HfCl}_2]$ (**14**). Elemental analysis shows that complex **14** contains additional products. Dissolving the mixture in a minimum amount of toluene followed by the vacuum transfer of large amounts of hexane affords the precipitation of a yellow powder

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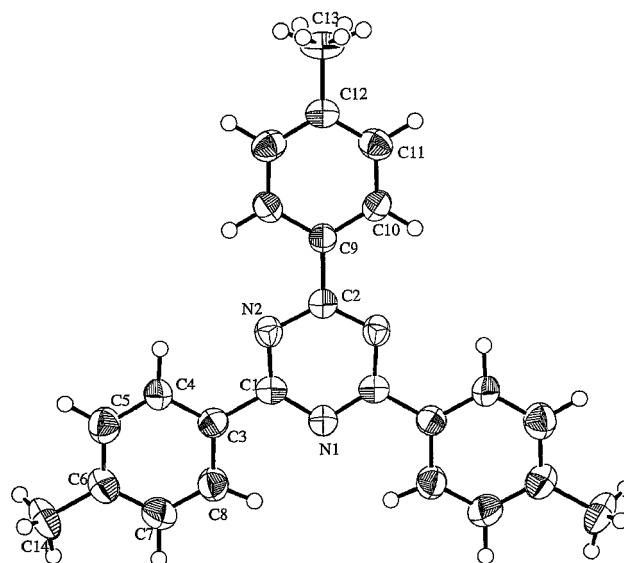


Figure 6. ORTEP diagram (50% probability ellipsoid) of triazine **15**.

Table 6. Selected Bond Lengths [Å] and Angles [deg] for Complex **15**

N(1)–C(1)	1.336(5)
N(2)–C(1)	1.333(5)
N(2)–C(2)	1.344(4)
C(1)–C(3)	1.469(6)
C(2)–C(9)	1.479(8)
C(1)–N(1)–C(1)#1	116.6(6)
C(1)–N(2)–C(2)	115.4(5)
N(2)–C(1)–N(1)	123.9(5)
N(2)–C(1)–C(3)	117.7(4)
N(1)–C(1)–C(3)	118.4(4)
N(2)–C(2)–N(2)#1	124.7(6)

material that was found to be silent in ^1H NMR. This powder is paramagnetic, exhibiting, at room temperature, an ESR signal (X-band) centered at 3360 G and $\Delta H = 12$ G, with a g value of 2.0017 characteristic for a Hf(III) complex.³⁰ One of the most intriguing questions in the formation of the Hf(III) complex is the elucidation of the reducing agent entity. From the diethyl ether washing solutions of the powder material, we were able to crystallize the organic compound tris-*p*-tolyl-1,3,5-triazine (**15**), the product of the trimerization of *p*-tolunitrile. The formation of this triazine indicates that Hf(III) induces the reverse reaction as indicated in eq 2, yielding *p*-tolunitrile and the lithium salt $\text{LiN}(\text{TMS})_2$. The former compound trimerizes to tris-*p*-tolyl-1,3,5-triazine. The Hf(III) presumably is obtained by the reduction of $\text{HfCl}_4 \cdot 2\text{THF}$ with $[4\text{-CH}_3\text{-PhC}(\text{NSiMe}_3)_2\text{-Li}(\text{TMEDA})]$, as observed for similar Ti and Zr complexes.³¹ Interestingly, from the low-temperature X-ray analysis (Figure 6, Table 6), the triazine was found to be a polymorphic compound of the recent structure published in the literature.³² The difference between the two crystalline materials resides in the packing disposition of the molecules between the main plain of the triazine ring with respect to the $\mathbf{a0b}$ plane. X-ray cell parameters and refinement data are presented in Table 10.

(30) Fakhr, A.; Mugnier, Y.; Gautheron, B.; Laviron, E. *J. Organomet. Chem.* **1986**, 302, C7 and references therein.

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(32) Thalladi, V. R.; Muthuraman, M.; Nagia, A.; Desiraju, G. R. *Acta Crystallogr.* **1999**, C55, 698.

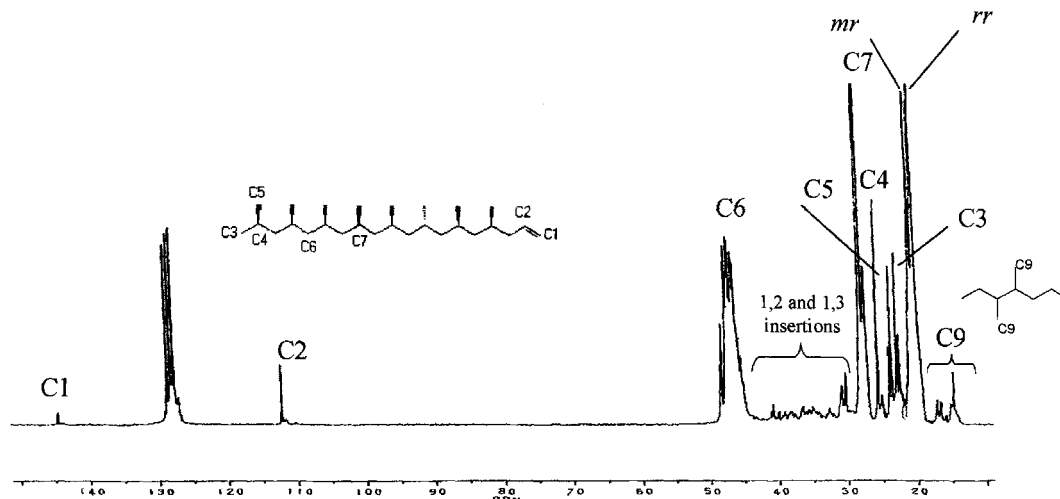


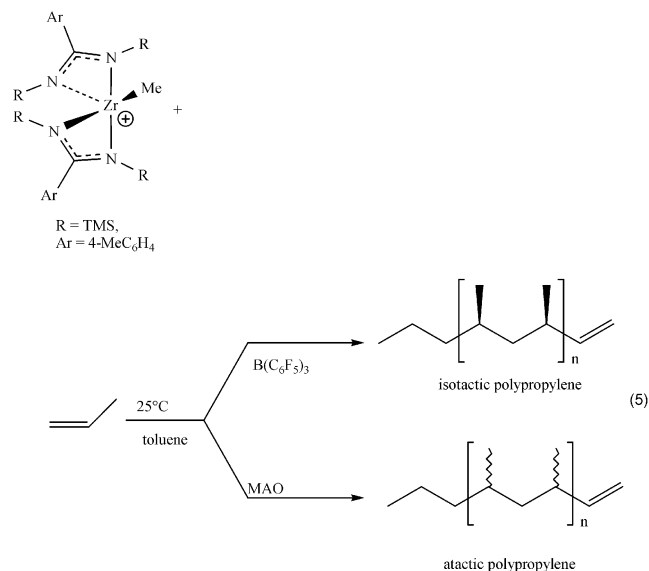
Figure 7. ^{13}C NMR of the polypropylene obtained catalyzed by complex **9** at room temperature.

Catalytic Polymerization Studies. Polymerization reactions were performed with the dimethyl complexes **9–12** activated by MAO or $\text{B}(\text{C}_6\text{F}_5)_3$. Because of the large differences in polymer properties obtained with these complexes at the various reaction conditions, the polymerization results are presented separately for complexes **9–12**.

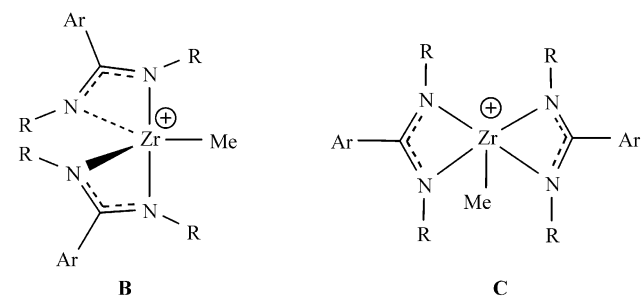
Polymerization of Propylene at Atmospheric Pressure Catalyzed with Complex **9.** This complex was found to be a good precursor for the polymerization of propylene at atmospheric pressure at 25 °C. When activated with MAO (Al:Zr molar ratio 250:1) in toluene, complex **9** produces large amounts (8.1×10^5 gPP/mol Zr·h) of an oily polymer with medium molecular weight $M_w = 38\,000$, resembling an atactic polypropylene. ^{13}C NMR triad and pentad analysis of this polymer shows that, contrary to the 10 expected signals for the methyl groups of an atactic polypropylene, only two major signals are observed in the region between 19.5 and 21.9 ppm (Figure 7).³³ A very similar spectrum has been recently observed in the characterization of polypropylene polymerized by α -diimine nickel complexes.³⁴ The two major signals belong to the corresponding mr and rr tryads. A very elegant analysis of similar type of polymers has been recently published.³⁴ The small signals in the region of 15 to 19 ppm and the signals between 29 and 41 ppm corroborate the presence of 2,1 and 1,3 misinsertions. Moreover, it is possible to conclude that β -Me elimination is the major termination mechanism, as represented by the signals observed at 146 and 113 ppm, the signals between 22 and 26 ppm for the vinylic CH (C1), CH_2 (C2), and the terminal carbons of the isobutylene unit (C3, C4, and C5) in Figure 7, respectively.³³

When precursor **9** was activated with $\text{B}(\text{C}_6\text{F}_5)_3$ (molar ratio B:Zr = 1), under the same reaction conditions as with MAO, a highly *isotactic* polypropylene was obtained (mmmm = 98%), contrary to the results obtained with MAO (eq 5). The activity of this catalytic system (1.2×10^5 gPP/mol Zr·h) is somewhat lower than the activity of complex **9** activated with MAO. It is important to point out that complex **9** has a C_2 -symmetry

octahedral geometry, suggesting that, when activated by MAO, theoretically an isotactic polymer, as obtained with $\text{B}(\text{C}_6\text{F}_5)_3$, should also be expected.³⁵



The “atactic polymer”, obtained with MAO, can be rationalized by two plausible mechanisms besides the 2,1 insertions: (1) formation of a “cationic” five-coordinated trigonal bipyramidal complex (**B**) or a square planar pyramidal intermediate (**C**), as a new active complex, with almost no stereodifferentiation at the propylene insertion, and (2) an intramolecular epimerization reaction of the growing polypropylene chain at the last-inserted monomeric unit (Scheme 1).^{36,37}



(33) Resconi, L.; Piemontesi, F.; Franciscano, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.

(34) McCord, E. F.; McLain, S. J.; Nelson, L. T. J.; Arthur, S. D.; Coughlin, E. B.; Ittel, S. D.; Johnson, I. K.; Tempel, D.; Killian, C. M.; Brookhart, M. *Macromolecules* **2001**, *34*, 362.

Scheme 1. Proposed Mechanism for the Intramolecular Epimerization of the Growing Polypropylene Chain at the Last-Inserted Monomeric Unit

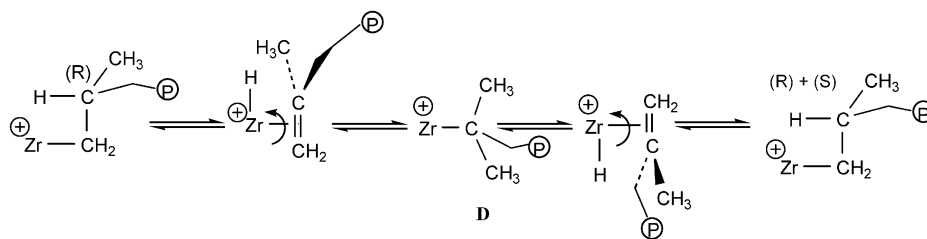


Table 7. Data for the Polymerization of Propylene Promoted by Complex **9** Using Different Solvents, Temperature, and MAO Amounts

entry	solvent	Al:Zr	T °C	P atm	activity ^a A × 10 ⁻⁵	Mn	Mw	MWD	mmmm ^c %	Mp °C
1	toluene	250	25	9.2	1.1 ^b	261 000	440 000	1.69	86 ^d	142
2	CH ₂ Cl ₂	250	25	9.2	2.2	36 000	86 000	2.35	11	oil
3	CH ₂ Cl ₂	400	25	9.2	7.5	10 750	26 750	2.49	90	146
4	CH ₂ Cl ₂	1000	25	9.2	7.9	23 500	42 470	1.81	96	147
5	CH ₂ Cl ₂	1000	25	9.2	7.9	58 100	82 600	1.42	98	149
6	CH ₂ Cl ₂	250	0	5.1	0.5	10 200	18 900	1.85	86	138
7	CH ₂ Cl ₂	250	25	9.2	2.2	10 700	26 700	2.49	90	146
8	CH ₂ Cl ₂	250	50	17.0	26.6	149 700	271 000	1.81	96	152
8	toluene	B(C ₆ F ₅) ₃	25	9.2	2.8 ^e	26 000	51 300	1.96	98	154
						3000	9300	3.10	7	oil

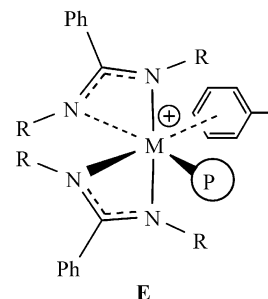
^a gr PP/mol Zr·h. ^b Mixture of isotactic (50%) and atactic (50%) fractions of polypropylene. ^c Measured by ¹³C NMR. ^d Isotacticity of the isotactic fraction. ^e 70% atactic and 30% isotactic.

The elucidation of which of the two plausible mechanisms is responsible for the production of an “atactic polypropylene” was achieved by performing the reactions under pressure (liquid propylene). For the first mechanism, none or small changes in the stereoregularity of the polymer will be predicted, whereas for the second mechanism, a highly isotactic polymer will be expected.

High-Pressure Polymerization of Propylene Catalyzed by Complex **9.** When the reaction catalyzed by **9** activated with MAO is carried out at high pressure, a highly stereoregular polymer is formed. A summary of the polymerization results is presented in Table 7. To acquire the best experimental conditions, we have started the polymerizations by studying the effect of the solvent. By performing the polymerization in dichloromethane, larger activities, stereoregularities, and melting points of the polymers were observed, as compared to the results exhibited in toluene (entries 1 and 2). This increase in activity is plausible as a consequence of the polarity of the CH₂Cl₂, causing a greater charge separation between the cationic benzamidinate alkyl complex and the MAO anion, encouraging the insertion of the monomer, as compared to toluene.

For toluene, a putative π -bond of the ring to the cationic center of complex (**E**) possibly takes place forming a cationic η^6 -toluene compound.³⁸ This intermediate inhibits the insertion

of the monomer and the termination of the polymer chain, allowing larger molecular weights and narrower molecular weight distributions, as compared to the polymers obtained in CH₂Cl₂.



The polymerization of propylene under higher pressure in CH₂Cl₂ yields an isotactic polypropylene with small amounts of stereodefects, while in toluene a mixture of isotactic and atactic products was obtained. The formation of two different polypropylene fractions in toluene can testify about the presence of two different active catalytic species. The nature of the intermediate responsible for the formation of the atactic fraction has not been fully elucidated yet. On the basis of NMR experiments, it seems that, in toluene, one of the benzamidinate ligations opens to a η^1 coordination, and the solvent occupies the vacant site. Interestingly, similar heteroallylic ligations (alkoxysilyl-imido) have exhibited dynamic behaviors.³⁹

Up to a molar ratio of Al:Zr = 400, the activity of the catalytic complex enhances with an increase in the MAO amount (entries

- (35) Recently a C₂-symmetry titanium complex has been shown to be active for the polymerization of propylene forming highly syndiotactic polymer that is formed through the chain-end mechanism. See ref 17a,b.
 (36) (a) Busico, V.; Cipullo, R.; Caporaso, P.; Angeloni, G.; Segre, A. L. *J. Mol. Catal. A: Chem.* **1998**, *128*, 53. (b) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M. *Macromolecules* **1997**, *30*, 6251. (c) Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971. (d) Busico, V.; Caporaso, L.; Cipullo, R.; Landriani, L.; Angelini, G.; Margonelli, A.; Segre, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 2105. (e) Leclerc, M.; Brinzing, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024 and references therein. (f) Busico, V.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. *Macromolecules* **1995**, *28*, 1887. (g) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329.
 (37) The additional “allylic mechanism” for the epimerization has been proposed, see: Resconi, L. *J. Mol. Catal.* **1999**, *146*, 167. This mechanism was found to be not a major pathway due to the lack of internal vinylidene and isobutenyl groups.

- (38) (a) Lancaster, S. J.; Robinson, O. B.; Bochmann, M.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **1995**, *14*, 2456. (b) Gillis, D. J.; Tudoret, M. J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543. (c) Eisen, M. S.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10358. (d) Eisen, M. S.; Marks, T. J. *Organometallics* **1992**, *11*, 3939. (e) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1747.
 (39) (a) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506. (b) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511.

Table 8. Data for the Polymerization of Propylene Promoted by Complex **10** with MAO

entry	solvent	Al:Ti ^a	T °C	P atm	activity ^b A × 10 ⁻⁵	Mn	Mw	MWD	mmmm %	type of polymer
1	CH ₂ Cl ₂	1000	25	1.0	0.0					
2	CH ₂ Cl ₂	1000	25	9.2	1.9	55 400	113 800	1.51	18	elastomer
3	toluene	1000	25	1.0	0.0					
4	toluene	1000	25	9.2	1.9	51 300	93 700	1.83	21	elastomer
5	CH ₂ Cl ₂	1000	-25	1.5	0.6				26	solid ^c
6	CH ₂ Cl ₂	1000	-10	3.0	0.3	102 700	163 000	1.57	23	elastomer
7	CH ₂ Cl ₂	1000	0	4.5	0.6	79 700	138 100	1.73	22	elastomer
8	CH ₂ Cl ₂	1000	10	7.0	1.0	68 900	117 600	1.71	22	elastomer
9	CH ₂ Cl ₂	1000	50	17.0	1.7	46 700	82 300	1.76	18	oil
10	CH ₂ Cl ₂	300	25	9.2	0.4	57 400	89 700	1.56	20	elastomer
11	CH ₂ Cl ₂	300 ^d	25	9.2	0.4	48 400	74 300	1.53	19	elastomer
12	CH ₂ Cl ₂	300 ^e	25	9.2	0.4	55 400	86 500	1.56	20	elastomer
13	CH ₂ Cl ₂	300 ^f	25	9.2	0.2	47 700	81 300	1.71	22	elastomer
14	CH ₂ Cl ₂	500	25	9.2	0.3	43 300	114 300	2.64	21	elastomer
15	CH ₂ Cl ₂	2000	25	9.2	2.6	59 800	116 700	1.95	13	elastomer
16	CH ₂ Cl ₂	3000	25	9.2	3.9	67 900	115 500	1.70	14	elastomer

^a Moles of catalyst = 7.8×10^{-6} . ^b gr PP/mol Ti · h. ^c Solid with no elastomeric properties and low solubility in hot trichlorobenzene although enough to measure mmmm content. ^d 15.6×10^{-6} mol of catalyst. ^e 31.2×10^{-6} mol of catalyst. ^f 46.8×10^{-6} mol of catalyst.

2–4). Further augmentation of MAO concentration does not influence the polymerization rate, but rather the properties of the polypropylene. Likewise, by raising the Al:Zr ratio, the melting points, molecular weights, and isotacticities of the polymers increase with a concomitant reduction in the molecular weight distribution (MWD). By performing the reaction at elevated temperatures, higher activities, stereoregularities, and molecular weights of polypropylene are achieved (entries 5, 6, and 7). These results suggest that an increase of the temperature induces faster insertion rates as compared to the rate of the epimerization, resulting in higher isotacticities.

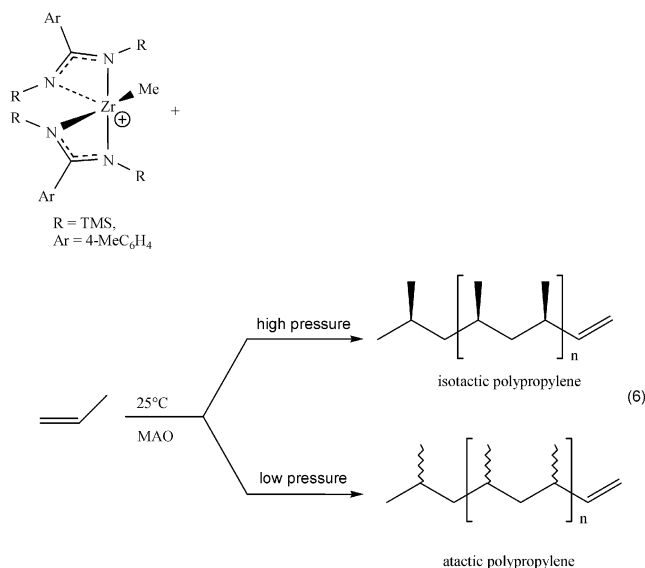
Worthy of note is that in the polymerization of propylene, performed by complex **9** activated with B(C₆F₅)₃, in toluene (entry 8), two polymeric fractions (70% atactic and 30% highly isotactic) are attained as is observed with the MAO. In CH₂-Cl₂, no polymerization is observed.

Comparing the stereoregularities of the polymers obtained at atmospheric or at high pressure, when complex **9** was activated by MAO or B(C₆F₅)₃, it is remarkably the substantial effect of the counterion. When B(C₆F₅)₃ is used at atmospheric pressure in toluene, a highly isotactic polymer is obtained, while two polymer fractions are accountable at higher monomer concentrations. The opposite effect is observed for MAO allowing large isotacticities at high pressures, but only in dichloromethane. Therefore, the stereoregularity of polypropylene promoted by the system “**9** + MAO” can be tailored as presented in eq 6.

It is important to point out that ¹³C NMR analysis of the chain ends of the polymers, obtained at high monomer concentration, also shows that the β-methyl elimination is the exclusive termination chain mechanism for these catalytic systems.

Statistically, we can deduce that at atmospheric pressure, the epimerization is observed every small number of insertions, forming a -mmrrmmrrmmrrmmrr- microstructure responsible for the two major signals with similar integration, and the almost absent signal for the mmmr pentad, as presented in Figure 7. The lack of 2,1 and 1,3 misinsertion signals in the ¹³C NMR for the polymers obtained at high pressures indicates the rapidity of the 1,2 insertion, as compared to the misinsertions.

A further endorsement that the mechanism presented in Scheme 1 is responsible for the epimerization of the last inserted unit was obtained by reacting complex **9** with MAO and



1-octene.^{23,40} Because the polymerization of 1-octene is extremely slow, it will be expected that if the epimerization is an operative pathway, a β-hydrogen elimination can take place from either the two methyl groups or the methylene group attached to the polymer chain (**D** in Scheme 1). In the first route, no changes in the alkene are expected, but in the second pathway, an isomerization of the double bond will be observed. The fact that 1-octene was isomerized to a mixture of octenes displays strong evidence for the formation of the intermediate complex **D** in Scheme 1.

Polymerization of Propylene Promoted by the Titanium Benzamidinate Complex 10. When the polymerization of propylene is performed using the titanium complex **10**, in most cases, an elastomeric polypropylene is formed with properties depending on the polymerization conditions. Results for the polymerization of propylene catalyzed by complex **10** activated with MAO are presented in Table 8.

Table 8 shows that, contrary to complex **9**, complex **10** is not active in the polymerization of propylene at atmospheric pressure either in CH₂Cl₂ or in toluene (entries 1 and 3). The solvent–metal interaction seems to be much stronger in titanium

(40) Averbuj, C.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 8755.

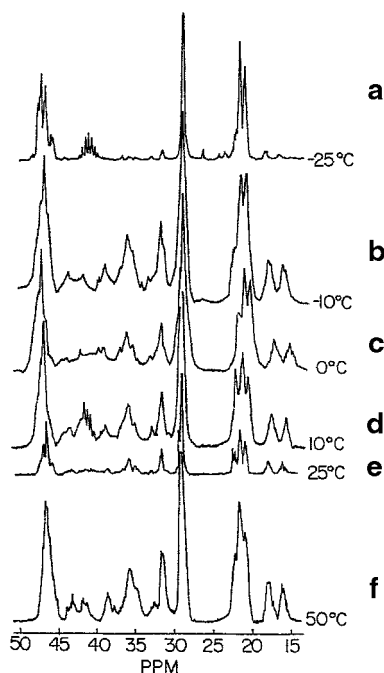


Figure 8. ^{13}C NMR spectra of polypropylene obtained at different temperatures by complex **10** activated with MAO. The temperature of the polymerization is indicated at each spectrum.

than in zirconium because of the effective charge at the metal center, indicating that at low pressure for **10** both solvents inhibit almost completely the monomer insertion. At high monomer concentration, **10** activated by MAO is an active precursor in both solvents (entries 2 and 4). At $-25\text{ }^\circ\text{C}$, a solid polypropylene is formed. This polymer contains almost no 2,1 or 1,3 misinsertions (Figure 8a) and is almost immiscible in hot trichlorobenzene. The steady augmentation of the temperature up to $25\text{ }^\circ\text{C}$ leads to a continuous increase of the polymerization rate, an increase in the number of the 2,1 and 1,3 misinsertions, and a decrease in the polymer molecular weight (entries 5–8 and Figure 8b–e), with no major change in the mmmm content. In this range of temperatures (-10 – $25\text{ }^\circ\text{C}$), elastomeric polymers are formed.⁴¹ At $50\text{ }^\circ\text{C}$, a small change in the activity is observed, while the molecular weight of the polymer continues to decrease producing a viscous oil (entry 9) (Figure 8f).

(41) For elastomeric polymerization using metallocenes, see: (a) Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 380 and references therein. (b) Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A: Chem.* **1998**, *136*, 23 and references therein. (c) Maciejewski Petoff, J. L.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316 and references therein. (d) Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. I. *J. Am. Chem. Soc.* **1998**, *120*, 2039. (e) Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908. (f) Carlson, E. D.; Krejchi, M. T.; Shah, C. D.; Terakawa, T.; Waymouth, R. M.; Fuller, G. G. *Macromolecules* **1998**, *31*, 5343. (g) Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707. (h) Maciejewski Petoff, J. L.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909. (i) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174. (j) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217. (k) Llinas, G. H.; Dong, S. H.; Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242. (l) For recent formation of elastic polypropylene with metallocenes due to a large number of stereoregular insertions "mistakes", see: Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Laskelä, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348. (m) For a recent publication regarding $\eta^3 \rightarrow \eta^1$ dynamic coordination and the effect in the polymerization of propylene, see: ref 19, Plat, D. *The Reactivity of Group IV Aminophosphine Complexes*; Ph.D. Thesis; Technion, Israel, 2000 and Shaviv, E.; Sc, M. *Heteroallylic Early Transition Metal Complexes*; Thesis; Technion, Israel, 2000. (n) For elastomeric polypropylene obtained by other group 4 complexes, see refs 18, 19, and 31.

The ^{13}C NMR spectrum (Figure 8) of the polymers shows that at $50\text{ }^\circ\text{C}$, large signals are present in the region between 32 and 45 ppm. These signals belong to the 2,1 and 1,3 misinsertions of propylene forming ethyl and butyl domains at the polymer chain.^{2f,34,42a} The increase of misinsertions observed with the elevation of the temperature accounts for the formation of the various forms of polypropylene (isotactic, elastomeric, and oily).

It is important to point out the effect of the amount of MAO. The higher the MAO amount is, the better the polymerization activity is, although beyond the Al:Ti ratio of 300 a plateau is reached, regarding the molecular weight of the polymers (entries 10, 14–16). The effect of the amount of the catalyst was measured by keeping the Al:Ti ratio constant, but increasing the amount of the catalyst (entries 10–13). Hence, similar activities are always observed regardless of the higher concentrations of the catalyst, presumably due to the formation of inactive dimeric species.

The different types of polymers that are achieved under pressure at room temperature by either complexes **9** (highly isotactic) or **10** (highly epimerized and a large number of 2,1 and 1,3 insertions) can be rationalized due to the α -agostic interactions for both complexes. The strong interactions in complex **9** inhibit the β -hydrogen elimination (less epimerizations), whereas for the titanium complex **10**, this interaction has been shown to be much weaker.^{41b} This effect also accounts for the absence of 2,1 misinsertions promoted with complex **9**. The strong interaction seems to be responsible for the occupation of the active coordination site by the hydrogen preventing the 2,1 misinsertion.

Influence of Substituents at the Benzamidinate Ligands on the Catalytic Activity of Complexes 11 and 12. A conceptual question regarding the catalytic activity of the benzamidinate complexes involves the effect of different groups at the aromatic ring. To shed some light, we have prepared and studied complexes **11** and **12**, which are isolobal to complexes **9** and **10**, respectively. In the former complexes, a hydrogen atom is at the *para*-position of the aromatic rings. The polymerization results obtained for the unsubstituted benzamidinate complexes (**11**, **12**) under similar reaction conditions are presented in Table 9.

Comparison of the activities for the zirconium complexes **9** and **11** (Tables 7 and 9) shows that for the unsubstituted complex **11**, the activity in toluene is larger than that of complex **9** in either toluene or CH_2Cl_2 . Larger activity is also observed for the unsubstituted titanium complex **12** as compared to complex **10** (Tables 8 and 9).

The polypropylene obtained with complex **11** is characterized by a high molecular weight (Mw of $\sim 1.9 \times 10^6$). The molecular weights of the polymers obtained with complex **12** in CH_2Cl_2 are much lower than those obtained by complex **10**, whereas in toluene the contrary is observed (compare entries 2, 4, and 14 in Table 8 with entries 8, 5, and 7 of Table 9, respectively). A plausible elucidation for the increase in activity of the unsubstituted complexes (**11** and **12**) in the polymerization of propylene, as compared to the complexes with the substituted benzamidinate ligands (**9** and **10**), relates to the difference in the electronic effects of both ligations on the cationic metal

(42) (a) *NMR of Polymers*; Bovey, F. A., Miray, P. A., Eds.; Academic Press: San Diego, CA, 1996. (b) Margl, P.; Deng, L.; Ziegler, T. *Organometallics* **1998**, *17*, 933.

Table 9. Data for the Polymerization of Propylene Promoted by Benzamidinate Complexes **11** and **12**^a

entry	cat.	solvent	Al:M	activity ^b A x 10 ⁻⁵	Mn	Mw	MWD	mmm ^c %	type of polymer
1	11	toluene	500	2.2	1600	3100	1.96	15	elastomer
2	11	toluene	1000	12.1	380 200	611 600	1.61	20	elastomer
3	11	toluene	2000	9.3	866 100	1 982 000	1.2	19	solid
4	12	toluene	500	2.2	92 400	169 900	1.84	12	elastomer
5	12	toluene	1000	28.5	125 000	310 100	2.48	17	elastomer
6	12	toluene	2000	14.0	137 000	211 700	1.54	27	elastomer
7	12	CH ₂ Cl ₂	500	1.8	12 000	35 100	2.91	9	elastomer
8	12	CH ₂ Cl ₂	1000	9.9	10 200	27 500	2.70	11	elastomer

^a 25 °C, 9.2 atm. ^b gr PP/mol M·h. ^c Measured by ¹³C NMR.

Table 10. Crystal Data and Refinement Details for Complexes **2**, **4**, **9**, **10**, **10*/13** and **15**

complex	2	4	9	10	10*/13	15
empirical formula	C ₄₀ H ₅₆ Li ₂ N ₆ Si ₄	C ₁₉ H ₃₉ LiN ₄ Si ₂	C ₃₀ H ₅₆ N ₄ Si ₄ Zr	C ₁₅ H ₂₈ N ₂ Si ₂ Ti _{0.50}	C _{14.78} H _{24.97} N ₂ Si ₂ Ti _{0.50}	C ₁₂ H _{10.50} N _{1.50}
formula weight	747.15	386.66	676.37	316.52	310.85	175.72
temperature	230(2) K	230(2) K	210(2) K	230.0(1) K	200.0(1) K	220.0(1) K
wavelength	0.7107 Å	0.71070 Å	0.71073 Å	0.71069 Å	0.71069 Å	0.71070 Å
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>I</i> 2/ <i>a</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> <i>m</i> <i>n</i> 21
unit cell dimensions	<i>a</i> = 11.4006(2) Å <i>b</i> = 24.2914(4) Å <i>c</i> = 16.7460(3) Å <i>α</i> = 90° <i>β</i> = 98.75 (6)° <i>γ</i> = 90°	<i>a</i> = 10.6540(4) Å <i>b</i> = 13.4360(6) Å <i>c</i> = 18.1020(8) Å <i>α</i> = 90° <i>β</i> = 91.6800(18)° <i>γ</i> = 90°	<i>a</i> = 11.1578(8) Å <i>b</i> = 11.8659(9) Å <i>c</i> = 15.8740(11) Å <i>α</i> = 100.1940(10)° <i>β</i> = 106.3370(10)° <i>γ</i> = 98.7370(10)°	<i>a</i> = 20.1172(5) Å <i>b</i> = 8.7559(2) Å <i>c</i> = 21.9639(5) Å <i>α</i> = 90° <i>β</i> = 95.2520(10)° <i>γ</i> = 90°	<i>a</i> = 20.039(10) Å <i>b</i> = 8.678(4) Å <i>c</i> = 21.829(10) Å <i>α</i> = 90° <i>β</i> = 94.72(5)° <i>γ</i> = 90°	<i>a</i> = 21.630(4) Å <i>b</i> = 9.458(2) Å <i>c</i> = 4.5734(9) Å <i>α</i> = 90° <i>β</i> = 90° <i>γ</i> = 90°
volume	4583.60(14) Å ³	2590.14(19) Å ³	1939.2(2) Å ³	3852.57(16) Å ³	3783(3) Å ³	935.5(7) Å ³
Z, calculated density	4, 1.083 Mg/m ³	4, 0.992 Mg/m ³	2, 1.158 Mg/m ³	8, 1.091 Mg/m ³	8, 1.092 Mg/m ³	4, 1.248 Mg/m ³
absorption coefficient	0.162 mm ⁻¹	0.146 mm ⁻¹	0.430 mm ⁻¹	0.369 mm ⁻¹	0.375 mm ⁻¹	0.074 mm ⁻¹
<i>F</i> (000)	1600	848	720	1368	1333	372
crystal size	0.15 × 0.3 × 0.5 mm	0.15 × 0.20 × 0.30 mm	0.50 × 0.40 × 0.40 mm	0.04 × 0.18 × 0.37 mm	0.15 × 0.23 × 0.31 mm	0.18 × 0.04 × 0.01 mm
<i>θ</i> range for data collection	1.49–25.50°	1.89–25.03°	1.37–26.40°	2.51–25.05°	2.04–25.04°	2.15–30.50°
limiting indices	0 ≥ <i>h</i> ≥ 13, 0 ≥ <i>k</i> ≥ 28, –19 ≥ <i>l</i> ≥ 19	0 ≥ <i>h</i> ≥ 12, 0 ≥ <i>k</i> ≥ 15, –21 ≥ <i>l</i> ≥ 21	–13 ≥ <i>h</i> ≥ 13, –10 ≥ <i>k</i> ≥ 14, –19 ≥ <i>l</i> ≥ 19	–23 ≥ <i>h</i> ≥ 18, 0 ≥ <i>k</i> ≥ 10, –26 ≥ <i>l</i> ≥ 17	–23 ≥ <i>h</i> ≥ 18, 0 ≥ <i>k</i> ≥ 10, 0 ≥ <i>l</i> ≥ 26	0 ≥ <i>h</i> ≥ 29, 0 ≥ <i>k</i> ≥ 13, –52 ≥ <i>l</i> ≥ 6
reflections collected/unique	8089/8089	4558/4558	10 962/7543	3406/3406	3432/3344	10 623/2438
completeness to highest <i>θ</i>	[<i>R</i> (int) = 0.0000] 99.7%	[<i>R</i> (int) = 0.0000] 99.6%	[<i>R</i> (int) = 0.0604] 99.6%	[<i>R</i> (int) = 0.0000] 99.7%	[<i>R</i> (int) = 0.0428] 100.0%	[<i>R</i> (int) = 0.0760] 91.5%
refinement method	full-matrix least- squares on <i>F</i> ²	full-matrix least- squares on <i>F</i> ²	full-matrix least- squares on <i>F</i> ²	full-matrix least- squares on <i>F</i> ²	full-matrix least- squares on <i>F</i> ²	full-matrix least- squares on <i>F</i> ²
data/restraints/parameters	8089/0/693	4558/0/308	7539/0/426	3406/0/199	3344/0/222	2438/0/155
goodness-of-fit on <i>F</i> ²	1.034	0.989	1.028	1.099	1.044	1.096
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0444, w <i>R</i> 2 = 0.1023	<i>R</i> 1 = 0.0648, w <i>R</i> 2 = 0.1475	<i>R</i> 1 = 0.0608, w <i>R</i> 2 = 0.1413	<i>R</i> 1 = 0.494, w <i>R</i> 2 = 0.1361	<i>R</i> 1 = 0.0927, w <i>R</i> 2 = 0.1697	<i>R</i> 1 = 0.0657, w <i>R</i> 2 = 0.1270
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0757, w <i>R</i> 2 = 0.1115	<i>R</i> 1 = 0.1485, w <i>R</i> 2 = 0.1715	<i>R</i> 1 = 0.1038, w <i>R</i> 2 = 0.1892	<i>R</i> 1 = 0.0711, w <i>R</i> 2 = 0.1450	<i>R</i> 1 = 0.1758, w <i>R</i> 2 = 0.1919	<i>R</i> 1 = 0.2407, w <i>R</i> 2 = 0.1980
largest diff. peak and hole	0.175 and –0.234 e Å ⁻³	0.276 and –0.222 e Å ⁻³	0.458 and –0.547 e Å ⁻³	0.352 and –0.224 e Å ⁻³	0.455 and –0.230 e Å ⁻³	0.195 and –0.174 e Å ⁻³

center. The induction Taft constants (σ^*), which quantitatively characterize the induction effect of an aliphatic substituent in an aromatic hydrocarbons, are +0.49 for the H atom and 0.00 for the CH₃ group.⁴³ Hence, the methyl group has a more negative inductive effect, that is, greater electron-donor properties, than the hydrogen atom, increasing the electron density at the phenyl ring and decreasing the positive charge at the metal center. The reduction of the cationic character at the metal center induces a weaker bond between an incoming molecule of propylene, reducing the polymerization activity of the complex.

The augmentation of the electron density at the metal center in complex **9** inhibits not only the polymerization rate, but also

the rate of the epimerization reaction (slowing down the β -hydrogen elimination), resulting in larger domains of the isotactic pentads, and therefore highly isotactic polymers. For the titanium complex **10**, besides the inhibition rate, no restraint takes place for the epimerization reaction, allowing the production of elastomeric polymers.

Structure of the Elastomeric Polypropylenes. As already mentioned above, in the polymerization of propylene at higher monomer concentrations using the complexes **10**, **11**, and **12**, an elastomeric polypropylene was formed. It is essential and fundamental to compare the chemical structures of the obtained elastomers with the structure of the elastomeric polypropylenes, described in the literature.

Three types of elastomeric polypropylene are known: (i) a large molecular weight atactic polymer,⁴⁴ (ii) polymers with

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alternating isotactic and atactic blocks,^{40a–k} and (iii) polymers obtained by the “dual-side” mechanism.^{40l} To elucidate the structure of the obtained elastomeric polypropylene, its ¹³C NMR spectra was compared with the spectrum of the “atactic oil” and the isotactic polypropylenes, prepared by the zirconium complex **9**. On the basis of the NMR data, for all of the samples, the statistical lengths of the isotactic blocks between two neighboring epimerization stereodeflects were calculated. According to these calculations, the length of an isotactic block before a stereodeflect was found to be between 35 and 45 CH₃ groups for an isotactic polymer (mmmm ≈ 90%) and between 7 and 8 CH₃ groups for the atactic sample (mmmm ≈ 7%). For the elastomeric polymers obtained with complex **10**, the length of the isotactic block was calculated to be between 11 and 27 CH₃ groups. Thus, for the elastomeric polypropylene, the length of the statistical isotactic fragment between two stereodeflects was found to be shorter than that obtained for an isotactic polymer and longer than that observed for an atactic sample. Therefore, it is plausible to assume that the elastomeric polypropylene prepared with these complexes differs, in principle, from the other three above-mentioned types of elastomers. Thus, contrary to the high molecular weight atactic elastomer,⁴³ our samples have an isotactic structure, in which longer isotactic domains are disposed between stereodeflects. Simultaneously, different from the alternating isotactic–atactic block elastomers,⁴⁰ where the alternating isotactic and atactic domains have commensurate lengths, our products are characterized by frequent alternation of the isotactic domains with many stereodeflects. As compared to the polymers obtained through the “dual-side” mechanism, which exhibit large mmmm contents (up to 72%),^{40l} our polymers reside with lower stereoregularities. In the “dual-site” mechanism, each site has a different symmetry, and, by the back-skipping of the polymeric chain, two stereochemistries for the insertions are possible. In our complexes, a back-skipping of the polymer chain will induce the same symmetry, thus inducing the same type of stereoregular insertion. The stereoregular errors are formed because of two competing reactions, the insertion of propylene and the intramolecular epimerization of the growing chain at the last inserted unit. The rate correlation of these two reactions influences the amount and length of the isotactic domains between the stereoerrors.

We have utilized atomic force microscopy (AFM) to discriminate between the crystalline and the amorphous areas in the homogeneous polymer. The use of AFM to characterize the morphology polymer samples on the nanometer scale is well documented in the literature.⁴⁵ Topography, phase imaging, and lateral force measurements are efficient tools to examine polymer structure and properties on the nanometer scale. Here, topographic and phase imaging techniques were used to

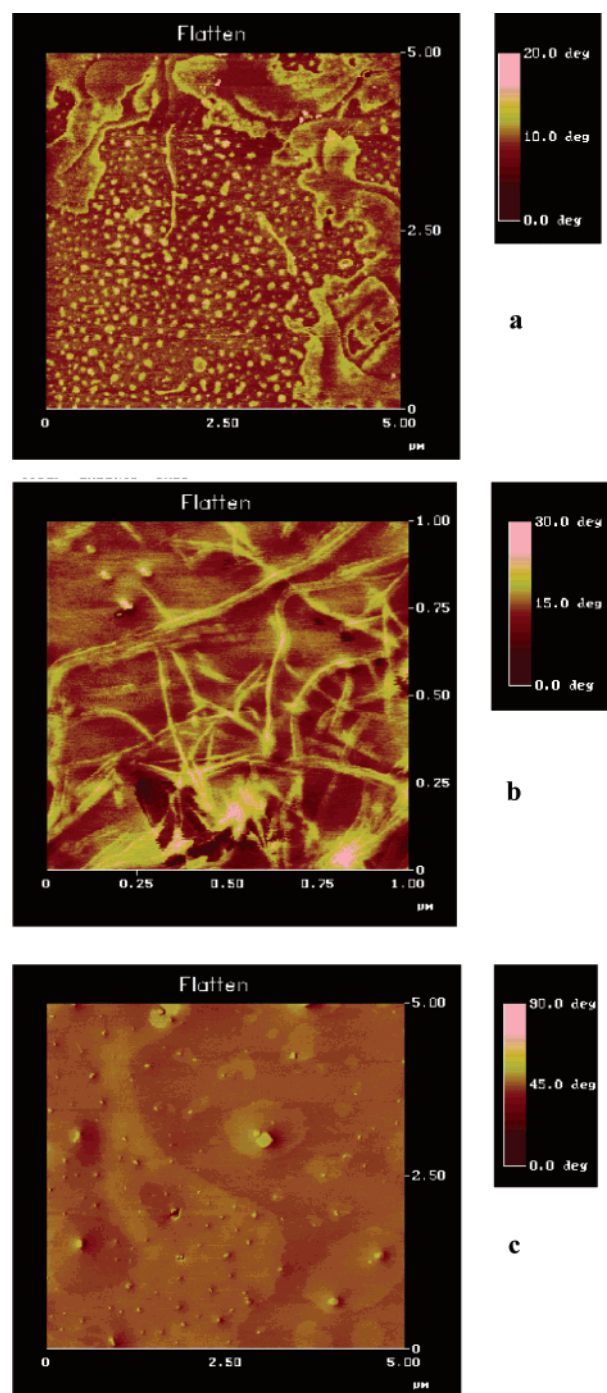


Figure 9. AFM pictures of different polypropylenes. (a) Isotactic polymer from Table 7, entry 4. (b) Elastomeric polymer from Table 8, entry 2. (c) Atactic polymer fraction from Table 7, entry 8.

characterize the morphology of the different types of polypropylene samples.

Samples of the different polymers were spin-coated on glass, and then left to dry at ambient temperature and atmosphere. Figure 9a–c depicts typical phase images of isotactic, elastomeric, and atactic polypropylene samples, respectively. Topographic images taken simultaneously fail to resolve any significant detail within the entire scan range, an indication that the differences in phase shift originate from differences in tip–surface interactions and not from topographical differences. The sample of the isotactic polymer consists of a mosaic of crystalline islands (brighter spots in the image) embedded in

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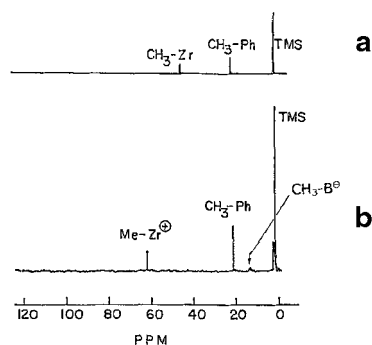


Figure 10. ^{13}C NMR spectrum of complex **9** (top) and the corresponding cationic complex obtained by the stoichiometry reaction with the cocatalyst $\text{B}(\text{C}_6\text{F}_5)_3$ (bottom).

an amorphous phase (darker areas) of the same material. The elastomeric polymer is composed of long interpenetrated and branched fibrils of crystalline character that interconnect amorphous regions. This phase image provides further support to the concept of microheterogeneous crystallinity of the elastomeric phase, caused by different crystalline domains that are characterized by a slightly different melting point. This set of heterogeneous crystalline phases is claimed to yield a broad and undefined melting zone. The atactic polymer is predominantly amorphous with a low density of crystalline domains.

Activation of the Benzamidinate Complexes by the Different Cocatalysts. The polymerization of propylene promoted by the benzamidinate complexes was carried out using either MAO or $\text{B}(\text{C}_6\text{F}_5)_3$ as cocatalysts. To shed some light on the structure of the active cationic complexes, we have followed the changes of the benzamidinate complexes when reacted with the $\text{B}(\text{C}_6\text{F}_5)_3$ cocatalyst under olefin starving conditions, by ^{13}C and ^{19}F NMR spectroscopy.

The ^{13}C NMR spectra of complex **9** and its mixture with an equivalent amount of $\text{B}(\text{C}_6\text{F}_5)_3$ in BrC_6D_5 are shown in Figure 10. The signal of the Zr-CH_3 (43 ppm) moves downfield (62.3 ppm) upon the reaction with the cocatalyst as expected for the formation of a cationic metal-alkyl group.^{4,46} A larger shift was observed for the corresponding titanium complex **10**, showing a displacement from 70 to 110 ppm in its cationic form.

It is important to point out that the spectrum presented in Figure 10b for the cationic complex was obtained after heating the reaction mixture to 90 °C for 2 h to achieve a complete conversion. For complex **10**, the shift of the methyl group is obtained regardless of any heating. Despite the similar character of the active species formed under activation of the complexes with $\text{B}(\text{C}_6\text{F}_5)_3$, they behave totally different in the polymerization of propylene. Thus, the activity of the cationic complex **9** at high pressure is rather small at room temperature, but it increases if it undergoes a preliminary heating stage and recooling to the reaction temperature. On the contrary, the precursor **10** activated with $\text{B}(\text{C}_6\text{F}_5)_3$ is inactive in the polymerization, regardless of any heating.

The ^{19}F NMR spectra of complex **9** with an equimolar amount of the cocatalyst, $\text{B}(\text{C}_6\text{F}_5)_3$, before and after heating, are shown in Figure 11a and b, respectively. At room temperature (Figure

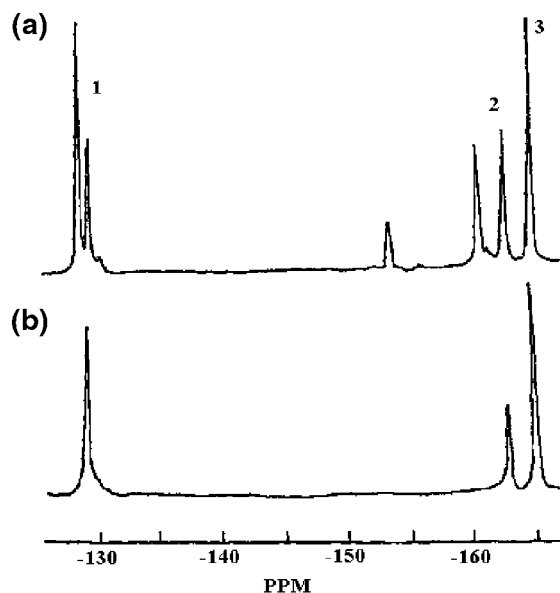


Figure 11. ^{19}F NMR spectra of complex **9** with $\text{B}(\text{C}_6\text{F}_5)_3$ at room temperature (a) and after heating (b).

11a), the spectra show two sets of signals. The signals marked 1, 2, and 3 belong to the formed cationic complex, whereas the other three signals belong to an intermediate unsolved structure. By heating and cooling the mixture, a reaction is observed achieving a quantitative conversion toward the cationic complex (Figure 11b). The chemical shift difference between the *m*- and *p*- ^{19}F of the anion $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3$ can also be indicative of the anion coordination.⁴⁷

Hence, values of $\Delta\delta$ (*m,p*-F) between 3 and 6 ppm indicate coordination, whereas values below 3 ppm indicate noncoordination. For the Zr complex, a difference of $\Delta\delta$ (*m,p*-F) = 2.28 ppm is observed, indicative for a noncoordinating ion pair, corroborating the results obtained in the polymerization of propylene by complex **9** in CH_2Cl_2 . The ^{19}F NMR spectra of complex **10** with an equimolar amount of the cocatalyst $\text{B}(\text{C}_6\text{F}_5)_3$ show the immediate formation of at least two inactive compounds (six new signals besides the starting cocatalyst) with no resemblance in the chemical shifts to other active or nonactive $\text{B}(\text{C}_6\text{F}_5)_3$ -containing metallocene complexes.⁴⁶

Conclusions

Several early-transition octahedral metal complexes containing the chelating benzamidinate ligation were prepared. These complexes exhibit a C_2 -symmetry as displayed in their X-ray diffraction studies. The reaction of the compounds with a cocatalyst produces the corresponding cationic complexes that are active catalysts for the polymerization of propylene. Depending on the nature of the complexes, either highly stereoregular or elastomeric polymers can be obtained. Moreover, the type of polymer can be modulated by the pressure of the monomer. The elastomeric polymers are characterized by an alternation of short isotactic domains with stereodefects that are encountered by the epimerization of the growing polymeric chain at the last monomeric insertion. The use of changing

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pressure to obtain a different block homo-copolymer is under investigation and will be reported shortly.

Experimental Section

General Procedure. All manipulations were carried out with the exclusion of oxygen and moisture using flamed Schlenk-type glassware and high vacuum (10^{-5} Torr) techniques. For storage of air-sensitive materials, a nitrogen-filled "Vacuum Atmospheres" glovebox with a medium capacity recirculator (1–2 ppm O_2) was used. The gases (argon, nitrogen, propylene) were purified by passage through a MnO oxygen removal column and a Davison 4 Å molecular sieves column. Analytically pure solvents were distilled under argon from potassium benzophenone ketyl (tetrahydrofuran), Na/K alloy (diethyl ether, hexane), Na (toluene), or P_2O_5 (dichloromethane). All solvents for vacuum line manipulations were stored in a vacuum over Na/K alloy. Nitrile compounds (Aldrich) and TMEDA were degassed and freshly distilled under argon. Methylalumoxane cocatalyst (Witco) was prepared from a 30% suspension in toluene by vacuum evaporation of the solvent at 25 °C/ 10^{-5} Torr. Tris(pentafluorophenyl)boron cocatalyst was prepared according to the literature.⁴⁸ $HfCl_4 \cdot 2THF$, $ZrCl_4$, and $TiCl_4$ were purchased and used as received (Aldrich). NMR spectra were recorded on Bruker AM-200 and AM-400 spectrometers. Chemical shifts for 1H NMR and ^{13}C NMR were referenced to internal solvent resonances and reported relative to $SiMe_4$. The polypropylene NMR experiments were conducted in 1,2,4-trichlorobenzene at 130 °C with 20% DMSO- d_6 . The NMR experiments of the benzamidinate complexes were conducted on Teflon valve-sealed tubes after vacuum transfer of the solvent in a high vacuum line. ^{19}F NMR experiments were performed in toluene, and the chemical shifts were reported relative to CCl_3F . Complexes **1**,²⁵ **2**,²⁵ **5**,²³ **6**,²³ **7**,^{21b,22d,i} **8**,^{21b,22d,i} **11**,^{21b,22d} and **12**^{21b,22d} were prepared as described in the literature.

Melting points of isotactic polypropylene were determined on a differential scanning calorimeter (DSC). Three runs (first heating, cooling, second heating) were performed at a heating rate of 10 °C/min in the temperature range 30–190 °C. The second-heating melting peak temperature was taken as a melting point.

Molecular weights of polymers were determined either by viscosimetric measurements⁴⁹ or by the GPC method. The latter was performed on a Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene (HPLC) as the mobile phase at 150 °C.

AFM measurements were performed on a DI3100 AFM machine (Veeco) equipped with an acoustic shield and vibration isolation table (TMC) using Si tips.

For complexes **9** and **13**, X-ray diffraction experiments were carried out with a Philips PW1100/20 four-circle diffractometer. Because of the extreme sensitivity of all synthesized complexes to oxygen and moisture, a suitable crystal for X-ray analysis was placed inside a glovebox in dry and degassed Parathon oil (Du-Pont). It was then mounted on a diffractometer, where it met a cold stream of nitrogen at 200 K. Reflections were collected, and intensities were corrected in the usual way except for absorption. The structure was solved by direct methods,⁵⁰ and refinement, based on F, was made by block-diagonal least-squares.⁵¹ All non-hydrogen atoms were refined anisotropically in two blocks. Hydrogen atoms were included at calculated positions and refined isotropically in one block. The $d(C-H)$ used was 1.08 Å. Measurement conditions and structure refinement are summarized in Table 10.

For compounds, **2**, **4**, **10**, and **15**, X-ray crystallographic experiments were carried out on a Nonius-Kappa CCD diffractometer with graphite-

monochromatized Mo K α radiation. The crystals were placed into a Parathon-N oil in a glovebox. Single crystals were mounted on the diffractometer under a stream of cold N_2 at 220 K. Data collection and reduction and cell refinements were carried out with the Nonius software package.⁵² The structure solution was carried out by the SHELXS 97⁵³ and SHELXSL 97⁵⁴ software packages, respectively. The ORTEP program incorporated in the TEXRAY structure analysis package was used for molecular graphics.⁵⁵ Relevant crystallographic information is summarized in Table 10.

Synthesis of $p\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2\text{Li} \cdot \text{TMEDA}$ (3**).** To a well stirred solution of 5.42 g (32.5 mmol) of $\text{LiN}(\text{TMS})_2$ in 50 mL of hexane at 0 °C was added 3.93 g (33.6 mol) of 4-methylbenzonitrile by a syringe in an argon flow. The mixture was stirred at room temperature for 3 h, and then 5.0 g (42.0 mmol) of TMEDA was added. The red-brown solution formed was stirred for an additional 3 h. After the reaction mixture was cooled overnight at –50 °C, a crystalline material precipitated that was cold filtered and dried under high vacuum to obtain 11.6 g (86%) of red-brown crystals of **3**: mp 112 °C (dec). 1H NMR (C_6D_6 , 200.13 MHz): δ = 7.22 (d, 3J = 8 Hz, 2H, Ph), 6.92 (d, 3J = 8 Hz, 2H, Ph), 2.1 (s, 3H, CH_3 -Ph), 1.98 (s, 12H, CH_3 -N), 1.74 (s, 4H, CH_2 -N), 0.08 (s, 18H, TMS). ^{13}C NMR (C_6D_6 , 50 MHz): δ = 182.0 (N-C-N), 138.9, 137.2, 128.9, 128.1, 126.8 (Ph), 56.5 (CH_2 -N), 45.6 (CH_3 -N), 21.4 (CH_3 -Ph), 3.0 (TMS).

Synthesis of Ligand $C_6H_5C(\text{NSiMe}_3)_2\text{Li} \cdot \text{TMEDA}$ (4**).** Complex **4** was prepared according to a modified literature procedure.²⁴ A suspension solution of 6.5 g (38.9 mmol) of $\text{LiN}(\text{TMS})_2$ in 100 mL of diethyl ether was reacted for 1 h with 4.62 g (39.8 mmol) of TMEDA. The reaction mixture was cooled to –10 °C, and 4.01 g (38.9 mol) of benzonitrile was added via a syringe under an argon flow. The reaction was stirred for 10 h at room temperature, and a crystalline product began to precipitate. Slow cooling of the reaction mixture to –40 °C overnight induced the precipitation of light yellow crystals, which were cold filtered and vacuum-dried to obtain 13.2 g (88%) of ligand **4**. For spectroscopic characterization, see ref 25.

Synthesis of $[4\text{-CH}_3\text{-C}_6\text{H}_4\text{C}(\text{NTMS})_2]_2\text{ZrMe}_2$ (9**).** 1.03 g (1.4 mmol) of complex **5** was dissolved in 50 mL of diethyl ether, and 2.16 mL of a 1.3 M solution of methyllithium in hexane (2.8 mmol) was added dropwise at –78 °C. The solvents were completely removed in a vacuum, the residue was redissolved in hexane (30 mL), and the resulting solution was filtered through a thin layer of dry Celite filter-aid to remove insoluble particles. After the solution was cooled overnight at –35 °C, pale yellow crystals were cold filtered and vacuum-dried to obtain 0.95 g (98%) of complex **9**. Anal. Calcd for $C_{30}H_{56}N_4Si_4Zr$ (676.36): C, 53.3; H, 8.4; N, 8.3. Found: C, 52.8; H, 8.2; N, 7.6. mp 135 °C (dec). 1H NMR (C_6D_6): δ = 7.16 (d, 3J = 8 Hz, 2H, Ph), 7.12 (d, 3J = 8 Hz, 2H, Ph), 1.99 (s, 3H, CH_3 -Ph), 1.04 (s, 3H, CH_3 -Zr), 0.17 (s, 18H, TMS). ^{13}C NMR (C_6D_6): δ = 184 (N-C-N), 138.8 (ipso carbon), 137.3, 130.0, 126.1 (Ph), 44.7 (CH_3 -Zr), 21.2 (CH_3 -Ph), 2.3 (TMS).

Synthesis of $[4\text{-CH}_3\text{-C}_6\text{H}_4\text{C}(\text{NTMS})_2]_2\text{TiMe}_2$ (10**).** In a manner similar to that described for the preparation of complex **9**, 1.68 g (2.5 mmol) of complex **6** was dissolved in 50 mL of diethyl ether and was reacted with 3.85 mL of 1.3 M (5.0 mmol) methyllithium solution in hexane. The reaction mixture was stirred for 8 h, and the solvents were vacuum evaporated. Next 30 mL of hexane was vacuum transferred to the residue, and LiCl was removed by filtration. Cooling the solution overnight at –40 °C resulted in the formation of brown crystals, which were cold filtered and vacuum-dried, producing 1.45 g (92%) of

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complex **10**. Anal. Calcd for $C_{30}H_{56}N_4Si_4Ti$ (632): C, 56.96; H, 8.86; N, 8.86. Found: C, 55.23; H, 8.08; N, 9.43. mp 98 °C (dec). 1H NMR (C_6D_6 , 200.13 MHz): δ = 7.25 (d, J = 7 Hz, 2H, Ph), 6.85 (d, J = 7 Hz, 2H, Ph), 2.0 (s, 6H, CH_3 -Ph), 1.90 (s, 6H, CH_3 -Ti), 0.15 (s, 18H, TMS). ^{13}C NMR (C_6D_6 , 50 MHz): δ = 189 (N-C-N), 139.1, 136.8, 128.6, 126.6 (Ph), 70.2 (CH_3 -Ti), 21.6 (CH_3 -Ph), 1.9 (TMS).

Synthesis of $[4-CH_3-C_6H_4C(NTMS)_2]_2HfCl_2$ (14**).** In a glovebox was charged a swivel frit with 0.573 g (1.6 mmol) of the dimeric ligand **1** prepared in diethyl ether²⁵ without TMEDA, and 1.49 g (3.2 mmol) of $HfCl_4 \cdot 2THF$. Next 50 mL of toluene was vacuum transferred, and the reaction mixture was stirred for 16 h at room temperature. All volatiles were vacuum evaporated, and 40 mL of toluene was vacuum transferred to allow the separation of LiCl. The inorganic salt was filtered, and toluene was vacuum evaporated to obtain a yellow oily material. The oil was washed several times with diethyl ether, and evaporation of the solvent allowed the formation of 0.22 g (34%) of a yellow solid. 1H and ^{13}C NMR analysis of the solid indicate the formation of complex **14**, although elemental analysis shows that additional materials are present, which are silent in NMR; see text above. 1H NMR ($CDCl_3$, 200.13 MHz): δ = 7.2–7.05 (m, 4H, Ph), 2.3 (s, 3H, CH_3 -Ph), 0.08 (s, 18H, TMS). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 187.1 (N-C-N), 137.6, 136.4, 128.9, 126.8 (Ph), 2.1 (TMS).

Propylene Polymerization Experiments. The catalytic polymerization of propylene was studied using complexes **9–12**. Cationic complexes were prepared by activation of these precatalysts by either MAO or $B(C_6F_5)_3$. Polymerization at atmospheric pressure was carried out in a 100 mL flamed round-bottom flask and in NMR J-Young tubes. Experiments at higher pressures were performed either in a 100 mL heavy-wall glass or in stainless steel reactors. The reactor was charged inside a glovebox with a certain amount of the catalytic precursor, cocatalyst, and a magnetic stirrer. The reactor was connected to a high vacuum line, and, after introducing the solvent (7–10 mL) via a syringe under an argon flow, it was frozen at liquid nitrogen temperature and pumped-down. For the polymerization at atmospheric pressure, the reactor was warmed to the reaction temperature, and propylene was used to back fill the vessel, and it was all maintained at 1.0 atm with a mercury manometer. When polymerization was performed at higher pressures, to the frozen reactor was vacuum transferred a certain amount of liquid propylene. The temperature was then raised in a thermostated

bath, and the stirring began. The pressure in the reactor was measured by means of a manometer. After being stirred for a certain period, the mixture was quenched by exhausting the unreacted propylene, followed by the fast introduction of 40 mL of CH_3OH/HCl (1:1). Polypropylene was filtered, washed with water until neutral solution was obtained, washed with acetone, and dried under vacuum. The organic fraction from the filtrate solution was separated, dried, and the solvent was evaporated. In most cases, this solution shows no atactic fraction but when appreciated the amount of it was inserted in the corresponding table.

Purification of Polypropylene from Aluminum Salts. Quenching the polymerization reactions, in which MAO was used as a cocatalyst, by $MeOH:HCl$ produces aluminum salts that are absorbed into the polymer. These inorganic salts are difficult to remove by just washing the polymer. We have been able to clean most of the salts by dissolving the polymer in a hot solution of either 1,2,4-trichlorobenzene, Decaline, or *p*-xylene (120 °C). The hot solution is filtered, and the filtrate is poured into cold acetone to reprecipitate the polypropylene. The latter was then washed with acetone in the Soxhlet apparatus to remove any traces of high boiling point solvents, followed by drying under vacuum.

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Supporting Information Available: Additional crystallographic details, tables of all bond distances, angles, and anisotropic thermal parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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