Determination of the Catalytic Active Species in the Polymerization of Propylene by Titanium Benzamidinate Complexes

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The catalytic behavior of the monomeric titanium bis(benzamidinate) [η-C$_6$H$_5$-C(NSiMe$_3$)$_2$]$_2$TiCl$_2$ (**1**), the dimeric titanium mono(benzamidinate) {[η-C$_6$H$_5$-C(NSiMe$_3$)$_2$]TiCl$_3$]}$_2$ (**2**), and the monomeric titanium mono(benzamidinate) complex η-C$_6$H$_5$-C(NSiMe$_3$)$_2$]TiCl$_3$]·THF (**3**) activated by methylalumoxane (MAO) has been compared in the polymerization of ethylene and propylene. Despite structural and symmetrical differences, the activities of all precatalysts were found to be alike, indicating that rearrangements toward similar active species are operative during the polymerization regardless of the starting materials. To shed some light on the mechanistic pathways for the formation of such active species from the different titanium benzamidinate complexes and on the role of the aluminum cocatalyst in the activation process, corresponding aluminum benzamidinate dichloro and dimethyl complexes were synthesized and compared to the titanium complexes. The formation of the different active sites was monitored using NMR and ESR spectroscopy, trapping experiments with [60]fullerene, and MALDI-TOF mass spectroscopy. The results obtained for the different benzamidinate titanium complexes and proposed mechanistic pathways for their activation reactions with MAO and their fate after the addition of the olefins are presented and discussed in this publication. In addition, viscoelastic and rheological mechanical properties of the polymers are disclosed.

Introduction

The flourishing application of "well-defined" single-site group 3 and 4 metallocene catalysts for the polymerization of α-olefins,[1] together with sophisticated investigations on the role of the ligand composition and structure in the stabilization of the active centers,[2] has facilitated the search of the nonmetallocene systems as alternative catalysts for this polymerization process.[3] Among the various organometallic compounds synthesized during the past decade, the complexes of early transition metals with the bidentate *N,N′*-bis(trimethylsilyl) benzamidinate ligations [η-RC(NR′)$_2$]$^-$ (where R = C$_6$H$_5$ or substituted phenyls, R′ = alkyl, aryl, or SiMe$_3$) have been widely described

as promising alternatives to the cyclopentadienyl complexes.[4] The benzamidinate complexes are normally obtained as a mixture of racemic C_2-symmetry *cis*-octahedral structures (**A**), which usually contain two ligands in a chelating coordination mode (M = group 4 early transition metals, X = halides, amines, or alkyl groups).
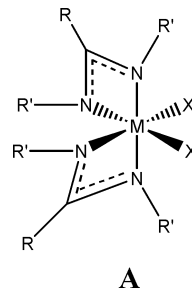
A

Compared to the cyclopentadienyl ligands, the benzamidinate ligations strongly differ from them with unique electronic

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properties.[4i,j] As a four-electron donor, the anionic moiety [RC(NSiMe$_3$)$_2$]$^-$ polarizes the M−N bonds, promoting greater electrophility of the metal center, as compared to the six electrons of the cyclopentadienyl ligands. The possibility to simply modify the steric and electronic properties of the benzamidinate-based ligations, 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 the synthesis of various organometallic complexes as potential catalytic precursors for polymerization and other α-olefin transformations.[5]

The catalytic properties of several group 4 bis(benzamidinate) complexes in the polymerization of α-olefins have been previously investigated.[4j,5b,6] When activated with methylalu-moxane (MAO) or other cocatalysts, these complexes demonstrated high catalytic activity for the polymerization of ethylene, propylene, and styrene.[5b,7] It was shown that the stereoregularity of the obtained polymers depends on the composition of the early transition metal benzamidinate complexes and the conditions under which the polymerization reactions were performed. Thus, for example, we have found that for some benzamidinate zirconium complexes the change of the monomer concentration during the process allowed the formation of various types of polypropylene (atactic, isotactic, or elastomeric).[7]

Among a great variety of benzamidinato-transition metal compounds, the monomeric titanium bis(benzamidinate) [η-C$_6$H$_5$-C(NSiMe$_3$)$_2$]$_2$TiCl$_2$ (**1**)[6] and the dimeric titanium mono(benz-amidinate) {[η-C$_6$H$_5$-C(NSiMe$_3$)$_2$]TiCl$_3$]}$_2$ (**2**)[5b,6e,8] complexes have been synthesized and studied as catalytic precursors for the polymerization of α-olefins. The reaction of benzonitrile with lithium bis(trimethylsilyl)amide produces the bidentate lithium salt [η^2-C$_6$H$_5$-C(NSiMe$_3$)$_2$Li] (eq 1) as either a monomeric, dimeric, or oligomeric complex depending on the solvent (TMEDA, ether, or hexane) used.[9] The consecutive reaction of 2 equiv of the latter ligands with titanium tetrachloride in toluene, at room temperature, yields a brown-red solution, from which 60−70% of pure complex **1** was isolated (eq 2)[4a−c,7]
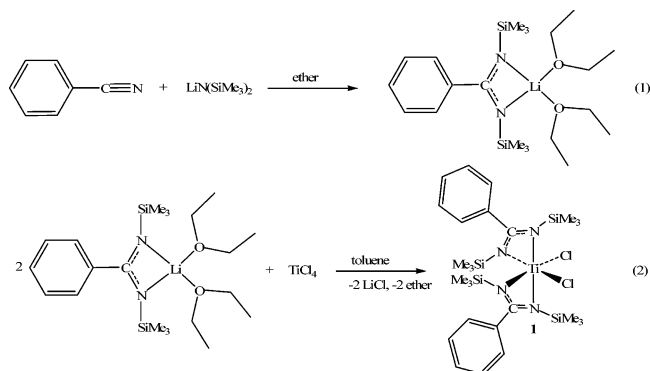

When the lithium complex reacts with Me$_3$SiCl in toluene, the neutral silylated benzamidinate ligand is formed[7a] (eq 3). Reaction of TiCl$_4$ with stoichiometric amounts of this neutral ligand in dichloromethane produces 92% of complex **2**[7b] (eq 4).

Interestingly, the dimeric complex **2** can be easily converted into the corresponding monomeric complex by using an electron-donor solvent or additional nucleophilic ligands, such as PPh$_3$.[5b,6e] Thus, in tetrahydrofuran at room temperature, the dimer produces a red crystalline solid of monomeric complex η-C$_6$H$_5$-C(NSiMe$_3$)$_2$]TiCl$_3$]·THF (**3**), in which one molecule of THF is coordinated to the titanium center (eq 5).
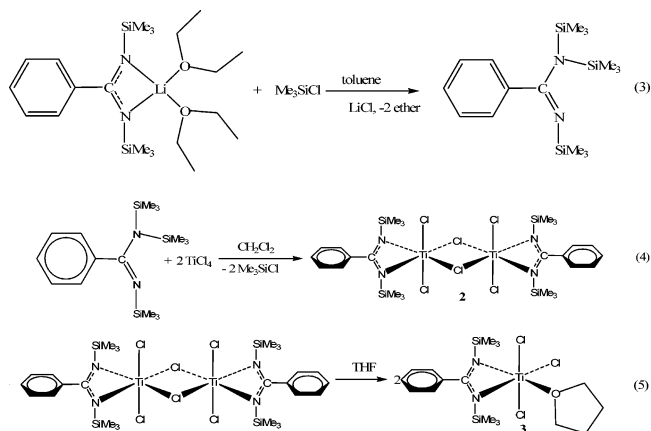
Thus, complexes **1** and **2**, having a similar chemical nature, differ by the space symmetry and number of ligations surrounding the metal center and, as a consequence, are expected to exhibit different reactivities and stereoselectivity in the polymerization of α-olefins. Hence, the mono(benzamidinate) titanium complexes **2** and **3** activated by MAO were found to be active for the polymerization of styrene, whereas the bis(benzamidi-nato) titanium complex **1** was completely inactive in this process under similar reaction conditions.[5b,6e] For ethylene, the polymerizations have been performed at low and high pressure with the zirconium bis(benzamidinate) dialkyl complexes.[10] The corresponding mono(benzamidinate) zirconium trialkyl complex has shown lower activities as compared to the bis(benzamidi-nate) complex.[6f,10] It is notable that theoretical calculation has predicted a higher activity in the polymerization of ethylene for the mono-benzamidinate derivative.[11]

Furthermore, regarding titanium, none of the mono(benz-amidinate) complexes **2** and **3** were found to be active for the polymerization of propylene at a monomer pressure of 1 atm.[5b,6e] This result is similar to our findings, in which the bis(benz-amidinate) titanium dichloride complex (**1**) activated with MAO also does not polymerize propylene at atmospheric pressure.[7] However, when complex **1** was used in the polymerization of

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propylene at higher pressures (liquid propylene ~10 atm), an elastomeric polypropylene was produced.[7]

Our main goal was to investigate the influence of the compositional and structural features of the mono- and bis-(benzamidinato) titanium complexes on their activity for the polymerization of ethylene and propylene at high pressure and on the properties of the polymers produced. In addition, to shed some light on the mechanistic pathways for the formation of the active species from the different titanium benzamidinate complexes and on the role of the aluminum cocatalyst in the activation process, corresponding aluminum benzamidinate dichloro and dimethyl complexes were synthesized. The catalytic activity of these aluminum complexes in the polymerization of propylene and the properties of the achieved polymers were compared with those obtained by the titanium complexes. In addition the formation of the different active sites was monitored using NMR and ESR (C_{60} trapping experiments) spectroscopy and MALDI-TOF mass spectroscopy. The results obtained regarding the active complexes and their fate in their reactions with MAO and olefins are presented and discussed in this publication. In addition, viscoelastic and rheological properties of the polymers are disclosed.

Experimental Section

General Procedures. All manipulations with air-sensitive materials were performed with the exclusion of oxygen and moisture in Schlenk-type glassware and a high-vacuum (10^{-6} Torr) line. For storage of materials, a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1−2 ppm O_2) was used. The gases (argon and nitrogen) were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were distilled under N_2 from Na/K-benzophenone (tetrahydrofuran), Na/K alloy (hexane), Na (toluene), or P_2O_5 (dichloromethane). All solvents for vacuum line manipulations were stored in a vacuum over Na/K alloy. Benzonitrile and TMEDA were freshly distilled under argon and degassed. C_{60}, $AlMe_3$, and $AlCl_3$ (Aldrich) was used as received. Methylalumoxane (Witco) was prepared from a 30% suspension in toluene by vacuum evaporation of the solvent at 25 °C/10^{-5} Torr. Complexes [η-C_6H_5-C(NSiMe$_3$)$_2$]$_2$TiCl$_2$ (**1**), {[η-C_6H_5-C(NSiMe$_3$)$_2$]-TiCl$_3$}$_2$ (**2**), and [η-C_6H_5-C(NSiMe$_3$)$_2$]TiCl$_3$·THF (**3**) were prepared as described in the literature.[4a−c,5b,6e]

The NMR measurements of the benzamidinate complexes were conducted on Teflon J. Young valve-sealed NMR tubes after vacuum transfer of the solvent in a high-vacuum line and recorded on Bruker Avance 300 or 500 MHz spectrometers. MALDI-TOF LD+ and LD− experiments were performed on a Waters MALDI mass spectrometer. ESR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.4 GHz) digital ESR spectrometer equipped with a Bruker N_2-temperature controller. All spectra were recorded at microwave power 10, 1 mW, 100 kHz magnetic field modulation of 1.0−0.5 G amplitude. Digital field resolution was 2048 points per spectrum, allowing all hyperfine splittings to be measured directly with accuracy better than 0.2 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia software.

Synthesis of Benzamidinate Aluminum Dichloride Complex 6. Li benzamidinate [PhC(NTMS)$_2$]Li[6f,7a] (2.7 g, 0.01 mol) was dissolved in 250 mL of dry toluene under inert conditions and cooled to −78 °C. Then 1.33 g (0.01 mol) of aluminum trichloride was dissolved in 50 mL of dry toluene in a dropping funnel and added dropwise to the lithium benzamidinate ligand. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The resulting solution was filtered through a fritted glass, and the solution was concentrated by vacuum to produce a solid product. The resulting monochloroaluminum benzamidinate com-

plex was crystallized from toluene−hexane (4:1) solution at −40 °C. The resulting brown crystals were filtered and dried under vacuum to obtain 2.11 g (58%). Anal. Calc for $C_{13}H_{23}N_2Si_2Cl_2Al$: C, 43.33; H, 6.37; N, 7.76; Cl, 19.67. Found: C, 42.65; H, 6.54; N, 7.38; Cl, 19.58. ^{1}H NMR (C_7D_8, 500 MHz): δ_H 0.08 (s, 18H, TMS), 7.11 (br, 5H, Ph). ^{13}C NMR (C_7D_8, 125 MHz): δ 0.07 (TMS); 123, 127, 131 (Ph). ^{29}Si NMR (C_7D_8, 99.3 MHz): δ 3.84 ppm.

Synthesis of Benzamidinate Aluminum Dimethyl Complex 7. Benzamidine PhC(NTMS)N(TMS)$_2$[9] (3.36 g, 0.01 mol) was suspended in 150 mL of dry hexane under inert conditions and cooled to −78 °C. Then 0.72 g (0.01 mol) of trimethyl aluminum (as 10% solution in hexane, Aldrich) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The resulting solution was concentrated by vacuum, removing part of the hexane until precipitation commenced. The white powder was filtered and dried under vacuum to obtain 1.9 g (59%). Anal. Calc for $C_{15}H_{29}N_2Si_2Al$: C, 56.25; H, 9.06; N, 8.75. Found: C, 56.82; H, 9.22; N, 8.71. ^{1}H NMR (C_7D_8, 500 MHz): δ_H 0.11 (s, 18H, TMS), 6.9 (br, 5H, Ph), 0.99 (s, 6H, Al*Me*$_2$). ^{13}C NMR (C_7D_8, 125 MHz): δ 0.05 (TMS); 7.13 (Al-*Me*); 122, 128, 132 (Ph). ^{29}Si NMR (C_7D_8, 99.3 MHz): δ 3.83 ppm.

Propylene Polymerization Experiments. The polymerization of propylene was studied using complexes **1**−**5** as catalytic precursors. The complexes were activated by methylalumoxane at different molar Al:Ti ratios. The polymerization was performed in a 100 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was charged with a certain amount of complex and MAO inside a glovebox and connected to a high-vacuum line. After introducing 5−6 mL of the solvent (CH_2Cl_2 or toluene) under an argon stream, the reactor was cooled to 123 K and vacuum evacuated. Then 30−40 mL of liquid propylene was vacuum transferred into the reactor. The temperature was then raised in a thermostated bath and the stirring began. The pressure in the reactor was measured with a manometer. After stirring for a definite period of time, the reaction was quenched by exhausting the unreacted C_3H_6 in a well-ventilated hood, followed by the introduction of a 30−40 mL mixture of acetylacetone and water (1:20) to decompose all the MAO, inducing the formation of Al(acac)$_3$. The polymer was filtered, washed with methanol and acetone, and dried under vacuum at 50 °C.

Ethylene Polymerization. The polymerization of ethylene was studied using complexes **1** and **2** as catalytic precursors. The complexes were activated by methylalumoxane at a Ti:Al molar ratio of 1:1000. The polymerization was performed in a 100 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was charged with a certain amount of complex and MAO inside a glovebox and connected to a high-vacuum line. After introducing 5−6 mL of toluene under an argon stream, the reactor was filled with ethylene at a pressure of 20 atm. The pressure was kept constant during the polymerization. After stirring for a definite period of time, the reaction was quenched by exhausting the unreacted ethylene in a well-ventilated hood, followed by the introduction of a 30−40 mL mixture of acetylacetone and water (1:20) to decompose all the MAO. The polymer was filtered, washed with acetone, and dried under vacuum at 50 °C.

Fractionation of Polymers. The polymer samples were fractionated by extraction with refluxing hexane. A 250 mL round-bottom flask was charged with the solvent (100 mL) and attached to a Soxhlet extractor. The polymer (~1 g) was packed into a cellulose thimble placed into the extractor. After 72 h of extraction the solvent was evaporated under vacuum from both hexane-soluble and hexane-insoluble fractions. The results are expressed as a percentage of the total amount of polymer.

Polymerization of Propylene under ESR Monitoring. A Teflon J. Young valve-sealed NMR tube was charged in the presence or absence of fullerene (2 mg/mL solution in toluene) with the

Table 1. Data for the Polymerization of Propylene Using Precatalysts 1, 2, and 3 Activated by Methylalumoxane

entry	cat.[b]	Al:Ti ratio	solvent	yield of polymer, g	activity,[c] $A \times 10^{-5}$	M_w	mwd[d]	*mmmm* %
				Complex **1**				
1	16.0	500	CH_2Cl_2	0.20	0.043	51 000	2.83	12.8
2	16.0	1000	CH_2Cl_2	1.93	0.40	47 000	3.13	14.9
3	17.0	2000	CH_2Cl_2	4.28	0.84	29 000	5.81	15.7
4	16.0	1000	toluene	3.23	0.69	59 000	3.70	10.9
				Complex **2**				
5	23.9	500	CH_2Cl_2	1.69	0.24	80 000	3.20	34.1
6	25.1	1000	CH_2Cl_2	3.10	0.38	51 000	3.76	20.6
7	25.1	2000	CH_2Cl_2	5.31	0.71	38 000	6.33	18.4
8	25.1	1000	toluene	4.73	0.63	58 000	3.97	11.9
				Complex **3**				
9	20.4	1000	CH_2Cl_2	2.30	0.38	55 000	3.77	14.7
10	20.4	1000	toluene	3.37	0.55	62 000	3.26	9.9

[a] 23°C, 10.2 atm, 6 mL of solvent, 40 mL of C_3H_6, 180 min. [b] mol Ti $\times 10^{-6}$. [c] g PP $\times$ mol Ti^{-1} $\times$ h^{-1}. [d] Molecular weight distribution.

corresponding complex, MAO, and a deuterated solvent inside a drybox. The NMR tube was connected to a high-vacuum line, frozen, pumped, thawed, and filled with propylene to 1 atm. The consumption of the propylene were monitored via a pressure gauge and refilled after reaching 700 mmHg. The ESR spectrum was measured after 1, 2, 6, and 12 refills of propylene.

Characterization of the Polymers. NMR spectra of the polymers were conducted in deuterated tetrachlorethane at 85 °C and recorded on a Bruker Avance 500 MHz spectrometer. The preheating of our polymer samples at 85 °C dissolved in 0.4 mL of tetrachloroethane-d_2 (4 h) yielded clear homogeneous solutions. ^{13}C NMR spectra of random polymer samples were measured at 85 and 120 °C, exhibiting reproducible pentad data.[12] Chemical shifts for ^{1}H and ^{13}C NMR were referenced to internal solvent resonances and reported relative to SiMe$_4$.

Molecular weights of polymers were determined by the GPC method on a Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene as a mobile phase at 150 °C and referenced to polystyrene standards.

Melting crystallization behavior of the polymers was examined using a Perkin-Elmer DSC-7 differential scanning calorimeter. Three runs (heating−cooling−heating) at a rate of 10 deg/min in the range 30−190 °C were performed for each sample of polymer. The second heating exothermal peak temperature was taken as a melting point.

Prior to studying their properties, the polymers were first devolatalized by processing on Collin roll mills and then compression molded at 180 °C using a Collin heated plate hydraulic press. Viscoelastic properties of the compression-molded samples were tested in both molten and solid state using an ARES dynamic mechanical thermal analyzer (Rheometric Scientific). The solid materials were tested in a torsion deformation mode using rectangular samples cut from the compression-molded plates. Dynamic temperature ramp experiments at 1 Hz oscillation frequency were conducted in the temperature range −50 to +100 °C at a heating rate of 5 deg/min. The applied deformation was about 0.2%.

The rheological properties of the molten polymers were tested at 180 °C using a parallel plate (25 mm) setup in a dynamic frequency sweep mode. The oscillation frequency varied from 0.05 to 15 Hz with the deformation amplitude of 2%. The complex viscosity data were approximated using the Carreau model. Shore A hardness of the elastomeric compression-molded samples was measured using a digital instrument according to the ASTM D2246.

Results and Discussion

In our search for catalysts for the polymerization of olefins, we have studied and compared the activity and selectivity of complexes **1** and **2** activated by MAO in the polymerization of ethylene. We have found that these complexes are active in the polymerization of ethylene, producing HDPE (mp = 130 °C)

at 20 atm exhibiting unexpectedly equal activities (5.8×10^3 g PE/(mol cat $\times$ h $\times$ atm) for complex **1** and 5.6×10^3 g PE/(mol cat $\times$ h $\times$ atm) for complex **2**). The similar activities spurred us to evaluate the relationship between the number of ancillary ligations in similar metal complexes, their symmetry, and their catalytic reactivity. To estimate these effects, a comparison study in the polymerization of propylene was performed using complexes **1**−**3**, and the results are shown in Table 1.

As well as complex **1**, complexes **2** and **3** were found to be active in the polymerization of propylene only at high pressure. The polymerization activities for all these complexes in toluene are somewhat larger than those obtained in dichloromethane (compare entries 2 and 4, 6 and 8, 9 and 10). In CH_2Cl_2, at the Al:Ti molar ratio of 500, the activity of **1** is smaller than that of complex **2** (entries 1 and 5), whereas at Al:Ti = 1000 the activities of all precatalysts in this solvent were found to be alike (entries 2, 6, and 9). In toluene, the polymerization activities of the complexes also differed insignificantly. These results induce us to consider that possible *similar active species* are operative in the polymerization process regardless of the starting materials.

For all the complexes, the elastomeric polypropylene produced in toluene has somewhat higher molecular weight than the polymers formed in dichloromethane. In addition, the polymers were characterized by a wide polydispersity. Raising the MAO concentration in the catalytic mixture decreases the molecular weights of the polymers and increases their molecular weight distribution. This result normally indicates that the aluminum transfer mechanism is operative, inducing the lower molecular weights fractions. However, according to the ^{13}C NMR analysis of all the obtained polymers, the double-bond chain-end signals were found to be characteristic for a β-hydrogen elimination process.[13] Interestingly, for corresponding zirconium benzamidinate complexes we have shown that the chain termination pathway involves β-methyl elimination.[7a,b] The formation of lower molecular weight polymers is therefore a result of the formation of different species with probably different activity, inducing higher molecular weight distributions.

Despite the different structural features of the used precatalysts, *the molecular weights of the polymers created under the same conditions were unexpectedly found to be alike* (compare entries 2, 6, and 9 for CH_2Cl_2, or 4, 8, and 10 for toluene). As regards the stereoregularity of the monomer insertion, augmen-

(12) Yoder, J. C.; Bercaw, J. E. *J Am. Chem. Soc.* **2002**, *124*, 9.
(13) Resconi, L.; Piemontesi, F.; Franciscono, G., Abis, L.; Fiorani, T. *Organometallics* **1992**, *114*, 1025.

Table 2. Data for the Fractionation of the Polymers PP-1 and PP-2, Obtained in Entries 4 and 8 (Table 1): Properties of the Hexane-Soluble (PP-HS) and Hexane-Insoluble (PP-HI) Polymeric Fractions

sample	wt %	M_w	mwd	*mmmm*, %
PP1 (whole polymer)	100	59 000	3.1	10.9
PP1-HS	98.2	55 000	3.2	10.0
PP1-HI	1.8	238 000	3.3	74.4
PP2 (whole polymer)	100	58 000	3.8	11.9
PP2-HS	96.7	56 000	3.1	10.0
PP2-HI	3.3	216 000	3.6	74.5

tation of the MAO concentration results in similar isotacticities for the polymers created by complex **1** in CH_2Cl_2 and in a slight decrease in stereoregularity for the polymers produced by complex **2**. The high polydispersity of the obtained polypropylenes, which is presumably a consequence of the presence of various active species, producing polymers with a wide spectrum of molecular weights and different tacticities, encouraged us to perform fractionations of the whole polymers using refluxing hexane, and the results are given in Table 2.

The data of Table 2 show that the main part (97−98%) of polypropylene is a hexane-soluble (HS) fraction. The molecular weight of the HS fraction for **PP-2** (polymer obtained by complex **2**) is equal to that of the polymer **PP-1** (polymer obtained by complex **1**). For both polymers, the isotacticities of the hexane-soluble and, accordingly, hexane-insoluble fractions were found to be also *equal*.

The results of the fractionation of the polypropylenes **PP-1** and **PP-2** confirm the compositional heterogeneity of the polymers, which were found to be a mixture mostly consisting of an elastomeric fraction, with properties similar to elastomers described by Resconi[14] (hexane-soluble fraction), and a high molecular weight polymeric fraction with larger isotacticity (hexane-insoluble fraction). It is important to point out that the tacticity of the hexane-soluble fraction was found to be similar to that observed for Resconi's elastomeric polymers;[12] however, the MW was noticeably lower. One possible reason for the elastomeric behavior of such low tacticity and low MW polymers is the presence of comparatively large amounts of ethyl and butyl fragments, formed as a result of misinsertions, as found for α-diimine late transition metal complexes in the polymerization of propylene.[15]

The ^{13}C NMR spectra of the different polymeric fractions are presented in Figure 1. As can be concluded from Figure 1, the NMR characterization of different polymer fractions indicates that the hexane-soluble fractions of samples **PP-1** and **PP-2**, as well as the hexane-insoluble fractions, are almost identical as regards the activity, tacticity, and stereoerrors. Moreover, the comparison of the pentad and triad distribution for the soluble fractions of **PP-1** and **PP-2** (Table 3) shows also absolute similarity of these samples.

To explain these unexpected similarities, it is conceivable that during the polymerization process the different complexes undergo rearrangements, forming equal number of species, similar in their structure, which are active for the polymerization reaction. To corroborate this hypothesis, one of such active species was postulated to be the corresponding aluminum benzamidinate complex that can be formed as a result of the interaction of the studied titanium benzamidinates with methylalumoxane. To confirm experimentally this assumption, the
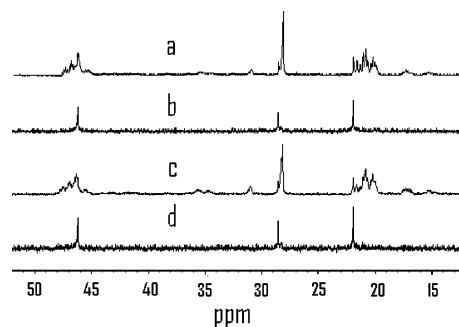
(14) Resconi L.; Jones, R. L.; Rheigold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

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

Figure 1. ^{13}C NMR spectra of different fractions of polypropylenes **PP-1** and **PP-2**: (a) **PP-1**, hexane-soluble fraction; (b) **PP-1**, hexane-insoluble fraction; (c) **PP-2**, hexane-soluble fraction; (d) **PP-2**, hexane-insoluble fraction. All polymers were obtained with the same equimolar amount of the corresponding catalysts, 6 mL of toluene, Ti:Al = 1:1000, RT, 4 h, 10.2 atm propene.

Table 3. Pentad and Triad Distribution for Hexane-Soluble Fractions of PP-1 and PP-2

pentad analysis	**PP-1**, %	**PP-2**, %
mmmm	10.2	10.0
mmmr	9.9	8.5
rmmr	5.2	4.8
mmrr	11.5	11.2
mmrm+rmrr	20.5	21.9
mrmr	10.3	10.1
rrrr	8.1	9.8
rrrm	12.4	13.1
mrrm	10.9	10.6
triad analysis	**PP-1**, %	**PP-2**, %
mm	25.3	22.3
mr	43.3	43.2
rr	31.4	34.5

aluminum benzamidinate dichloride (**6**) and dimethyl (**7**) complexes were synthesized by the reaction of the lithium benzamidinate ligand [η-C_6H_5-C(NSiMe_3)_2Li] with $AlCl_3$ or the reaction of the neutral benzamidinate ligand [C_6H_5-C(=NSiMe_3)-(NSiMe_3)_2] with $AlMe_3$,[16] correspondingly (Scheme 1).

We have investigated the features of activation of complexes **1** and **2** with methylalumoxane followed by ^{29}Si NMR, discriminating various species formed at different steps of the activation (Figure 2). The spectra obtained for those complexes were compared to the spectra of the aluminum benzamidinate complexes **6** and **7**.
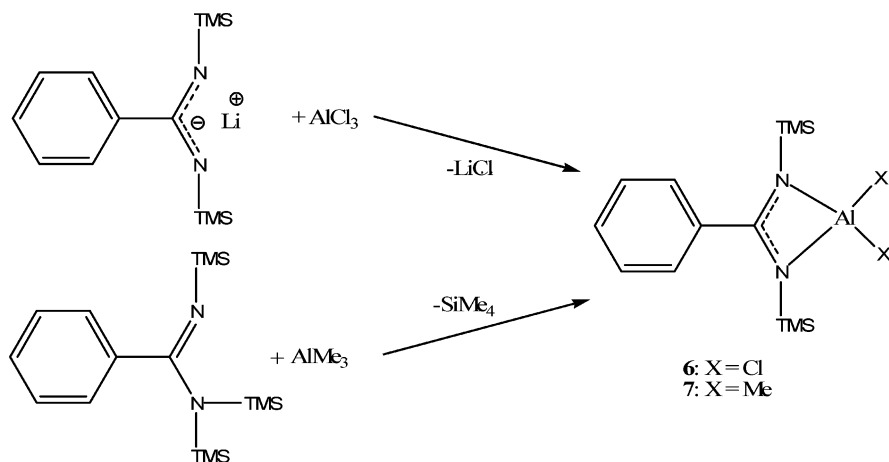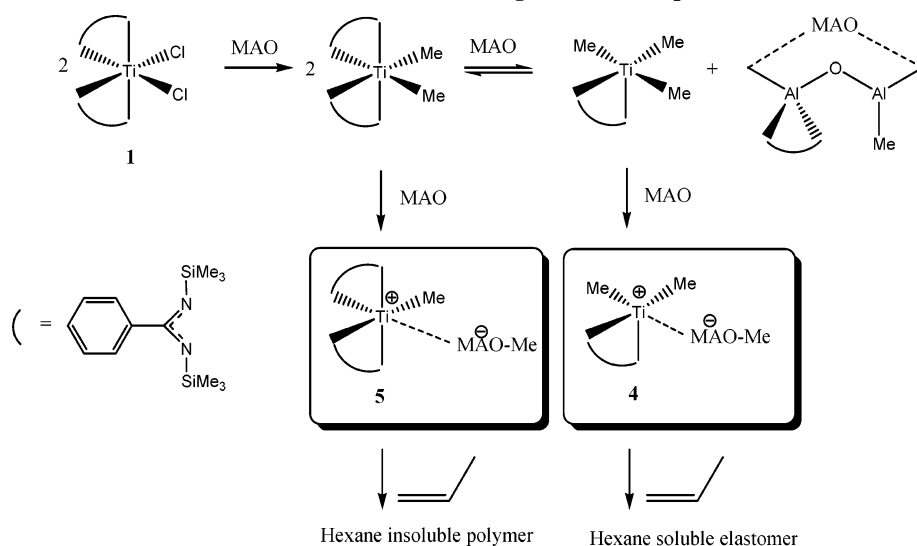
In Figure 2, the spectrum a exhibits the clean signal of the pure complex **1**. This signal has no matches with the signals obtained in spectrum b of complex **1** activated with MAO. It is important to point out that the central signals in spectrum b match the signal obtained in both spectrum c and d, corresponding to the aluminum dichloro benzamidinate (**6**) and dimethyl aluminum benzamidinate (**7**) complexes, respectively. Similarly, spectrum e of the pure complex **2** exhibits only one single signal, but after the addition of MAO (f) the same three signals as obtained with complex **1** (spectrum b) are observed (the intensities are somewhat different due to the amount of MAO used and the formation of Ti(III) species, vide infra). Hence, on the basis of our previous results for cationic bis-(benzamidinate) complexes,[7b,17] we can substantiate that the small signal at the lowest chemical shift in spectrum b belongs to the bis(benzamidinate) titanium methyl cationic complex, whereas the large signal at the highest magnetic field corresponds to the mono(benzamidinate) alkyl cationic complex.[15]

(16) For a similar synthesis see: Barker, J.; Aris, D. R.; Blacker, N. C.; Errington, W.; Phillips, P. R.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1999**, *586*, 138.

Scheme 1.   Synthesis of Aluminum Benzamidinate Complexes

6: X = Cl
7: X = Me

Scheme 2.   Plausible Rearrangement of Complex 1

Hexane insoluble polymer   Hexane soluble elastomer

The formation of the aluminum complex involves the metathesis of the benzamidinate ligand from the titanium complexes to the aluminum center at MAO. After adding a large concentration of MAO (>1:20 for complex **1** and >1:2 for

Figure 2. ^{29}Si NMR monitoring of the formation of new species from complexes **1** and **2** in toluene-d_8: (a) pure complex **1**, (b) complex **1** + MAO at a 1:20 respective ratio, (c) pure complex **6**, (d) pure complex **7**, (e) pure complex **2**, (f) complex **2** + MAO at a respective 1:1 ratio.[18]

complex **2**), all signals including the signals from the aluminum benzamidinate complexes disappeared from the spectra. This behavior was found to be a result of the formation of Ti(III) species, which were indicated using ESR analysis (vide infra).

The activities of complexes **6** and **7** in the high-pressure polymerization of propylene were found to be an order of magnitude less reactive ($\sim$0.5 × 10^4 g PP × mol Al^{-1} × h^{-1}) than for the corresponding titanium precatalysts **1** and **2**. The molecular weight, polydispersity, and tacticity of the elastomers produced by the aluminum benzamidinate complexes were also found to be close to the hexane-soluble (HS) polymeric fractions obtained by the titanium complexes. At the same time, the low activity of complexes **6** and **7** activated by MAO allowed us to conclude that the formation of the hexane-soluble fraction (more than 90% of the whole polymers produced by the catalytic systems **1**/MAO and **2**/MAO) that may be produced by species obtained by the partial migration of the benzamidinate ligand from Ti to Al is insignificant. Hence, the formation of the polydisperse hexane-soluble elastomeric polypropylenes mainly depends on the presence of the other two active intermediates (unless NMR-silent but catalytically active species are obtained).

The additional two signals on the ^{29}Si NMR spectra (Figure 2b,f) are representative of two different complexes, each of
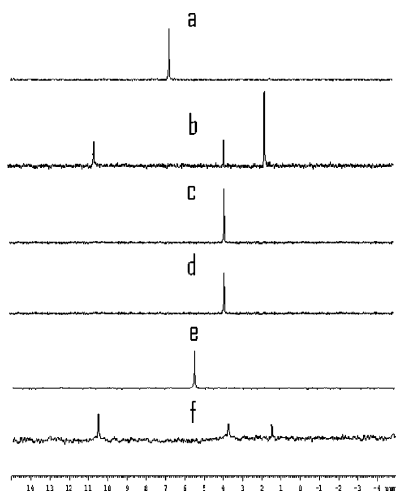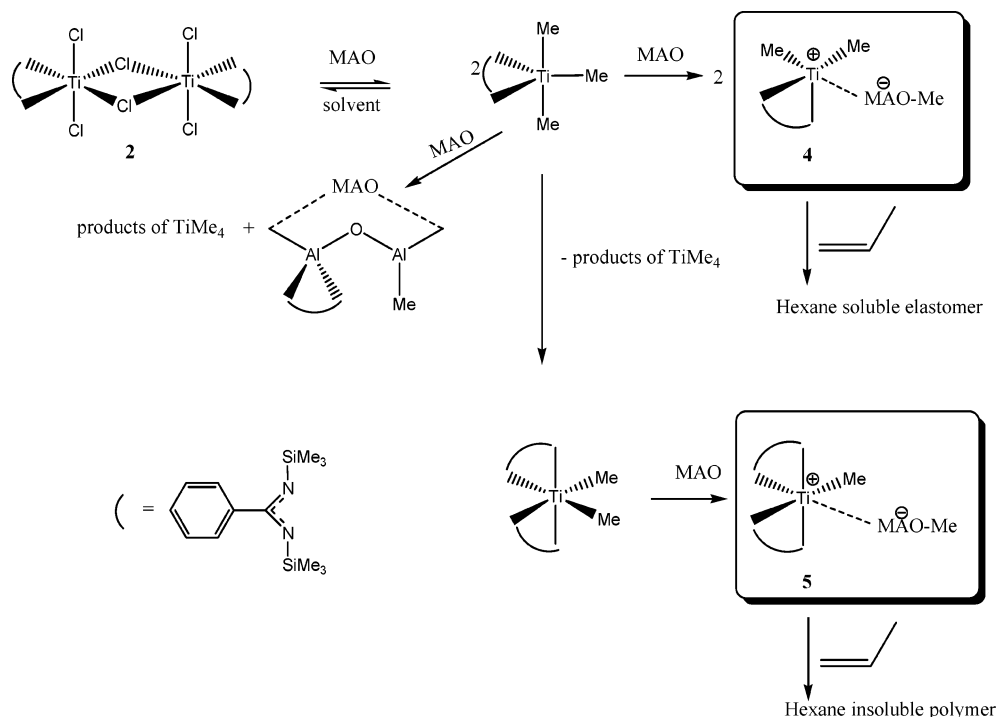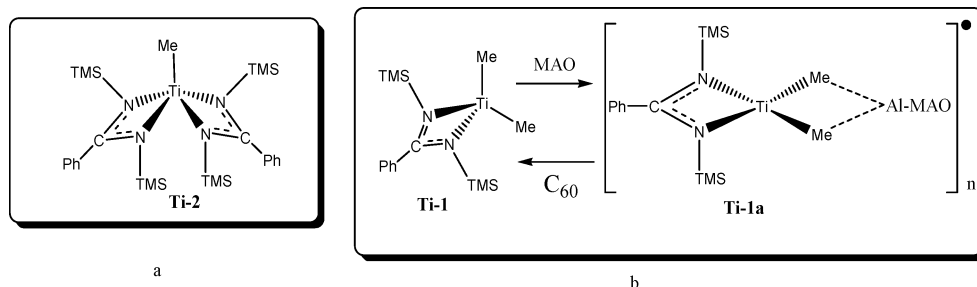
(17) Volkis, V. Benzamidinate Complexes as Active Catalysts for the Polymerization of α-Olefins and Silanes. Ph.D. Thesis. Technion−Israeli Institute of Technology, 2000.

Scheme 3. Plausible Mechanism for the Disproportionation of Complex 2

Scheme 4. Proposed Ti(III) Intermediates in the Activation of Complexes 1 and 2 with MAO

which is probably responsible for the formation of different fractions. Assuming that a bis(benzamidinate) titanium methyl complex, with C_2 symmetry, is responsible for the small isotactic hexane-insoluble fraction, a second monomeric mono(benzamidinate) titanium cationic alkyl complex must be responsible for the formation of the elastomeric hexane-soluble polymer.[19] Hence, it is reasonable that complex **2** rearranges the same as complex **1**, forming the same active species. Plausible mechanisms for the rearrangements for complexes **1** and **2** are described in Schemes 2 and 3.

The rearrangement mechanisms can be explained by elementary reactions well known for group 4 metal complexes.[20] In Scheme 2, the rearrangement of complex **1** starts with the formation of the corresponding dimethyl titanium bis(benzamidinate) complex by the reaction with MAO. The methide abstraction will form the cationic complex **5**, or if a metathesis is operative, one benzamidinate ligand will be transferred to the aluminum center, as observed in the ^{29}Si NMR. The

corresponding methide abstraction from the benzamidinate titanium trimethyl with MAO will yield the corresponding cationic complex **4**. In Scheme 3, the dimeric complex **2** reacts with MAO toward the monomeric complex in a fashion similar to that in the formation of complex **3**. Upon its reaction with MAO, this complex can induce either methide abstraction, forming complex **4**, or the metathesis reaction, eliminating TiMe$_4$ and producing the aluminum benzamidinate moiety. In addition, a ligand redistribution of the benzamidinate titanium trimethyl will produce also complex **1** and TiMe$_4$[5b,21] (a second possibility regards the ligand redistribution of the cationic titanium benzamidinate dialkyl complex, although if operative, it should be much slower).[5b,6e,22] The abstraction of a methide ligand from complex **1** with MAO will form complex **5**.

As mentioned above, in the reaction of either complex **1** or **2** with MAO some Ti(III) intermediates were found and characterized by ESR. Figure 3 illustrates the ESR of the intermediates formed, when MAO was added to the toluene solution of complex **1** at Ti:Al ratio 1:1000. The ESR spectra of the paramagnetic intermediates were measured at room temperature and at low temperatures as frozen glasses. The ESR

(18) The benzamidinate aluminum complexes (**6** and **7**) are unaffected by the presence of an excess of MAO. Moreover, the reaction of the neutral benzamidinate ligand with an excess of MAO exhibits the same ^{29}Si NMR signal, at 3.83 ppm, as obtained for complexes **6** and **7**.

(19) Low-temperature polymerization of monobenzamidinate titanium dialkyl cationic complexes has been shown to produce stereoregular syndiotactic polypropylene (*rr* = ~50%); see refs 19a,b.

(20) Bresler, L. S.; Ivanova, V. P.; Khachaturov, A. S. *Zh. Strukt. Khim.* **1976**, *17*, 257.

(21) Wu, Y.-D.; Peng, Z.-H.; Chan, K. W. K.; Liu, X.; Tuinman, A. A.; Xue, Z. *Organometallics* **1999**, *18*, 2081.

(22) (a) Liguori, D.; Centore, R.; Tuzi, A.; Grisis, F.; Sessa, I.; Zambelli, A. *Macromolecules* **2003**, *26*, 5451. (b) Liguori, D.; Grisis, F.; Sessa, I.; Zambelli, A. *Macromol. Chem. Phys.* **2003**, *204*, 164.
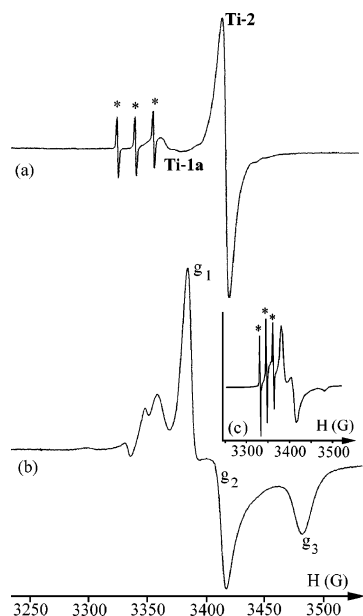
Figure 3. ESR characterization of complex **1** activated by MAO in toluene: (a) at room temperature (for determination of g-factor spectrum recorded with 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO), $g = 2.0059$, the three lines of TEMPO marked by stars); (b) at 150 K without TEMPO; (c) at 170 K with TEMPO.

spectrum at 290 K (Figure 3a) illustrates two single isotopic signals: a minor signal with an upfield shifted g-factor (compared to organic radicals) at $g_{iso} = 1.982$ (**Ti-1a**) (line width = 26.0 G) and a major signal, at $g_{iso} = 1.959$ (**Ti-2**) (line width = 8.3 G). The signal of the latter species (**Ti-2**) in frozen glass is characterized by a three-axis anisotropy of the g-factor,[23] which results in three ESR signals ($g_1 = 1.985$, $g_2 = 1.969$, and $g_3 = 1.927$), as shown in Figure 3b (Figure 3c shows the calibration at low temperature with TEMPO = 2,2,6,6-tetramethylpiperidine-N-oxyl). The observed strong anisotropy of the g-factor in frozen glasses and the low value of the g_{iso}-factor in solution are typically exhibited by paramagnetic Ti(III) complexes.[24] The broad resonance of the minor signal (**Ti-1a**) was found to have a weak anisotropy of the g-factor in frozen glass. This widening of the signal is normally a result of spin exchange processes within agglomeration of various titanium species, which probably contain aluminum from MAO (Scheme 4b). Intriguingly, a similar signal of aggregates has been observed by Baird et al. for Cp*TiCl₃ activated by MAO.[25] On the basis of the steric equivalence between cyclopentadienyl ligands and benzamidinates, it seems plausible that the structure of the agglomeration species involves only one benzamidinate ancillary ligand per metal center, as observed for the corresponding metallocenes.[22] Regarding the signal observed for the titanium species with the strong anisotropy, we can relate this signal to the trigonal bipyramidal intermediate **Ti-2**, with two benzamidinate ligands (Scheme 4a), having the three expected symmetry axes.[21a]

When the activation of complex **1** with MAO was performed in the presence of fullerene C_{60} (used as a radical-trapping
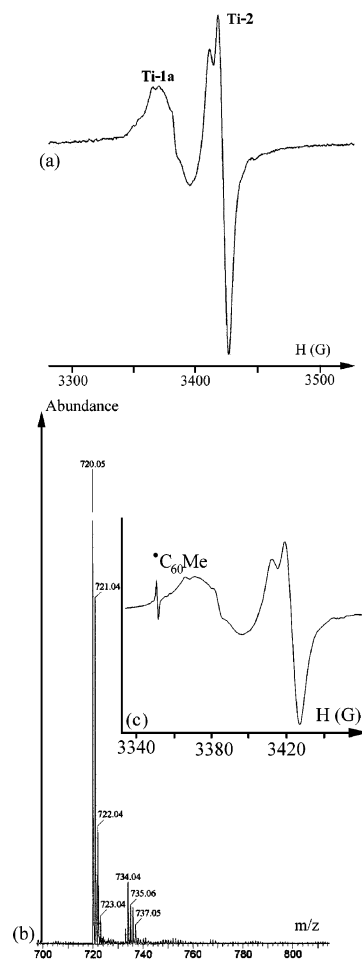

Figure 4. ESR and MALDI-TOF monitoring of the mixture of complex **1** with fullerene C_{60} activated by MAO: (a) ESR spectrum at 290 K in toluene, (b) MALDI-TOF spectrum, (c) ESR spectrum of the reaction mixture under visible light ($\lambda > 600$ nm).

agent),[23b] the intensity of the **Ti-1a** signal on the ESR was found to be higher (Figure 4a) compared with the same signal without the preaddition of C_{60}. This result indicates that the addition of C_{60} induces the formation (breaks or avoids the aggregates) of an additional intermediate maintaining its chemical nature due to the similar exhibited g-factor and the temperature anisotropy. The irradiation of this reaction mixture in the cavity of the ESR spectrometer by visible light ($\lambda > 600$ nm) gives rise only to reversible dissociation of the dimer of the fullerenyl radicals $MeC_{60}-C_{60}Me \rightleftharpoons 2\ {}^{\bullet}C_{60}Me$, and the corresponding signal was also observed (Figure 4c).[26] MALDI-TOF analysis shows one methyl radical trapped on one fullerene molecule (Figure 4b). The formation of the methyl radical is via the reduction of the dimethyl Ti(IV) complex with MAO, producing the Ti(III) and the methyl radical.

The ESR analysis of the active species, formed from complex **1** activated by MAO, without fullerene, at different steps of the polymerization reaction with propylene (performed in the NMR tube) shows that the intensity of the **Ti-2** species decreases

(23) Bolton, J. R.; Wertz, J. E. *Electron Spin Resonance: Elemental Theory and Practical Applications*; Chapman and Hall: New York, 1986.

(24) (a) Lukens, W. W.; Smith, M. R., III; Andersen, R. *J. Am. Chem. Soc.* **1996**, *118*, 1719, and references therein. (b) Bonoldi, L.; Abis, L.; Fiocca, L.; Fusco, R.; Longo, L.; Simone, F.; Srea, S. *J. Mol. Catal. A: Chem.* **2004**, *219*, 47. (c) Ye, Z.; Wang, W.-J.; Zhu, S. *J. Appl. Polym. Sci.* **2003**, *89*, 2474. (d) Pattiasina, J. W.; Heeres, H. J.; van Bolhuis, F.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *Organometallics* **1987**, *6*, 1004.

(25) Williams, E. F.; Murray, M. C.; Baird V. C. *Macromolecules* **2000**, *33*, 261, and references therein.

(26) (a) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1184. (b) Tumanskii, B. L.; Kalina, O. G. *Radical Reactions of Fullerenes and Their Derivatives*; Kluwer Academic Publishers: Dordrecht: The Netherlands, 2001. (c) Taylor, R. *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*; Imperial College Press: London, 1999.
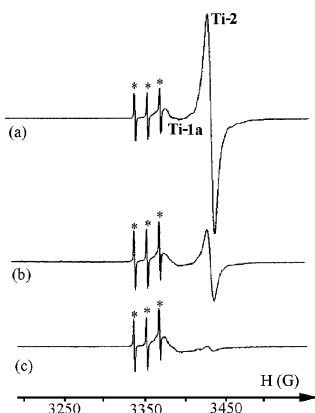
Figure 5. ESR monitoring of the active species formed from complex **1** during propylene polymerization reaction in a ESR tube: (a) before polymerization, (b) after two back-fillings, (c) after six back-fillings (lines of TEMPO marked by stars).
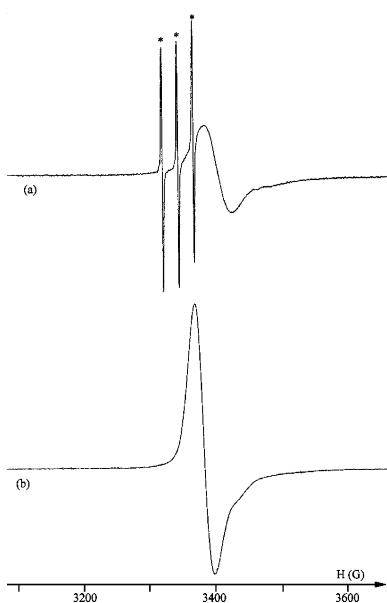

Figure 6. ESR monitoring of complex **2** activated by MAO in toluene: (a) at room temperature (lines of TEMPO marked by stars), (b) at 150 K.

very rapidly during the polymerization (Figure 5). The signal of **Ti-1a** remains unchangeable, indicating that this kind of species is not active in the polymerization process. After six fillings of the ESR tube (see Experimental Section), the **Ti-2** species completely disappeared from the spectrum, forming the polymer and regenerating Ti(IV) species.[27]

When the same reaction was carried out in the presence of C_{60} as a function of the addition of propylene, the same trend was obtained. The signal of **Ti-2** totally disappeared but the signal of **Ti-1a**, which was obtained with relative high intensity (Figure 4a), was reduced to the same intensity as observed without fullerene. This result indicates that some of the nonagglomerate species (proposed to be **Ti-1**) observed in the signal of **Ti-1a** are oxidized to Ti(IV).[24]

Similar ESR studies were also performed for complex **2**. In contrast to complex **1**, and to corroborates the formation of the presumably mono(benzamidinate) species (**Ti-1** and/or **Ti-1a**), the activation of complex **2** with MAO in toluene induces the

(27) For other Ti(III) octahedral allylic complexes that are oxidized to Ti(IV) by propene during the polymerization, see: Ray, B.; Neyroud, T. G.; Kapon, M.; Eichen Y.; Eisen, M. S. *Organometallics* **2001**, *20*, 3044.
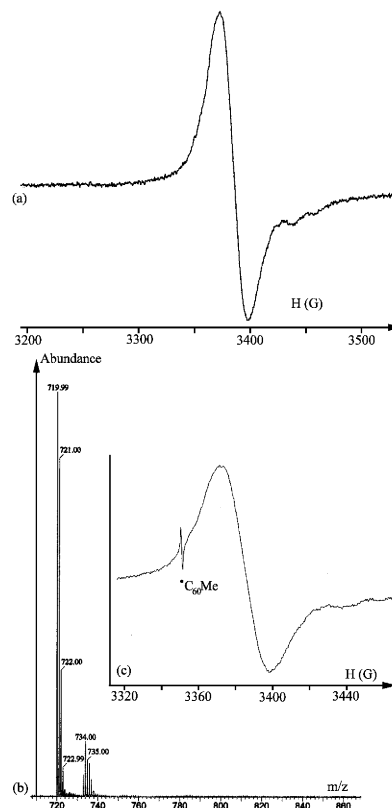

Figure 7. ESR and MALDI-TOF monitoring of the mixture of complex **2** with fullerene C_{60} activated by MAO: (a) ESR spectrum at 290 K in toluene, (b) MALDI-TOF spectrum, (c) ESR spectrum of reaction mixture under visible light ($\lambda > 600$ nm).
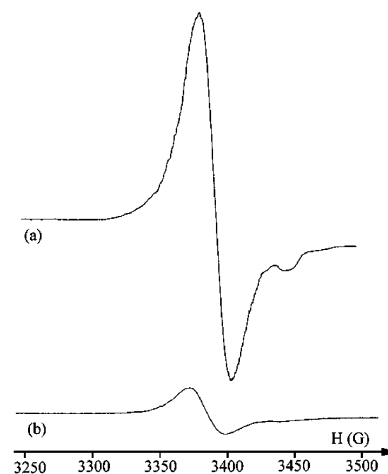

Figure 8. ESR monitoring of the active species formed from complex **2** during propylene polymerization reaction: (a) before polymerization, (b) after two back-fillings.

formation of a large **Ti-1** and **Ti-1a** ESR signal having temperature behavior similar to that of the same signal obtained in the activation of complex **1** (Figure 6). The signal of **Ti-2** is absent from this ESR spectrum, indicating that no disproportionation is obtained from the cationic complexes. The presence of the fullerene C_{60} did not affect the activation of complex **2** (compare ESR in Figures 6 and 7). In addition, the irradiation of the ESR tube with visible light allows, as shown before, the production of the C_{60}-Me radicals, as observed in the ESR (Figure 7c). MALDI-TOF characterization of such samples also showed the methyl radicals trapped on the fullerene (Figure 7b).
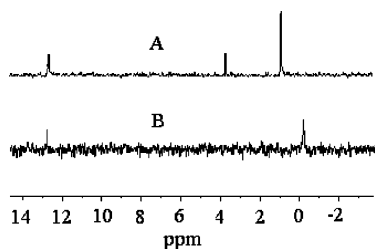
Figure 9. ^{29}Si NMR of the active species formed from complex **1** with C_{60} activated by MAO; effect of propylene: (A) before polymerization, without fullerene, at Ti:Al ratio 1:20, (B) after the beginning of polymerization, Ti:Al ratio 1:1000, in the presence of fullerene.

It is important to point out that the intensity of the ESR signal of **Ti-1a/Ti-1** obtained in the activation of complex **2** with MAO decreases after the addition of propylene, and a small signal equal in intensity to the signal of **Ti-1a** found for complex **1** remains regardless the amount of propene added (Figure 8). This result corroborates that in the activation of complex **2** the proposed mono(benzamidinate) titanium trimethyl intermediate is reduced to the corresponding mono(benzamidinate) Ti(III) species (**Ti-1** in Scheme 4b), which can react with MAO, forming additional agglomerates (**Ti-1a**). With propylene, the species **Ti-1** is oxidized to Ti(IV), producing the expected polymer, whereas the signal of the agglomerated inactive species **Ti-1a** is unaffected.

Comparison of the polymerization results for complexes **1** and **2** under regular conditions in the presence of fullerene C_{60} as a radical-trapping agent (added after the activation with MAO) shows no difference in activity. This allows us to conclude that all observed Ti(III) intermediates have very low polymerization activity if at all operative, or are produced and transformed to corresponding Ti(IV) species when exposed to propene. Interestingly, when fullerene C_{60} was added to complex **1** before its activation with MAO, the resultant catalytic system produced only 2% of the polypropylene, as compared to the corresponding polymerization without fullerene. The polymer was characterized as an isotactic solid (*mmmm* = 75% and broad mp, starts at 144, max at 151.2 °C; narrow crystallization signal at 112 °C, ΔH_m = 272 J/mol). It is remarkable that the 2% is exactly the same amount of the hexane-insoluble fraction of polypropylene that resulted under regular conditions!! Hence, it seems plausible that C_{60} can coordinate to the mono(benzamidinate) complex **4** (eq 6), impeding the insertion of propene, whereas due to steric hindrance in complex **5**, containing two benzamidinate ligands, this coordination is not operative and the stereoregular polymer is obtained.
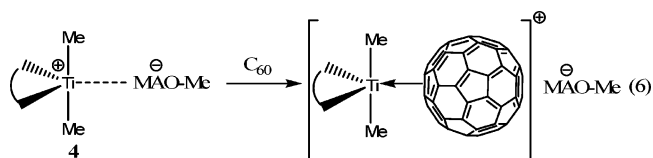
In parallel, we have followed the activation of the titanium benzamidinate complexes in the presence of fullerene using also ^{29}Si NMR. For example, when fullerene was added to complex **1** before the activation by MAO, two ^{29}Si signals from Ti-centered species were observed only after the addition of propylene (Figure 9). The downfield signal is exactly at the same chemical shift as obtained for complex **5**, whereas the second signal was obtained upfield shifted by ∼2.0 ppm, as expected for complex **4** upon coordination with C_{60}.

The thermal, mechanical, and rheological properties of the polymers **PP-1** and **PP-2** were also investigated. The purified nonfractionated polymers were found to be similar in their processability. Polymer **PP-1** or **PP-2** produced by complex **1** or **2**, respectively, activated with MAO was easily processed on roll mills at 100−120 °C and compression molded at 100 °C.

DSC thermograms of the polymers are smooth, showing no thermal effects on heating or cooling in the range 30−190 °C, thus indicating a low-crystalline structure of the samples.

As may be seen from the DMTA curve for **PP-1** (Figure 10a), there is a monotonic gradual decrease of the storage modulus (G') with the temperature increase in the range −50 to −10 °C, followed by an abrupt drop indicative of the glass transition. The single strong peak on tan δ versus temperature at about 0 °C (characteristic for the polypropylene glass transition), together with the 3 orders of magnitude decrease of G'', is evidence of the mainly amorphous structure of the tested polymer.

The rheological behavior of the polymers is represented by shear viscosity versus shear rate dependencies at 180 °C obtained from the oscillatory tests (Figure 10b). In the molten state, the polymer demonstrates typical viscoelastic rheological behavior. Both the storage (G') and loss (G'') modulus increase with the oscillation frequency. In the studied frequency range, G', a measure of the elastic properties, rises with the frequency faster than G'', as a result of viscous properties. Thus, with the frequency increase, the melts become more elastic. At low oscillation frequency (low shear rate), the melts show liquidlike behavior ($G'' > G'$), typical for molten non-cross-linked thermoplastics. For the sample **PP-1** the G'/G'' crossover probably occurs at higher frequency, beyond the studied range.

The complex viscosity (η*) of the melts (Figure 10b), a measure of their overall resistance to flow, was also found to be similar for both polymers **PP-1** and **PP-2**. η* changes with
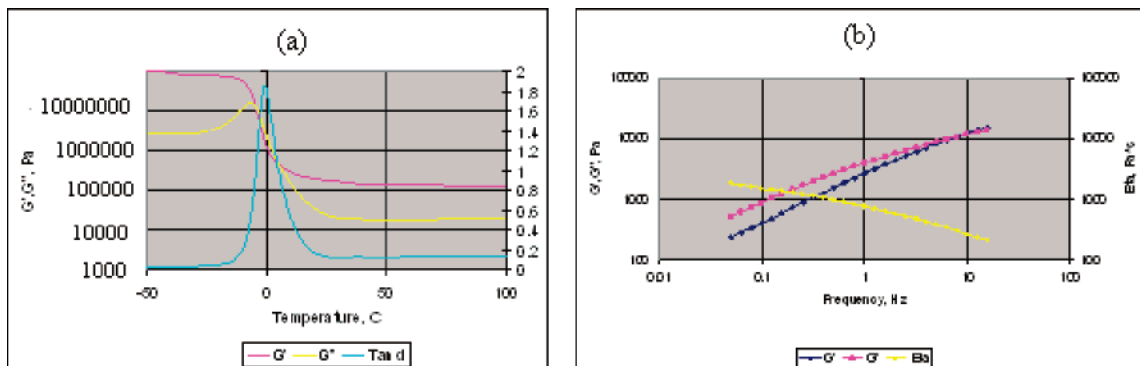

Figure 10. DTMA thermogram for the polypropylene **PP-1** (a) and frequency dependences of the storage and loss moduli, and of the complex viscosity for the blend of polymer **PP-1** measured at 180 °C (b).

the shear rate, demonstrating behavior typical for molten polymers: Newtonian plateau in the range of low frequencies and decrease of viscosity with increasing of shear rates (non-Newtonian behavior).

Conclusion

The catalytic properties of the monomeric titanium bis(benzamidinate) $[\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]_2TiCl_2$ (**1**), the dimeric titanium mono(benzamidinate) $\{[\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]TiCl_3]\}_2$ (**2**), and the monomeric titanium mono(benzamidinate) complex $\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]TiCl_3\cdot THF$ (**3**) activated by MAO were studied in the polymerization of ethylene and propylene. Being similar by their chemical nature, but different by their space symmetry and number of ligations surrounding the metal center, complexes **1**−**3** were expected to exhibit diverse reactivities and stereoselectivity in the polymerization of α-olefins. Unexpectedly, the catalytic behavior of all complexes was found to be similar in the polymerization of ethylene and propylene. Moreover, the difference in properties of the resultant polymers produced by the different benzamidinate complexes (tacticities, fractional composition, molecular weight, and viscoelastic and rheological properties) was found to be insignificant. Fractionation of the polymers shows the formation of a solid isotactic hexane-insoluble minor fraction and an elastomeric hexane-soluble major fraction. The hexane-soluble fractions of all samples, as well as the hexane-insoluble fractions, were almost identical as regards their properties. These unexpected similarities are explained via likely rearrangements of the complexes, forming an equal number of species, similar in their structure, that are active for the polymerization reaction. Aluminum benzamidinate complexes were synthesized and are also obtained in the reaction of the titanium complexes with MAO, but their contribution to the total amount of polymer is very small.

The activation of complexes **1** and **2** by MAO was followed by ^{29}Si NMR, which discriminated between various species (complexes **4** and **5**) formed at different steps of the activation. In addition to species **4** and **5**, during the activation of either complex **1** or **2** with MAO some Ti(III) intermediates were found and characterized by ESR at room temperature and in frozen glasses. Trapping experiments with C_{60}, ESR studies, MALDI-TOF spectroscopy, and NMR showed that Ti(III) complexes are not active in the polymerization but rather are oxidized by propene to Ti(IV), similar to other Ti(III) allylic complexes.[24]