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Active Intermediates of Ethylene Polymerization over 2,6-Bis(imino)pyridyl Iron Complex Activated with Aluminum Trialkyls and Methylaluminoxane

Konstantin P. Bryliakov,*[,†,‡] Nina V. Semikolenova,[†] Vladimir A. Zakharov,[†] and
Evgenii P. Talsi[†,‡]

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090,
Pr. Lavrentieva 5, Novosibirsk, Russian Federation, and
Department of Natural Sciences, Novosibirsk State University,
630090, Novosibirsk, ul. Pirogova 2, Russian Federation

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Summary: The intermediates of olefin polymerization over homogeneous catalysts based on bis(imino)pyridine iron(II) chloride (LFeCl$_2$, L = 2,6-bis[(1-2,6-dimethylphenylimino)ethyl]pyridine) with different activators (trimethyl-, triisobutyl-, trioctylaluminum and MAO) have been studied by ^{1}H and ^{2}H NMR. In conditions approaching real polymerization, neutral species of the type [LFe(II)Cl(μ-R)$_2$AlR$_2$] or [LFe(II)R(μ-R)$_2$AlR$_2$] dominate in the reaction solution in LFeCl$_2$+AlR$_3$ systems, whereas in LFeCl$_2$/MAO systems, ion pairs [LFe(II)(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$ (at Al/Fe < 200) and [LFe(II)(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (at Al/Fe > 500) are the predominant species.

In recent years, new active bis(imino)pyridine iron(II)-based catalysts for ethylene polymerizaion have attracted considerable interest. Upon acivation with methylaluminoxane (MAO)[1−4] or trialkylaluminum compounds,[5−10] these complexes yield high-density linear polyethylene. Attempts to understand the mechanism by which these catalysts operate have been reported in the literature.[7,11−14] On the basis of close similarity of the ^{1}H NMR spectra observed upon activation of LFeCl$_2$ (**1**, Scheme 1) catalyst {L = 2,6-bis[(1-2,6-dimethylphenylimino)ethyl]pyridine} with AlMe$_3$ in CH$_2$Cl$_2$ and with MAO in toluene, it was assumed that similar neutral intermediates (rather than ion pairs) are formed in catalytic systems **1**+AlMe$_3$ and **1**+MAO.[7]

In this work, we have found that the above occasional similarity is observed only if AlMe$_3$ is dissolved in CH$_2$Cl$_2$ and MAO in toluene. When toluene is used as a solvent for both activators, formation of quite different intermediates, **1**+AlMe$_3$ and **1**+MAO systems, is clearly seen. We report here a ^{1}H and ^{2}H NMR spectroscopic study of the intermediates formed upon activation of **1** with AlMe$_3$, Al(iBu)$_3$, and Al(nOct)$_3$ in comparison with those formed with MAO.

Results and Discussion

^{1}H NMR Spectra of the Systems 1+MAO and 1+AlR$_3$. Interaction of **1** with MAO (hereinafter in spectroscopic studies the sample of MAO-3 containing 1 mol % of Al as AlMe$_3$ was used, see Experimental Section) and AlR$_3$ was investigated by ^{1}H and ^{2}H NMR in toluene-d_8 and toluene in the temperature range −60 to +35 °C. The ^{1}H NMR spectrum of the starting complex **1** was well described in an earlier work of ours.[7] Peak assignment was done based on relative intensities of the peaks and line widths (the latter correlates with the proximity to the paramagnetic center).[7,14] Upon interaction with MAO, **1** converts into new species **2** (at Al/Fe ratios of 10−200) and **3** (at Al/Fe ratios of 500−1000). The ^{1}H NMR data for complexes **2** and **3** can be found in Figure 1 and Table 1. In toluene solution (i.e., in the solvent used in polymerizations), they are stable at room temperature for hours. Both **2** and **3** are heterobinuclear species with the AlMe$_2$ moiety bound to complex **1** by Me or Cl bridges (Scheme 2). The assignment of the AlMe$_2$ peak (denoted as X) was confirmed by ^{2}H NMR spectra in the experiments with deuterated MAO and Al(CD$_3$)$_3$. The ionic structures for **2** and **3** could be reasonably assumed on the basis of similarity of the ^{1}H NMR spectrum of **2** with that for complex **2′** ([LFe(II)(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$) observed in the **1**+AlMe$_3$+CPh$_3$B(C$_6$F$_5$)$_4$ system, for which formation of ion pairs should be expected (Table 1).[7]

Previously, complex **3** was erroneously assigned to neutral species of the type **4** (Scheme 2) on the basis of close similarities of the observed ^{1}H NMR spectra of catalytic systems **1**+AlMe$_3$ in CH$_2$Cl$_2$ and **1**+MAO in

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* Corresponding author. Fax: +7 3832 34 3766. E-mail: bryliako@catalysis.nsk.su.
[†] G. K. Boreskov Institute of Catalysis.
[‡] Novosibirsk State University.

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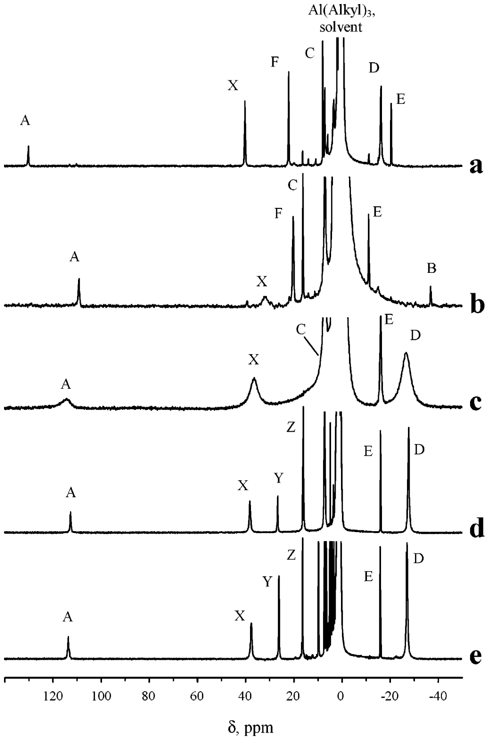

Figure 1. ^{1}H NMR spectra (toluene-d_8, 20 °C) of complexes **2**–**6** formed upon interaction of **1** with different activators: (a) MAO, Al:Fe = 100; (b) MAO, Al:Fe = 1000; (c) Al_2Me_6, Al:Fe = 30; (d) Al(iBu)$_3$, Al:Fe = 30; (e) Al(nOct)$_3$, Al:Fe = 30. The reason for line broadening with $AlMe_3$ (c) is not clear.

toluene,[7] assuming that ionic intermediates in the reaction of **1** with $AlMe_3$ could not be formed. The comparison of NMR spectra of intermediates in one and the same solvent (toluene) was not done in the previous publication due to broadening of NMR peaks of the **1**/$AlMe_3$ system in toluene (in contrast to the **1**/$AlMe_3$ system in CH_2Cl_2). In this paper, we have found that, irrespective of this broadening, reliable ^{1}H NMR data for the intermediate formed in the **1**/$AlMe_3$ system in toluene could be obtained (Figure 1c and Table 1). Peaks observed in the **1**/$AlMe_3$ system in toluene were similar to those detected in the other **1**/AlR_3 systems and dramatically differed from those for intermediates **2** and **3** formed in the **1**/MAO system (especially peaks B and F in the very low and very high field, which were not observed in the **1**/MAO system (Table 1)). Thus, we assume that a neutral species is formed in the **1**/$AlMe_3$ system L(Me)Fe(II)(μ-Me)$_2$AlMe$_2$ or L(Cl)Fe(II)(μ-Me)$_2$AlMe$_2$ (**4**) and cation-like intermediates [LFe(II)(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$ (**2**) and [LFe(II)(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**3**) are formed in the **1**/MAO system. The reason for the confusing close similarities of NMR spectra of **1**/$AlMe_3$ in CH_2Cl_2 and **1**/MAO in toluene is still obscure. Nevertheless, it is clear that various intermediates are formed in **1**/$AlMe_3$ and **1**/MAO systems in toluene.

The assignment of the $AlMe_2$ peak (denoted as X) and the Fe-Me-Al peak of **4** was confirmed in the experiments with Al(CD_3)$_3$, by ^{2}H NMR spectra (see footnotes for Table 1). The number of $AlMe_2$ protons of **4** could be reliably determined from integration of corresponding intense and distinct ^{1}H NMR peak X in comparison with corresponding peaks of L (all peaks of L with corresponding integral intensities were detected). The number of bridging Fe-Me-Al protons of **4** could be determined from integration of the corresponding ^{2}H NMR peak at 630 ppm in comparison with that of $AlMe_2$ at 36 ppm (the obtained ratio was 1:1). The terminal Fe-Me group of **4** was not detected spectroscopically. Thus, on the basis of ^{1}H and ^{2}H data, we cannot discriminate between the structures L(Me)Fe(II)(μ-Me)$_2$AlMe$_2$ and L(Cl)Fe(II)(μ-Me)$_2$AlMe$_2$ for complex **4**. However, in general terms, the structure of **4** (L(Me)Fe(II)(μ-Me)$_2$AlMe$_2$ or L(Cl)Fe(II)(μ-Me)$_2$AlMe$_2$) is determined reliably. In the case of the **1**/MAO system, the formation of cation-like species [LFe(II)(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$ (**2**) and [LFe(II)(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**3**) was proposed on the basis of various NMR patterns for **2**, **3** (**1**/MAO system), and **4** (**1**/$AlMe_3$ system) and the similarity of the ^{1}H NMR spectrum observed for **2** and that of the species formed in the **1**/$AlMe_3$/B(C_6F_5)$_3$ system (Table 1). The assumption that **3** is "more alkylated" than **2** is based on the fact that **2** is observed at low and **3** at high Al/Fe ratios.

Formation of mainly the heterobinuclear ion pair [LFe(II)(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**3**) upon activation of 2,6-bis(imino)pyridyl iron complex **1** with MAO at high Al/Fe ratios agrees well with corresponding data for metallocene/MAO systems where similar heterobinuclear ion pairs [L$'_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ or [L$'_2$Ti(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ strongly dominate in the reaction solution at high Al/Zr or Al/Ti ratios.[15,16] ^{1}H NMR spectra of heterobinuclear ion pairs are not sensitive to variations in the nature of their Me-MAO$^-$ counteranions, since the perturbing Me-MAO$^-$ anion is only in outer-sphere contact with the coordinatively saturated cation. Thus heterobinuclear ion pairs display one rather sharp NMR pattern.

We note that peaks B and F (in the very low and very high field, respectively) are common for all **1**+AlR_3 systems: the same signals are observed in ^{1}H NMR spectra of complexes **5** (formed in the **1**+Al(iBu)$_3$ system at Al/Fe ratios of 30–1000) and **6** (which was monitored in **1**+Al(nOct)$_3$ at Al/Fe ratios of 50 and 100) (Table 1). In the **1**+MAO system, these peaks were not observed, thus indicating formation of substantially different complexes in the **1**+MAO and **1**+AlR_3 systems, implying different electron spin density distribution. In the first case, formation of heterobinuclear ion pairs could reasonably be assumed, whereas in all **1**+AlR_3 systems, neutral heterobinuclear species are present. In contrast to the **1**+MAO system (where **2** converts into **3** with increasing Al/Fe ratio), in **1**+AlR_3 systems a single species of type **4**–**6** is observed in a wide range of Al/Fe ratios (Al/Fe = 15–100 for R = Me and nOct; Al/Fe = 30–1000 for R = iBu). Complexes **4** and **6** are stable for hours at room temperature, whereas **5** almost disappears within 10 min. Possible structures of the species formed are presented in Scheme 2.

Polymerization Studies. The data for polymerization activities of the **1**+MAO and **1**+AlR_3 systems at an Al/Fe molar ratio of 500 are compared in Table 2. In the polymerization conditions used, **1** demonstrated

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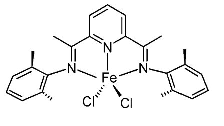
Table 1. Chemical Shifts (δ, ppm) in ^{1}H and ^{2}H NMR Spectra of Fe^{II} Complexes

complex, nucleus	solvent	T, °C	**A** (Py−H$_m$)	**B** (Py−H$_p$)	**C** (Ar−H$_m$)	**D** (Ar−Me)	**E** (Ar−H$_p$)	**F** (N=C(Me))	**X**	**Y**	**Z**
2,[a] ^{1}H	tol-d_8	20	130.2	NF[i]	7.9	−16.5	−20.5	21.6	40.2		
2′,[b] ^{1}H	CD$_2$Cl$_2$	10	141.8	NF	7.6	−23.2	−21.3	19.5	44.2		
3,[c] ^{1}H	tol-d_8	20	109.1	−37.0	16.1	NF	−11.2	20.2	31.9		
4,[d] ^{1}H	tol-d_8	20	114.3	358.3	ca. 8	−26.8	−16.1	−276.5	36.4		
4,[e] ^{2}H	tol-d_8	20							36.2 [f, g]		
5,[d] ^{1}H	tol-d_8	20	112.6	360.7	ca. 8	−27.8	−16.1	−277.1	38.1	26.6	16.9
6,[d] ^{1}H	tol-d_8	20	113.4	359.6	ca. 8	−27.2	−16.1	−277.1	37.4	25.9	16.1[h]

[a] At Al/Fe ratio of 100. [b] Complex **2′** observed in the **1**+AlMe$_3$+CPh$_3$B(C$_6$F$_5$)$_4$ system, adopted from ref 7. [c] At Al/Fe ratio of 1000. [d] At Al/Fe ratio of 30. [e] Experiment **1**+Al(CD$_3$)$_3$, Al/Fe = 30. [f] At low temperature, this peak splits into two signals: 47.8 and 60.5 at −60 °C. [g] The Fe-Me-Al peaks can be observed in the low field: 621.7 at −60 °C. [h] Multiple other peaks observed in the range 2−8 ppm. [i] NF, not found.

Scheme 1. Structure of Complex 1



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Scheme 2. Structures Proposed for Complexes 2−6

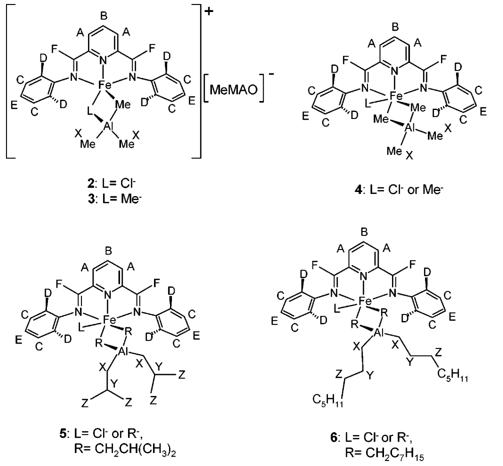

Table 2. Ethylene Polymerization over LFeCl$_2$ with Different Aluminum Organic Activators

no.	activator	activity kg PE/mol Fe·min·bar[a]	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1	MAO	490	13.5	45	3.3
2	AlMe$_3$	450	8.9	106	12
4	Al(iBu)$_3$	375	10.7	115	10.8
5	Al(n-octyl)$_3$	510	7.3	46	6.3

[a] Polymerization at 35 °C, in toluene, reaction time 15 min; [Fe] = 1.4 × 10^{-5} M, Al (cocatalyst)/Fe = 500(mol/mol) at ethylene pressure of 2 bar.

close activities with all activators. However, the stability of **1**+AlR$_3$ systems was lower in comparison with that of **1**+MAO: typically, the polymerization rate in the former system dropped ca. 5-fold within the first 15 min,[8] whereas the system **1**+MAO-3 exhibited high and stable activity for half an hour. The values of MM and MMD of the obtained polymer samples depend on the activator composition (Table 2). Polymer produced by the **1**+MAO system is characterized by narrower MMD, whereas for polymers obtained with trialkyl aluminum activators, MMD was noticeably broader. These data show that different active species are formed in the **1**+MAO and **1**+AlR$_3$ systems, although they exhibited close catalytic activities.

Intermediates **2**−**4** are stable in toluene at room temperature, while polymerization activity of the corresponding catalytic systems drops within several minutes. Probably, addition of monomer dramatically decreases the stability of iron intermediates. The rapid catalyst degradation could be partially responsible for broad MMD characteristics for the catalytic systems studied. One of the possible ways of iron catalyst degradation is the reduction of Fe(II) into Fe(I). Further studies are needed to verify this assumption.

The polymerization data show that the activities of **1**/MAO-3 and **1**/AlR$_3$ are very similar (Table 2). Thus, both "cation-like" complex **3** and neutral complexes **4**−**6** provide appropriate sites for monomer coordination, and the structures of the active sites for complexes **3**−**6** are rather close. It is reasonable to assume that the first step of polymerization is the replacement of AlR$_3$ in the coordination sphere of intermediates **3**−**6** by the monomer, followed by monomer insertion into the Fe−R bond. In this case one should expect a small difference in activity for various AlR$_3$. The small difference in activity of ion pair **3** and neutral species **4**−**6** could be explained in two different ways: (1) the activity of the Fe−R bond toward ethylene insertion is mainly determined by the nature of the tridentate bis(imino) pyridine ligand and is less affected by the nature of the fifth or sixth ligand; (2) after monomer insertion, complexes **3**−**6** convert into intermediates of very similar structures. Further studies are needed to clarify this question.

^{1}H NMR Monitoring of the System 1+Al(iBu)$_3$+C$_2$H$_4$. Recently, successful ^{1}H NMR observation of the polymeryl zirconium intermediates of polymerization was reported.[17,18] In this work, we studied the interaction of complex **5** with ethylene. After addition of ethylene to a liquid nitrogen frozen sample prepared from **1** and Al(iBu)$_3$ (Al/Fe = 100:1, ethylene/Fe = 20:1) and shaking at −40 °C, the ^{1}H NMR peaks of complex **5** were found to be broadened and slightly shifted, with a new peak at 14.2 ppm being observed (Table 3 and Figure 2). This could be attributed to the formation of ferrous complex with polymer ligand, having longer correlation times and hence wider resonances.[19] The previously unobserved paramagnetically shifted peak at 14.2 ppm could result from the protons of this growing polymer chain. At −40 °C, slow ethylene consumption

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Table 3. Chemical Shifts (δ, ppm) in ^{1}H NMR Spectra of Fe^{II} Complexes 5 and 5·polymer (5·p)

complex, nucleus	solvent	*T*, °C	**A** (Py−H$_m$)	**B** (Py−H$_p$)	**C** (Ar−H$_m$)	**D** (Ar−Me)	**E** (Ar−H$_p$)	**F** (N=C(Me))	**X**	**Y**	**Z**
5,[a] ^{1}H	tol-d_8	−40	152.3	463.7	NF[c]	−40.9	−23.3	−363.7	53.9	36.5	22.4
5·p,[a,b] ^{1}H	tol-d_8	−40	NF	NF	NF	−42.2	−27.4	NF	NF	NF	26.0

[a] At Al/Fe ratio of 100. [b] Peak of the growing polymer chain coordinated to the active iron species was observed at 14.2 ppm, ethylene peak at 5.39 ppm. [c] NF, not found.

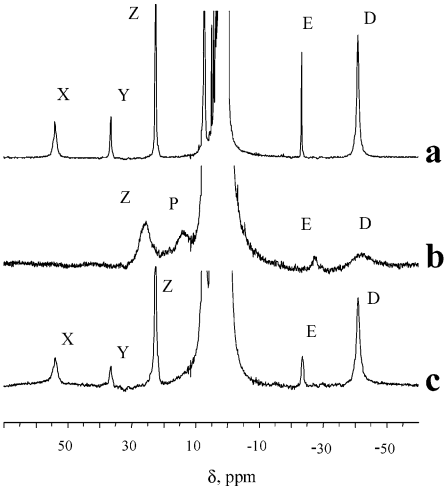

Figure 2. ^{1}H NMR spectra (toluene-d_8, −40 °C) of the system **1**+Al(iBu)$_3$ (Al/Fe = 100) (a); after addition of 20 equiv of ethylene and shaking the sample at −40 °C (b); and after warming to room temperature and repeated cooling to −40 °C (c). The broad peak marked as "P" probably corresponds to protons of the growing polymer chain coordinated to the active iron species.

was detected by the decrease of its ^{1}H NMR signal (5.39 ppm). After fast warming the sample to room temperature and repeated cooling to −40 °C, only narrow lines of the recovered species **5** were found, the peak at 14.2 ppm having disappeared and all ethylene being consumed. Apparently, after completion of the polymerization process, polymer ligand is replaced by AlR$_3$ to restore the active species **5**. This experiment supports the assumption that complex **5** is the precursor of the active site in the system **1**+Al(iBu)$_3$.

Conclusions

We have shown that neutral species **4**−**6** are formed in **1**+AlR$_3$ systems, whereas ion pairs **2** and **3** are formed in the **1**+MAO system. The structures of intermediates **2**−**6** could be determined from ^{1}H and ^{2}H NMR spectra. In conditions approaching real polymerization, only one ferrous complex dominates in particular catalytic systems: heterobinuclear ion pair **3** for the **1**+MAO system and neutral heterobinuclear complexes (**4**−**6**) for **1**+AlR$_3$ systems. Thus, in contrast to zirconocene/MAO[16,20] and titanocene/MAO[15] systems, where heterobinuclear and zwitterion-like ion pairs are the closest precursors of the polymerization active centers, for iron-based systems both heterobinuclear ion pair **3** and neutral heterobinuclear complexes **4**−**6** could be the active center precursors.

Experimental Section

General Procedures. Complex **1** was prepared as previously described.[21] Toluene-d_8 was dried over molecular sieves (4 Å), purified by refluxing over sodium metal, and distilled in dry argon. All solvents were stored and handled in a vacuum. All experiments were carried out in sealed high-vacuum systems using breakseal techniques. MAO-3 with total Al content of 40 wt % and 1 mol % of Al as AlMe$_3$[8] was obtained as a solid product by removal of the solvent in vacuo at 50 °C from commercial MAO (the latter was purchased from Witco). Al(nOct)$_3$ was purchased from Witco. Al(iBu)$_3$ and AlMe$_3$ were Aldrich commercial reagents. Al(CD$_3$)$_3$ was prepared as in ref 20, starting from CD$_3$I.

NMR Spectra. ^{1}H and ^{2}H NMR spectra were recorded using pulsed FT-NMR technique, on Bruker DPX-250 (at 250.13 MHz) and MSL-400 NMR (at 400.13 MHz) spectrometers, respectively, in cylindrical 5 mm glass sample tubes. Operating conditions: spectral width 125 kHz; spectrum accumulation frequency 2 Hz; number of transients 1000−10 000; 10−20° pulse at 1−2 μs (^{1}H) or 45° at 10 μs (^{2}H). The data were accumulated with 16−32K data points in the time domain. Chemical shifts were measured in ppm, with positive values in the low-field direction. For calculations of ^{1}H chemical shifts, the resonance of the CD$_2$H group of the toluene solvent was taken as 2.09 ppm (^{1}H).

Preparation of Samples for ^{1}H NMR. Calculated quantities of LFeCl$_2$ and activator (MAO, AlMe$_3$, Al(CD$_3$)$_3$, Al(iBu)$_3$, Al(nOct)$_3$) were combined in toluene under vacuum in NMR tubes and sealed off from a vacuum line. The samples were stored in liquid nitrogen and mixed at cooling prior to recording NMR spectra. If necessary, ethylene was added to liquid nitrogen frozen sample. Total Fe concentration was 0.001−0.004 M, and that of Al was 0.06−1 M, whereas Al/Ti ratios were in the range 15−1000.

Ethylene Polymerization Studies. Polymerization was performed in a steel 1 L autoclave. Complex **1** (0.001 g, 2.0 × 10^{-6} mol) was introduced into the autoclave in a vacuum-sealed glass ampule. The reactor was evacuated at 50 °C, cooled to 20 °C, and charged with the solution of a calculated amount of cocatalyst in 150 mL of toluene. After setting up the polymerization temperature (35 °C) and ethylene pressure (2 bar), the reaction was started by breaking off the ampule with the complex. During the polymerization time (15 min), ethylene pressure, stirring speed, and temperature were maintained constant. The experimental unit was equipped with an automatic computer-controlled system for ethylene feed and recording of the ethylene consumption.

Polymers MM and MWD Measurements. Weight-average (M_w) and number-average (M_n) molecular weights and molecular weight distributions (M_w/M_n) were obtained by the GPC method with a Waters-150 at 150 °C with trichlorobenzene as a solvent.

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Supporting Information Available: ^{1}H NMR spectra of **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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