Organometallics **2007,** *26,* 4810−4815

Activation of Bis(phenoxyimino)zirconium Polymerization Catalysts with Methylaluminoxane and $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$

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Received April 27, 2007

The intermediates of olefin polymerization over homogeneous catalysts based on bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride $\{(L^{^tBu})_2ZrCl_2\}$ (**1-^{t}Bu**), bis[*N*-(3-methylsalicylidene)-anilinato]zirconium(IV) dichloride $\{(L^{Me})_2ZrCl_2\}$ (**1-Me**), and bis[*N*-(salicylidene)anilinato]zirconium(IV) dichloride $\{(L^{H})_2ZrCl_2\}$ (**1-H**) with different activators {methylaluminoxane (MAO) and $AlMe_3/[CPh_3]^+$-$[B(C_6F_5)_4]^-$} have been studied by ^1H and ^{13}C NMR spectroscopy. Heterobinuclear ion pairs $[(L^{^tBu})_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$ (**2-^{t}Bu**) and $[(L^{^tBu})_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**2′-^{t}Bu**) are formed upon activation of **1-^{t}Bu** with MAO and $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$, respectively. These species are the precursors of the highly active intermediates of polymerization. In contrast, the activation of **1-Me** with MAO results mainly in the formation of the tight ion pair $[(L^{Me})_2ZrMe^+\cdots Me\text{-}MAO^-]$. This ion pair is the precursor to a poorly active intermediate of polymerization. In the catalytic systems **1-H**/MAO and **1-H**/$AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$, the aluminum ion pairs $[L^HAl(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+[Me\text{-}MAO]^-$ and $[L^HAl(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+[B(C_6F_5)_4]^-$, which were inactive in ethylene polymerization, are predominantly formed. The isomeric composition of **2′-^{t}Bu** is close to that of the initial complex **1-^{t}Bu**. The main route of the **1-^{t}Bu**/MAO catalyst deactivation is the ligand transfer to aluminum with the formation of the complex $L^{^tBu}AlMe_2$.

Recently, new and highly active group 4 polymerization catalysts based on phenoxyimine ligands have been discovered by Fujita and co-workers at Mitsui Chemicals.[1,2,4,5] These catalysts attract considerable interest with regard to their ability to conduct living olefin polymerization and lead to new polymeric materials.[1−24] To form the active centers, they must be activated by Lewis acidic cocatalysts such as methylaluminoxane (MAO) or $AlR_3/[CPh_3]^+[B(C_6F_5)_4]^-$. In a recent study of the living polymerization catalyst bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride $\{(L^F)_2TiCl_2\}$ (Scheme 1), it was shown that activation of $(L^F)_2TiCl_2$ with MAO or $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$ leads to the formation of the initiating active species $[(L^F)_2TiMe(S)]^+[Me\text{-}MAO]^-$ and $[(L^F)_2TiMe(S)]^+[B(C_6F_5)_4]^-$, respectively (S is a weakly coordinated solvent molecule). These species react with ethylene to afford the chain-propagating species $[(L^F)_2TiP]^+[Me\text{-}MAO]^-$ and $[(L^F)_2TiP]^+[B(C_6F_5)_4]^-$ (P is the growing polymer chain). The main route of $(L^F)_2TiCl_2$/MAO catalyst deactivation is the ligand transfer to aluminum with formation of the complex L^FAlMe_2.[11,20] Similar initiating species were observed in highly active polymerization catalysts obtained upon activation of bis[*N*-(phenyl)pyrrolylaldiminato]titanium(IV) dichloride $\{(L')_2TiCl_2\}$ and (*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato-*N′*-(phenyl)pyrrolylaldiminato)titanium(IV) dichloride $(L'L^FTiCl_2)$ with MAO (Scheme 1). They are

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(1) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett*. **1999**, 1263.

(2) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc*. **2001**, *123*, 6847.

(3) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc*. **2001**, *123*, 5134.

(4) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Angew. Chem., Int. Ed*. **2001**, *40*, 2918.

(5) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R; Nakano, H.; Tanaka, H.; Kojoh, S.-i.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc*. **2002**, *124*, 3327.

(6) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev***. 2003**, *103*, 283.

(7) Mitani, M.; Nakano, T.; Fujita, T. *Chem.—Eur. J*. **2003**, *9*, 2396.

(8) Tshuva, E. Y.; Goldberg, I; Kol, M. *J. Am. Chem. Soc*. **2000**, *122*, 10706.

(9) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed*. **2000**, *39*, 3626.

(10) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res*. **2004**, *37*, 231.

(11) Makio, H.; Fujita, T. *Macromol. Symp*. **2004**, *213*, 221.

(12) Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem. Soc. Jpn*. **2003**, *76*, 1493.

(13) Talarico, G.; Busico, V.; Cavallo, L. *Organometallics* **2004**, *23*, 5989.

(14) Lamberti, M.; Consolmagno, M.; Mazzeo, M.; Pellecchia, C. *Macromol. Rapid Commun*. **2005**, *26*, 1866.

(15) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714.

(16) Weiser, M.-S.; Wesolek, M.; Mülhaupt, R. *J. Organomet. Chem*. **2006**, *691*, 2945.

(17) Cherian, A. E. R.; Lobkovsky, E. B.; Coates, G. W. *Macromolecules* **2005**, *38*, 6259.

(18) Saito, J.; Suzuki, Y.; Makio, H.; Tanaka, H.; Onda, M.; Fujita, T. *Macromolecules* **2006**, *39*, 4023.

(19) Pärssinen, A.; Luhtanen, T.; Klinga, M.; Pakkanen, T.; Leskelä, M.; Repo, T. *Eur. J. Inorg. Chem*. **2005**, 2100.

(20) Bryliakov, K. P.; Kravtsov, E. A.; Pennington, D. A.; Lancaster, S. J.; Bochmann, M.; Brintzinger, H. H.; Talsi E. P. *Organometallics* **2005**, *24*, 5660.

(21) Bryliakov, K. P.; Kravtsov, E. A.; Broomfield, L.; Talsi E. P.; Bochmann, M. *Organometallics* **2007**, *26*, 288.

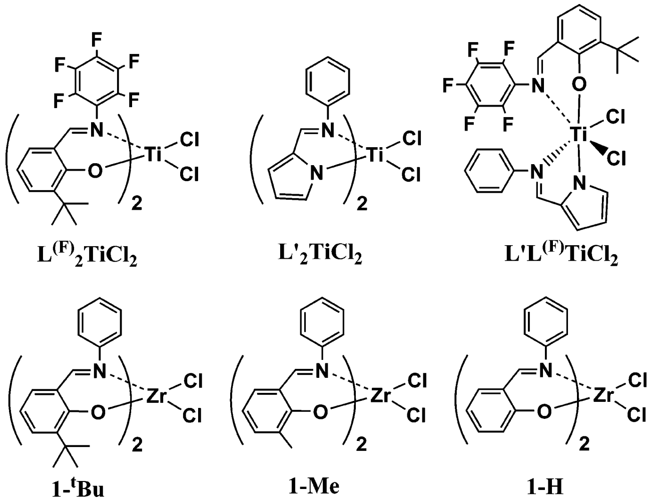
(22) Axenov, K. V.; Klinga, M.; Lehtonen, O.; Koskela, H. T.; Leskelä, M.; Repo, T. *Organometallics* **2007**, *26*, 1444.

(23) Yoon, J.; Mathers, R. T.; Coates, G. W.; Thomas, E. L. *Macromolecules* **2006**, *39*, 1913.

(24) Tohi, Y.; Makio, H.; Matsui, S.; Onda, M.; Fujita, T. *Macromolecules* **2003**, *36*, 523.

10.1021/om7004113 CCC: $37.00

Scheme 1. Structures of Titanium Complexes Studied Recently[11,20,21] and Zirconium Complexes Studied in This Work



outer sphere ion pairs $[(L')_2TiMe(S)]^+[Me\text{-}MAO]^-$ and $[L'L^FTiMe(S)]^+[Me\text{-}MAO]^-$.[21] Very recently, it was shown that activation of hafnium bis(phenoxyimino) dibenzyl complexes with $B(C_6F_5)_3$ led to the cationic bis(phenoxyimino)hafnium monobenzyl species, which was active in ethylene polymerization.[22] Thus, for some titanium and hafnium bis(phenoxyimine) and bis(pyrrolidoimine) catalysts, the active species of polymerization (or their precursors) were characterized, but there are no such data for zirconium-based counterparts.

Zirconium bis(phenoxyimino) dichloride complexes bearing phenylimino groups are much more active in ethylene polymerization than titanium and hafnium analogues. It was found that zirconium complexes with bulky substituent R in position 3 of the phenolic ring (R = *tert*-butyl, adamantyl, cumyl) are highly active in polymerization of ethylene, while those with smaller substituents (R = ^{i}Pr, Me) are poor catalysts.[2] To elucidate the reason for this dramatic effect of the substituent R on the catalytic activity, it is necessary to identify the intermediates formed upon activation of zirconium bis(phenoxyimine) catalysts with various substituents in the phenolic ring.

Some zirconium bis(phenoxyimine) catalysts are capable of producing polyethylene with uni-, bi-, and trimodal molecular mass distribution depending on the reaction conditions. This multimodality was attributed to the existence of various isomers of the initial zirconium complex and hence of the active intermediate.[24] Until now there were no experimental studies that allowed comparison of the isomeric composition of the initial bis(phenoxyimine) catalyst and that of the active species of polymerization.

In this work, we report the results of the ^1H and ^{13}C NMR study of the intermediates formed upon interaction of bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride ($(L^{tBu})_2ZrCl_2$) (**1-^{t}Bu**), bis[*N*-(3-methylsalicylidene)anilinato]zirconium(IV) dichloride ($(L^{Me})_2ZrCl_2$) (**1-Me**), and bis[*N*-(salicylidene)anilinato]zirconium(IV) dichloride ($(L^H)_2ZrCl_2$) (**1-H**) with MAO and $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$ (Scheme 1). The main goal of the study was to elucidate how the structure and stability of the intermediates correlate with the catalytic activity of the above systems and the structure of the produced polyethylene.

Results and Discussion

1-^{t}Bu/MAO System. The ^1H NMR spectrum of the initial complex **1-^{t}Bu** in toluene-d_8 at 20 °C displays sharp and well-resolved peaks (Table 1). After addition of MAO (Al:Zr = 300−500, 20 °C, toluene-d_8), **1-^{t}Bu** is converted to the complexes further denoted as **2-^{t}Bu** and **3-^{t}Bu** (Figure 1a, Table 1). **2-^{t}Bu** is unstable at room temperature and rapidly converts to **3-^{t}Bu** within 1/2 h (Figure 1b). The ^1H NMR spectrum of **3-^{t}Bu** coincides entirely with the previously reported ^1H NMR spectrum of $L^{tBu}AlMe_2$ (Table 1).[25] Thus, **3-^{t}Bu** is aluminum complex $L^{tBu}AlMe_2$. Previously, similar ligand transfer to aluminum was observed for titanium complexes $(L^F)_2TiCl_2$ and $(L')_2TiCl_2$ (Scheme 1).[11,20,21]

Table 1. Selected ^1H NMR Chemical Shifts (ppm, 20 °C, Toluene-d_8) for Complexes Formed upon Activation of 1-^{t}Bu, 1-Me, and 1-H with MAO and $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$

no.	species	N=CH	^{t}Bu	Al−Me	μ-Me
1	$(L^{tBu})_2ZrCl_2$ (**1-^{t}Bu**)	7.52	1.47		
2	$[(L^{tBu})_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ $[Me\text{-}MAO]^-\cdot$(**2-^{t}Bu**)	7.81	1.01	d	−0.82
3	$[(L^{tBu})_2Zr(\mu\text{-}Me)_2AlMe_2)]^+$ $[B(C_6F_5)_4]^-$ (**2-^{t}Bu**)	7.77	1.24	*d*	−0.91
4	$[(L^{tBu})_2Zr(\mu\text{-}Me)_2AlMe_2)]^+$ $[B(C_6F_5)_4]^-$ (**2-^{t}Bu**)[a]	7.76		−0.45	−0.67
5	$L^{tBu}AlMe_2$ (**3-^{t}Bu**)	7.51	1.51	−0.30	
6	$(L^{Me})_2ZrCl_2$ (**1-Me**)	8.01	*b*		
7	$[(L^{Me})_2Zr(\mu\text{-}Me)_2AlMe_2)]^+$ $[B(C_6F_5)_4]^-$ (**2-Me**)	7.64	*c*	−0.45	−0.87
8	$[L^{Me}Al(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+$ $[Me\text{-}MAO]^-$ (**5-Me**)	7.41		−0.67	−0.78
9	$[L^HAl(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+$ $[Me\text{-}MAO]^-$ (**5-H**)	7.48		−0.66	−0.75
10	$[L^HAl(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+$ $[B(C_6F_5)_4]^-$ (**5-H**)	7.46		−0.66	−0.72

[a] In 3:1 = toluene-d_8:decahydronaphthalene at −20 °C. [b] Me resonance at δ 1.5−2.5. [c] Me resonance at δ 2.01. [d] Broadened at 20 °C.

2-^{t}Bu exhibits the ^1H NMR resonances at δ 7.81 (imine) and 1.01 (^{t}Bu) and that at δ −0.82 (Figure 1a). The imine and ^{t}Bu resonances of **2-^{t}Bu** and **3-^{t}Bu** were previously observed by Makio and Fujita.[11] However, the identification of these species was not completed. On the basis of previous studies of metallocene[26−35] and post-metallocene[20,21] systems, two alternative structures can be suggested for **2-^{t}Bu**: heterobinuclear ion pair $[(L^{tBu})_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$ and outer sphere ion pair $[(L^{tBu})_2ZrMe(S)]^+[Me\text{-}MAO]^-$ (S = molecule of solvent). The attempt to use ^{13}C-enriched MAO for the recording of the ^{13}C NMR spectrum of **2-^{t}Bu** was unsuccessful due to the low solubility of the latter species. The heterobinuclear ion pairs formed upon activation of metallocenes with either MAO or $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$ have identical cationic parts.[31−35]

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(25) Pappalardo, D.; Tedesco, C.; Pellecchia, C. *Eur. J. Inorg. Chem.* **2002**, 621.

(26) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(27) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

(28) Chen, Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc*. **1998**, *120*, 6287.

(29) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(30) Zhou, J.; Lancaster, S. L.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223.

(31) Tritto, I; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247.

(32) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys*. **2000**, *201*, 558.

(33) Bryliakov, K. P.; Semikolenova, N. V.; Yudaev, D. V.; Zakharov, V. A.; Brintzinger, H.-H.; Ystenes, M.; Rytter, E.; Talsi E. P. *J. Organomet. Chem*. **2003**, *683*, 92.

(34) Bryliakov, K. P.; Talsi, E. P.; Bochmann, M. *Organometallics* **2004**, *23*, 149.

(35) Bryliakov, K. P.; Babushkin, D. E.; Talsi, E. P.; Voskoboynikov, A. Z.; Gritzo, H.; Schröder, L.; Damrau, H-R. H.; Wieser, U.; Schaper, F.; Brintzinger, H-H. *Organometallics* **2005**, *24*, 894.

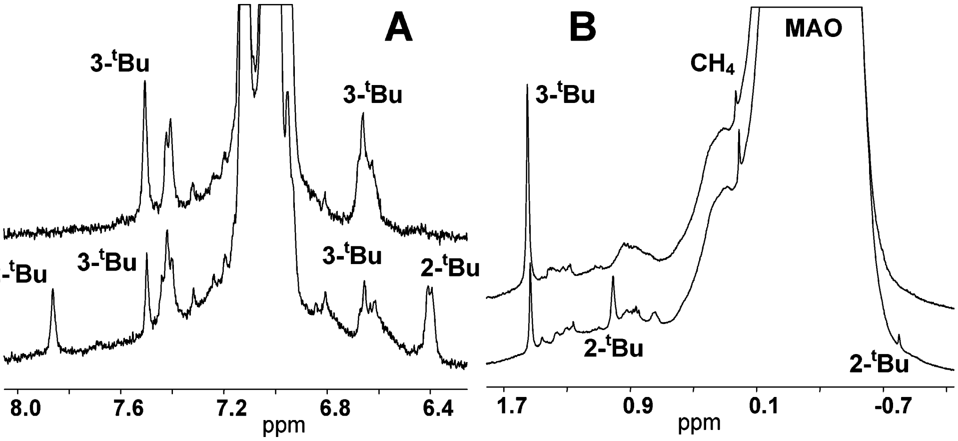

Figure 1. ^{1}H NMR spectra of the aromatic (A) and aliphatic (B) regions of the **1-^{t}Bu**/MAO sample 10 min (a) and 1 h (b) after storage of the sample at 25 °C in toluene-d_8 ([**1-^{t}Bu**] = 2 × 10^{-3} M, Al:Zr = 300). The amplification in (A) is 8 times larger than in (B).

Thus, we can use the data on the structure of the ion pair formed in the **1-^{t}Bu**/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ system for the assignment of the corresponding intermediate in the **1-^{t}Bu**/MAO counterpart.

1-^{t}Bu/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ System. The ^{1}H NMR spectrum of the sample **1-^{t}Bu**:AlMe$_3$:[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ = 1:10:1.1 in toluene-d_8 recorded 10 min after mixing of the reagents at room temperature displays three ^{1}H peaks in the range of imine protons at δ 7.77, 7.72, and 7.61, several peaks from ^{t}Bu protons in the range δ 1−1.5, and an intense peak at δ −0.91. After storage of the sample at room temperature, the observed picture is simplified and predominantly one complex remains in the solution. This complex, further referred to as **2′-^{t}Bu,** displays ^{1}H NMR peaks (δ 7.77 (imine), 1.24 (^{t}Bu), and −0.91) close to those for **2-^{t}Bu** (Table 1). As in the case of **2-^{t}Bu**, two alternative structures can be suggested for **2′-^{t}Bu**: [(L^{tBu})$_2$ZrMe(S)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ or [(L^{tBu})$_2$Zr(μ-Me)$_2$AlMe$_2$)]$^+$-[B(C$_6$F$_5$)$_4$]$^-$. To discriminate between these structures, it is important to measure the value of the $^1J_{CH}$ coupling constant for the resonance at δ −0.91. It was shown previously that for the terminal Zr−Me group $^1J_{CH}$ =120−125 Hz, whereas for bridging Zr−Me−Al or terminal Al−Me groups $^1J_{CH}$ = 112−114 Hz.[29, 32] To determine $^1J_{CH}$ for the resonance at δ −0.91, we have used ^{13}C-enriched AlMe$_3$ (95% ^{13}C). The ^{13}C-enriched AlMe$_3$ was available as a 1 M solution in decahydronaphthalene. The presence of decahydronaphthalene in the reaction mixture decreased the solubility of **2′-^{t}Bu** and thus prevented the detection of its ^{13}C NMR peaks. However, the ^{1}H NMR spectrum of the **1-^{t}Bu**/^{13}C-AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ system in a 3:1 = toluene-d_8:decahydronaphthalene mixture displayed very sharp and informative peaks, which allowed elucidation of the structure of **2′-^{t}Bu**.

The ^{1}H NMR spectrum of the sample **1-^{t}Bu**/^{13}C-AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (Zr:Al:B = 1:50:1.1) recorded at −20 °C 10 h after sample preparation shows two doublets of equal intensities in the region of negative chemical shifts as was expected for μ-Me and Al−Me resonances of heterobinuclear ion pair [(L^{tBu})$_2$Zr(μ-^{13}CH$_3$)$_2$Al(^{13}CH$_3$)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (see peaks denoted by the letters "c" and "d" in Figure 2a). At 20 °C, one of these doublets is broadened, whereas the other one remains sharp (Figure 2b, Table 1). The doublet at δ −0.66 ($^1J_{CH}$ = 112.4 Hz), sharp at both 20 and −20 °C, can be assigned to the μ-Me moiety, and that at δ −0.45 ($^1J_{CH}$ = 114.8 Hz), broadened at 20 °C, can be assigned to the Al−Me moiety (bridging Me groups seem to be less mobile than the terminal ones).[36] The ratio among the imine, μ-Me, and Al−Me peaks of **2′-^{t}Bu** was 2:6:6, in agreement with the structure [(L^{tBu})$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$-[B(C$_6$F$_5$)$_4$]$^-$. The determined $^1J_{CH}$ values (112.4 and 114.8 Hz) are within the range typical for μ-Me and Al−Me protons of heterobinuclear ion pairs.[29,32]

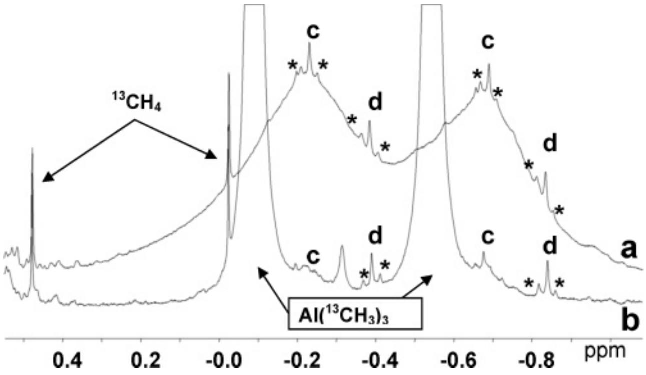

Figure 2. ^{1}H NMR spectra at −20 °C (a) and 20 °C (b) of the sample **1-^{t}Bu**:^{13}C-AlMe$_3$:[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ = 1:50:1.1 in 3:1 = toluene-d_8:decahydronaphthalene. The sample was stored for 10 h at 20 °C before recording of the NMR spectrum. ([**1-^{t}Bu**] = 2 × 10^{-3} M). Peaks denoted by the letters "c" and "d" belong to the Al^{13}CH$_3$ and μ-^{13}CH$_3$ groups of **2′-^{t}Bu,** respectively. The asterisks show peaks of the minor isomers of **2′-^{t}Bu**.

These data allow the conclusion that **2′-^{t}Bu** is a heterobinuclear ion pair, [(L^{tBu})$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$. Apparently, **2-^{t}Bu**, exhibiting a ^{1}H NMR spectrum similar to that of **2′-^{t}Bu**, is the heterobinuclear ion pair [(L^{tBu})$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$-[Me-MAO]$^-$ (Scheme 2). Remember that the activation of the titanium complex (L^F)$_2$TiCl$_2$ with MAO or AlMe$_3$/[CPh$_3$]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ leads to the outer sphere ion pairs [(L^F)$_2$TiMe(S)]$^+$-[Me-MAO]$^-$ and [(L^F)$_2$TiMe(S)]$^+$[B(C$_6$F$_5$)$_4$]$^-$.[20] Thus, the diverse structures of the initiating active species of polymerization are possible for various bis(phenoxyimine) catalysts ([L$_2$(M)Me(S)]$^+$ and [L$_2$M(μ-Me)$_2$AlMe$_2$]$^+$, M = Zr or Ti). Further studies are needed to elucidate what electronic and structural factors determine the structure of the initiating active species of polymerization.

It is worth noting that the μ-Me and Al−Me peaks of **2′-^{t}Bu** display two small satellite signals denoted with asterisks. The ratio among the main signal and the minor ones is about 1:5:1

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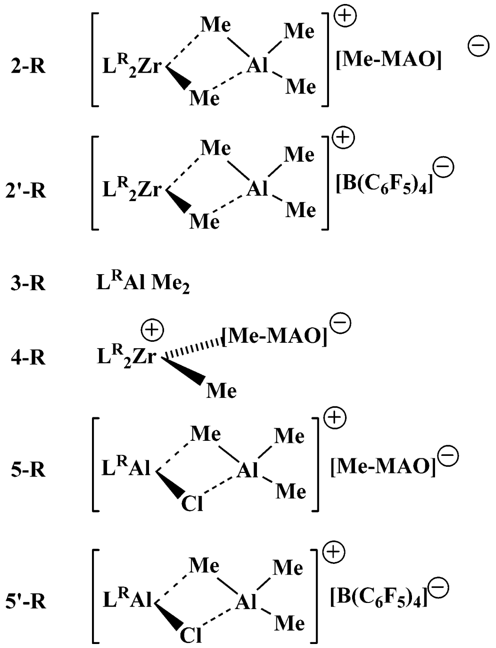
(36) In toluene-d_8 a μ-Me resonance of **2′-^{t}Bu** is observed at δ −0.91, whereas in a 1:1 = toluene-d_8:decahydronaphthalene mixture it is observed at δ −0.66 due to the effect of solvent.

Scheme 2. Proposed Structures of Complexes Formed upon Activation of 1-^{t}Bu, 1-Me, and 1-H with MAO and AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$



(Figure 2). Similar satellite peaks were observed for the initial complex **1-^{t}Bu** in $C_2D_2Cl_4$ by ^{1}H and ^{14}N NMR.[24] Bis(phenoxyimine) catalysts potentially possess five isomers.[2] On the basis of X-ray analysis data and DFT calculations, Fujita et al. assigned the main NMR signal of **1-^{t}Bu** to isomer a and the minor paired signals to isomer b, which is the only isomer that has chemically nonequivalent phenoxyimine ligands.[24] Similarly, the main and minor paired signals of **2′-^{t}Bu** can be assigned to heterobinuclear ion pairs with the structures a$_1$ and b$_1$, respectively. Thus, the isomeric composition of the intermediate **2′-^{t}Bu** is close to that for the initial complex **1-^{t}Bu.** The catalytic system **1-^{t}Bu/**MAO affords polyethylene with unimodal MMD.[24] Thus, for the **1-^{t}Bu/**MAO system, the presence of minor isomers of active species has no pronounced effect on the modality of the polymer. Further it will be more interesting to study the isomeric composition of the initiating active species of polymerization for those catalysts which produce multimodal polyethylene.

Data on the catalytic activities of the **1-^{t}Bu/**MAO (Al:Zr = 1000) and **1-^{t}Bu/**AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (Zr:Al:B = 1:100:1.1) systems are presented in Table 2. Data for well-known catalysts based on Cp$_2$ZrCl$_2$ are given for comparison. Under the polymerization conditions used, **1-^{t}Bu/**MAO demonstrates very high activity (Table 2, entry 1), exceeding that of the Cp$_2$ZrCl$_2$/MAO system (entry 7). The system **1-^{t}Bu/**MAO produces polymers with low molecular mass and narrow MMD ($M_w = 9.4 \times 10^3$, $M_w/M_n = 2.2$). The polymer samples obtained with the **1-^{t}Bu/**AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ system are characterized by a slightly higher molecular mass ($M_w = 14 \times 10^3$, $M_w/M_n = 2.6$).

1-Me/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ System. The ^{1}H NMR spectrum of the sample **1-Me**:AlMe$_3$:[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ = 1:10:1.1 in toluene-d_8, recorded 10 min after sample preparation, shows mainly peaks of the heterobinuclear ion pair [(L^{Me})$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ **(2′-Me).** The ^{1}H NMR spectrum of **2′-Me** is similar to that of **2′-^{t}Bu** (Table 1**)**. Thus, the structures of the initiating active species of polymerization formed in the **1-^{t}Bu/**AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and **1-Me/**AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ systems are similar. The dramatic difference in the productivity of the above systems (Table 2) can be caused by the various activities of the propagating intermediates of polymerization.

Table 2. Ethylene Polymerization over Phenoxyimine Complexes, Activated with MAO and AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ Cocatalysts[a]

entry	complex	cocatalyst	[Zr], × 10^6 M	C$_2$H$_4$ pressure (bar)	activity [(kg of PE/mol of Zr) bar min]
1	**1-^{t}Bu**	MAO	3.6	2	1820
2	**1-^{t}Bu**	borate	3.6	5	450
3	**1-Me**	MAO	25	5	17
4	**1-Me**	borate	25	5	7
5	**1-H**	MAO	25	5	0
6	**1-H**	borate	25	5	0
7	Cp$_2$ZrCl$_2$	MAO	14	2	42
8	Cp$_2$ZrCl$_2$	borate	14	3	43

[a] Polymerization conditions: (entries 1−6) 40 °C, 3 min, toluene 150 mL, cocatalyst MAO (Al:Zr = 1000), cocatalyst borate (Zr:AlMe$_3$:[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ = 1:100:1.1); (entries 7 and 8) 50 °C, 3 min, toluene 70 mL, cocatalyst MAO (Al:Zr = 1000), cocatalyst borate (Zr:AlMe$_3$:[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ = 1:100:1.1).

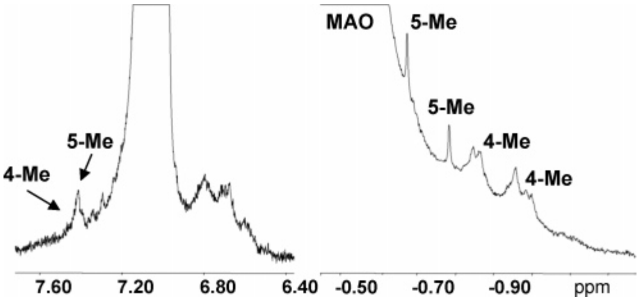


Figure 3. ^{1}H NMR spectrum of the sample **1-Me**/MAO recorded 20 min after sample preparation in toluene-d_8 at 20 °C ([**1-Me**] = 3 × 10^{-3} M, Al:Zr = 100).

1-Me/MAO System. The ^{1}H NMR spectrum of the sample **1-Me/**MAO (Al:Zr = 100) in toluene-d_8 recorded 1 h after sample preparation at 20 °C shows an imine signal at δ 7.41, two nonuniformly broadened signals near δ −0.85 and −0.97, and sharp peaks at δ −0.67 and −0.78 (Figure 3). The imine signal at δ 7.41 is a superposition of sharp and broad peaks. The observed spectrum does not change during several hours at room temperature. As was shown previously, the cationic part of the tight ion pairs [L$_2$(M)Me$^+\cdots$Me-MAO$^-$] can display various ^{1}H and ^{13}C NMR signals for various [Me-MAO]$^-$ counteranions, whereas the chemical shifts of the cationic part of [L$_2$M(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ are insensitive to the nature of [Me-MAO]$^-$.[31−35,37] As a result, [L$_2$(M)Me$^+\cdots$Me-MAO$^-$] species exhibit nonuniformly broadened, complicated signals, while [L$_2$M(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ species show relatively sharp and well-interpreted peaks. On the basis of these data, the broad signal near δ 7.41 and broadened signals near δ −0.85 and −0.97 can be assigned to the tight ion pair [(L^{Me})$_2$ZrMe$^+\cdots$Me-MAO$^-$] (**4-Me**) (Scheme 2). The sharp peaks at δ 7.41, −0.67, and −0.78 belong to the new complex **5-Me**. The nature of this complex will be discussed below. In contrast to the **1-^{t}Bu/**MAO system, where outer sphere ion pairs **2-^{t}Bu** are the major species, in the catalytic system **1-Me/**MAO, tight ion pairs **4-Me** dominate in the reaction solution. Thus, in the **1-^{t}Bu/**MAO system, the bulky ^{t}Bu substituent prevents the tight contact of [Me-MAO]$^-$ with zirconium and thus has a strong positive effect on the catalytic activity.

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[37] Babushkin, D. E.; Naundorf, C.; Brintzinger, H.-H. *Dalton Trans.* **2006**, 4539.

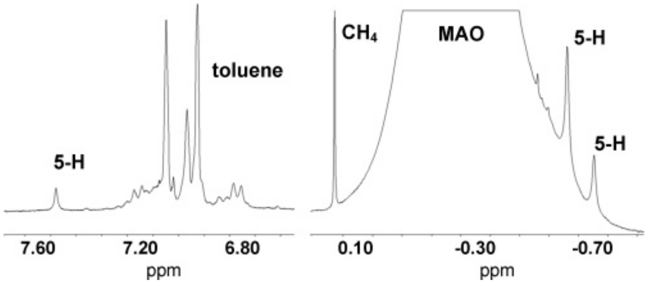


Figure 4. ^{1}H NMR spectrum of the sample **1-H**/MAO recorded 20 min after sample preparation in toluene-d_8 at 20 °C ([**1-H**] = 3 × 10^{-3} M, Al:Zr = 100).

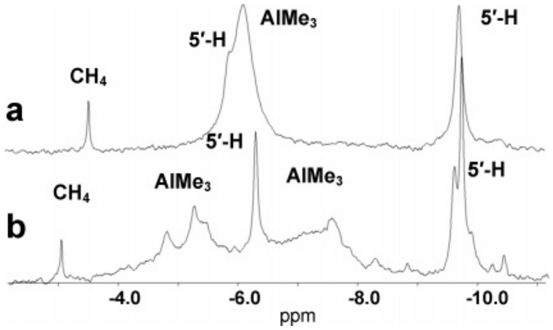
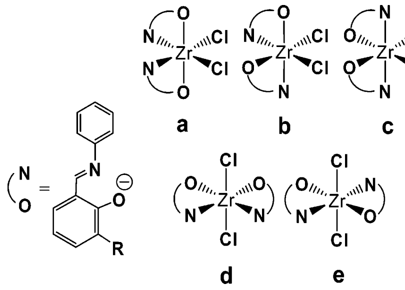
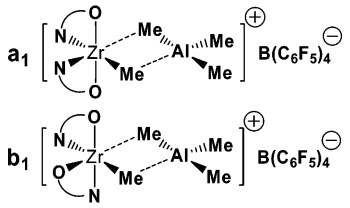


Figure 5. ^{13}C NMR spectrum of the sample **1-H**:^{13}C-AlMe$_3$:[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ = 1:10:1.1 recorded 30 min after sample preparation in toluene-d_8 at 20 °C (a) and −20 °C (b) ([**1-H**] = 3 × 10^{-3} M).

Scheme 3



Scheme 4



1-H/MAO System. The initial complex **1-H** is insoluble in toluene-d_8. The ^{1}H NMR spectrum of the sample **1-H**/MAO (Al:Zr =100) in toluene-d_8 shows sharp peaks of new complex **5-H**, which is stable for at least 1 month at room temperature (Figure 4). The ^{1}H NMR spectrum of **5-H** (δ 7.48 (1H), −0.66 (6H), and −0.75 (3H)) can be assigned to the aluminum ion pair [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$ (Scheme 2). To support this assignment, we have undertaken a ^{1}H and ^{13}C NMR study of the **1-H**/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ system using a ^{13}C-enriched sample of AlMe$_3$.

1-H/^{13}C-AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ System. The ^{1}H NMR spectrum of the system **1-H**/^{13}C-AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (δ 7.46 (1H), −0.66 (6H), and −0.72 (3H)) was very similar to that of the **1-H**/MAO analogue (Table 1). The ^{13}C NMR spectrum of the **1-H**/^{13}C-AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ system at 20 °C displays two peaks of complex **5′-H**. One of these peaks overlaps with that of AlMe$_3$ (Figure 5a). At −20 °C, the resonance of AlMe$_3$ is broadened and two peaks of **5′-H** at δ −6.4 (1C) and −9.9 (2C) are clearly seen (Figure 5b). The two-dimensional ^{13}C−^{1}H correlation spectrum revealed that the ^{13}C peak at δ −6.4 correlates with the ^{1}H NMR resonance at δ −0.72, whereas that at δ −9.9 correlates with the ^{1}H NMR resonance at δ −0.66. The $^1J_{\rm CH}$ values of 115 Hz determined for peaks at δ −6.4 and −9.9 correspond to those for the Al−Me−Al and Al−Me groups.[29,32] Thus, the observed spectrum belongs to the ion pair [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**5′-H**). Correspondingly, complex **5-H** should be the ion pair [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$. The assignment of **5′-H** or **5-H** to the zirconium species can be excluded, since the typical range of the ^{13}C chemical shifts for Zr−Me or Zr−Me−Al moieties is 30−50 ppm.[31,32] Thus, upon interaction of **1-H** with both MAO and AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ activators, the initial complex is decomposed with the formation of the aluminum ion pairs [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$ (**5-H**) and [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**5′-H**), which are inactive in ethylene polymerization. It is worth noting that the ^{13}C NMR spectrum of Figure 5b contains an additional signal close to that at δ −9.9. The nature of this signal is unclear.

The ^{1}H NMR spectrum of complex **5-Me** observed in the **1-Me/**MAO system is very similar to that of **5-H** (Figure 3 and Table 1). Most probably, **5-Me** is aluminum complex [L$^{\rm Me}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$.

Conclusions

For the first time, cationic species formed upon interaction of bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride ((L$^{\rm tBu}$)$_2$ZrCl$_2$) (**1-^{t}Bu**), bis[*N*-(3-methylsalicylidene)anilinato]zirconium(IV) dichloride ((L$^{\rm Me}$)$_2$ZrCl$_2$) (**1-Me**), and bis[*N*-(salicylidene)anilinato]zirconium(IV) dichloride ((L$^{\rm H}$)$_2$ZrCl$_2$) (**1-H**) with MAO and with AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ have been studied. It was shown that, in the catalytic systems **1-^{t}Bu/**AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$, **1-Me**/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$, and **1-^{t}Bu/**MAO, heterobinuclear ion pairs [(L$^{\rm tBu}$)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**2′-^{t}Bu**), [(L$^{\rm Me}$)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**2′-Me**), and [(L$^{\rm tBu}$)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**2-^{t}Bu**) are formed. In contrast, in the catalytic system **1-Me/**MAO, the tight ion pair [(L$^{\rm Me}$)$_2$ZrMe$^+\cdots$Me-MAO$^-$] (**4-Me**) is the major species in the solution. In the catalytic systems **1-H**/MAO and **1-H**/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$, the aluminum ion pairs with proposed structures [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[Me-MAO]$^-$ and [L$^{\rm H}$Al(μ-Me)(μ-Cl)AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ are predominantly formed. The relatively rapid deactivation of bis(phenoxyimino)zirconium/MAO catalysts correlates with a facile ligand transfer to aluminum observed for these catalysts by NMR. The much lower polymerization activity of the **1-Me/**MAO system than that of the **1-^{t}Bu/**MAO analogue correlates with more tight coordination of the [Me-MAO]$^-$ counterion to the active site of polymerization (or its precursor) observed by NMR for the former system.

Experimental Section

MAO was purchased from Witco GmbH (Bergkamen, Germany) as a toluene solution (total Al content 1.8 M, Al as AlMe$_3$ 0.5 M). Toluene-d_8 and decahydronaphthalene were dried over molecular sieves (4 Å), degassed in vacuo, and stored under dry argon. All operations were carried out under dry argon using a glovebox and standard Schlenk techniques or in sealed high-vacuum systems using break-seal techniques. Solids and toluene-d_8 were transferred and stored in a glovebox. Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1-^{t}Bu**),[2] bis[*N*-(3-methylsalicylidene)anilinato]zirconium(IV) dichloride (**1-Me**),[2] and bis[*N*-(salicylidene)anilinato]zirconium(IV) dichloride (**1-H**)[38] were prepared as described. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 250.130 and 62.89 MHz, respectively, on a Bruker DPX-250 MHz NMR spectrometer. Typical operating conditions for ^{13}C NMR measurements were as follows: spectral width 20 kHz, spectrum accumulation frequency 0.2−0.1 Hz, 100−2000 transients, 90° pulse at 7 μs. Multiplicities and coupling constants were derived from analysis of gated decoupled spectra. Operating conditions for ^{1}H NMR measurements: spectral width 5 kHz, spectrum accumulation frequency 0.5−0.2 Hz, number of transients 32−64, ca. 30° pulse at 2 μs. For calculations of ^{1}H and ^{13}C chemical shifts, the resonances of the methyl group of the toluene-d_8 solvent were taken as 2.11 and 20.40 ppm, respectively. The sample temperature measurement uncertainty and temperature reproducibility were less than ±1 °C.

Preparation of MAO and Al_2Me_6 Samples. Solid MAO was prepared from commercial MAO (Witko) by removal of the solvent in vacuo at 20 °C for 5 h. The solid product obtained (polymeric MAO with a total Al content of 40 wt % and an Al concentration as residual $AlMe_3$ of ca. 5 wt %) was used for the preparation of the samples. $^{13}CH_3$-enriched MAO was prepared by ligand exchange of 99% $^{13}CH_3$-enriched Al_2Me_6 (30 mol % total Me groups) and solid MAO (70 mol % total Me groups) in toluene solution followed by subsequent removal of volatiles under vacuum at room temperature to give a sample of ^{13}C-enriched MAO (ca. 30% ^{13}C) with the desired Al_2Me_6 content (polymeric MAO with a total Al content of 40% and an Al concentration as residual Al_2Me_6 of ca. 5 wt %). A more detailed description is presented in ref 34.

Preparation of 1-R/MAO Samples (R = ^{t}Bu, Me, and H). Calculated quantities of **1-R** (∼10^{-2} mmol of Zr), MAO or $AlMe_3$/$CPh_3^+B(C_6F_5)_4^-$, and toluene-d_8 (for ^{13}C measurements toluene was used) were combined under vacuum in NMR tubes. The samples were immediately cooled to −196 °C, and the tubes were sealed off from the vacuum line.

Ethylene Polymerization Studies. The experiments were carried out in a 0.5 L reactor in toluene at constant ethylene pressure and temperature for 30 min. **1-R** (0.5 mL of a 2×10^{-6} M solution in CH_2Cl_2) was introduced into the reactor in a vacuumized sealed glass ampule. The reactor was evacuated at 80 °C for 1 h, cooled to 20−25 °C, and then charged with 150 mL of toluene in which the calculated amount of activator was dissolved. The reactor was heated to 40 °C, and the desired ethylene pressure was settled. The reaction was started by breaking the ampule with **1-R**. The initial activity (see Table 2) was calculated from the polyethylene yield for the first 3 min of polymerization.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (Grant No. 06-03-32700) and the Royal Society (Grant No. 2004/R1-FSU).

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[38] Furuyama, R.; Saito, J.; Ishii, S-i.; Mitani, M.; Matsui, S.; Tohi, H.; Fujita, T. *J. Mol. Catal.* **2003**, *200*, 31.