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Effect of the nature of an organoaluminum activator on catalytic properties of phenoxyimine zirconium complexes in homo- and copolymerization reactions of ethylene

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Catalytic properties of the phenoxyimine zirconium complexes, *viz*., bis[*N*-(3,5-di-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1**) and its fluorinated analog, bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]zirconium(IV) dichloride (**2**), were studied. Ethylene homopolymerization and copolymerization of ethylene with α-olefins were chosen as catalytic reactions, and various organoaluminum compounds served as activators: commercial polymethylalumoxane (MAO) containing ~35 mol.% of trimethylaluminum (TMA), MAO purified from TMA ("dry" MAO), and "classical" organoaluminum compounds, namely, TMA and triisobutylaluminum (TIBA). Complex **1** is not activated by "dry" MAO but is efficiently transformed into the catalytically active state by commercial MAO, "conventional" TMA, and TIBA. These processes give low-molecular-weight polyethylenes (PE) characterized by high values of polydispersity indices and by polymodal curves of gel permeation chromatography (GPC). The order of decreasing the efficiency of activation for the cocatalysts is MAO > TIBA > TMA. Fluorinated complex **2** exhibits a high activity after its treatment with MAO and "dry" MAO, the activity is much lower upon mixing with TIBA, and complex **2** is inactive when using TMA. In the copolymerization of ethylene with hex-1-ene and dec-1-ene, complex **1** treated with MAO is highly active but gives a low level of insertion of the comonomer (1—2 mol.% in the copolymer). Complex **2** activated with "dry" MAO is more efficient in the copolymerization of ethylene with propylene or hex-1-ene but, like complex **1**, it does not produce copolymers with a high content of the comonomer. The both catalysts provide the insertion of α-olefin as isolated units separated by extended sections of the chain consisting of ethylene units.

Key words: zirconium, phenoxyimine complexes, trimethylaluminum, methylalumoxane (MAO), triisobutylaluminum, catalysis, polymerization, copolymerization, polyethylene.

Phenoxyimine (FI) complexes of IV Group metals represent a wide class of efficient and polyfunctional catalysts for homo- and copolymerization of olefins.[1,2] Catalytic properties of these catalysts are controlled with allowance for a specific process. The catalytic properties can be modified by both changing their geometric and electronic structures (choice of the composition and structure of the chelating ligand and the type of transition metal) and using organometallic compounds (activators) of various composition and nature.[3—6]

The titanium FI complexes, whose ligand includes the fluorine substituent in the *ortho*-position of the =N—Ph fragment and the phenoxyketimine substituents with alkyl or aromatic substituents at the carbon atom of imine, when activated with polymethylalumoxane (MAO) are capable of performing "living" polymerization of ethylene and propylene even at elevated temperatures (50—70 °C).[7—15] The activity and stereoselectivity of the catalysts in propylene polymerization vary in a wide range depending on the type of substituents in the ketimine or phenoxide fragments. Even the nature of the substituent in the *para*-position remote from the transition metal affects the catalytic properties. The bulky substituents in the *ortho*-position of the phenoxide moiety favor the high activity of the catalyst, which can vary in wide ranges (up to two orders of magnitude), depending on the number or arrangement of fluorine substituents in the =N—Ph fragment.[3]

In the presence of the fluorinated zirconium FI catalysts, the "living" polymerization of ethylene is not observed, but the molecular weight (MW) of the polyethyl-

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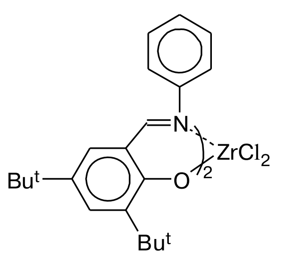
ene (PE) samples obtained with these catalysts is 20—30 times that of the MW of the samples synthesized on the complexes with non-fluorinated**[16,17]** or with cycloalkylimine ligands.**[18,19]** The activity of the zirconium FI catalysts is also controlled in a very wide range by changing the structure of the chelating ligands**[3—6]** and it considerably exceeds the activity of the titanium analogs.

The FI catalysts are very sensitive to the presence of trialkylaluminum compounds in the reaction medium. In the presence of trimethylaluminum (TMA), whose content in commercial MAO reaches 30—40 mol.%, the FI catalysts are deactivated by the exchange between the ligand of the complex and the methyl groups of TMA to form $LAlMe_2$.**[20—22]** The deactivation is inhibited, when a bulk substituent is present in the *ortho*-position of the phenoxide fragment.

When activated with MAO, the titanium FI complexes exhibit, as a rule, different reactivities towards the insertion of ethylene, propylene, and especially, higher α-olefins, which impedes the use of these complexes in the synthesis of random or alternating olefin copolymers. However, the reduction of the imine fragment to amine under the action of triisobutylaluminum (TIBA) (combined cocatalyst $AlBu^i_3/CPh_3B(C_6F_5)_4$) affords a catalyst capable of performing the polymerization of higher α-olefins (hex-1-ene, oct-1-ene, dec-1-ene, 4-methylpent-1-ene) in heptane with a high rate. As a result, atactic high-molecular-weight poly-α-olefins with a large content of regiodefects in the macromolecular chain are formed.**[23]** The catalyst is inefficient in toluene. For the synthesis of copolymers of ethylene with propylene and higher α-olefins, MAO purified from TMA is used as an activator of the zirconium FI complexes.**[24—26]** In copolymerization the fluorinated complexes exhibit a higher efficiency and form copolymers with a considerably higher MW, and the insertion of the copolymer occurs more efficiently than that for the non-fluorinated analogs.**[24]**

A few experimental data on the possibility of activation of the FI complexes by cocatalysts alternative to MAO or $AlBu^i_3/CPh_3B(C_6F_5)_4$ are known. According to the published**[27]** results, conventional organoaluminum compounds (OAC), such as $AlEt_3$, $AlHex_3$ (Hex is hexyl), and $AlMe_3$, are fairly efficient in the activation of the phenoxycycloalkylimine zirconium FI complexes in ethylene polymerization. However, their use results in the formation of a series of active sites forming polymodal polyethylene (PE). In terms of activity in ethylene polymerization the perfluorinated titanium FI complex activated by diethylaluminum chloride (DEAC) is comparable with the same complex activated by MAO, whereas $AlEt_3$ and $AlBu_3{}^i$ fail in activating this complex.**[28]** The PE formed has a high MW and a low value of polydispersity indices.

In this work, we present the data obtained by the study of the catalytic properties of two new zirconium compounds **1** and **2** supplementing the family of chelate FI complexes. It was of interest to study specific features of the catalytic behavior of the non-fluorinated and fluorinated catalysts based on complexes **1** and **2** in the homo- and copolymerization of higher α-olefins after their activation by MAO, "dry" MAO (MAO purified from TMA), and trialkylaluminum (TMA and TIBA) and to elucidate the role of alkylaluminum in the process of catalyst activation and chain transfer reactions.



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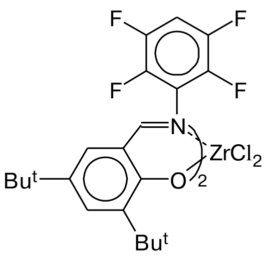

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Experimental

Toluene was twice distilled over $LiAlH_4$ in argon, and MAO with a content of ~35 mol.% as a solution in toluene (Aldrich) was used without additional purification. "Dry" MAO was prepared from 22.5 mL of a 1.5 *M* solution of MAO in toluene (Aldrich) by pumping out all volatile substances (solvent and TMA) with a vacuum fore pump for 6—7 h at ~20 °C. The white powder formed at the end of the procedure was dissolved in toluene (22.5 mL) and then used as a reactant. According to the data of ^1H NMR spectroscopy, the amount of trimethylaluminum remained in "dry" MAO decreased to ~5 mol.%. Ethylene of polymerization purity was additionally purified by passing through columns packed with activated 4 Å molecular sieves and Al_2O_3. The phenoxyimine ligands and complexes **1** and **2** were synthesized according to the procedures described previously.**[29—31]**

Complex 1. Found (%): C, 65.65; H, 6.68; Cl, 8.57; N, 3.65; Zr, 10.3. $C_{42}H_{52}Cl_2N_2O_2Zr$. Calculated (%): C, 64.76; H, 6.73; Cl, 9.10; N, 3.60; Zr, 10.71. ^1H NMR (toluene-d_8), δ: 1.23 (s, 18 H, 2 Bu^t); 1.51 (s, 18 H, 2 Bu^t); 6.60—6.90 (m, 10 H, 2 Ph); 7.51 (d, 2 H, 2 Ar, *J* = 2.2 Hz); 7.58 (s, 2 H, 2 N=CH). ^{13}C NMR (toluene-d_8), δ: 30.0, 31.4, 34.2, 35.5 (s, 2 Bu^t); 123.1, 123.7, 126.6, 127.5, 129.2 (m, 2 Ph); 132.0, 139.5, 141.7, 151.5, 158.3 (s, 2 Ar); 170.4 (s, 2 H, 2 N=C).

Complex 2. Found (%): C, 54.78; H, 4.97; F, 15.05; Cl, 7.75; N, 3.11; Zr, 9.28. $C_{42}H_{44}Cl_2F_8N_2O_2Zr$. Calculated (%): C, 54.65; H, 4.60; F, 16.5; Cl, 7.68; N, 3.03; Zr, 9.88. ^1H NMR (toluene-d_8), δ: 1.26 (s, 18 H, 2 Bu^t); 1.39 (s, 18 H, 2 Bu^t); 6.07 (m, 2 H, 2 C_6F_4H); 6.90 (d, 2 H, 2 Ar, *J* = 2.0 Hz); 7.59 (s, 2 H, 2 N=CH); 7.65 (d, 2 H, 2 Ar, *J* = 2.0 Hz). ^{13}C NMR (toluene-d_8), δ: 29.5, 31.2, 34.4, 35.5 (s, 2 Bu^t); 103.5, 127.5, 128.4, 137.2, 137.7 (m, 2 C_6F_4H); 122.6, 130.2, 134.1, 139.9, 142.8 (s, 2 Ar); 176.5 (s, 2 H, 2 N=C).

All procedures with compounds sensitive to air and moisture were carried out in a helium box or using the Schlenk technique.

Homo- and copolymerization of ethylene. Ethylene polymerization was carried out at a total pressure of ethylene and toluene vapor of 1 atm in a glass 100-mL flask equipped with a magnetic stirrer and special taps for introduction of components of the catalytic system and ethylene. Toluene (20 mL) and the necessary amount of an organoaluminum compound (MAO, "dry" MAO, TMA, or TIBA) as a solution in toluene were sequentially introduced into the reactor inside the helium box. The necessary amount of the precatalyst as a solution in toluene was placed in a special ampule attached to the reactor. After withdrawal from the box, the reactor was connected to glass vacuum setup and degassed. The reactor was heated to a specified temperature and the reaction mixture was saturated with ethylene. Polymerization was initiated by the introduction of the complex into the mixture. The pressure was maintained constant during polymerization and the ethylene consumption was detected by the pressure change in a measuring steel vessel equipped with a manometer. Polymerization was terminated by the introduction of a 10% solution of HCl in ethanol into the reactor. The polymer was filtered off, washed several times with an aqueous-ethanol mixture, and dried *in vacuo* at 50—60 °C to a constant weight.

The copolymerization of ethylene with hex-1-ene and dec-1-ene under atmospheric pressure was carried out analogously to ethylene polymerization, but for copolymerization the comonomers were introduced into the reactor together with the solvent in the amount corresponding to the required mole ratio to ethylene. The concentration of ethylene in toluene at a specified temperature was determined according to a known procedure.[32] It was found that at 30 °C the ethylene concentration was 0.14 mol L^{-1} atm^{-1}.

The copolymerization of ethylene with α-olefins at an elevated pressure was carried out at an ethylene pressure of 10 atm in a stainless steel temperature-controlled 200-cm^3 autoclave equipped with a mechanical stirrer. The reactor was pre-evacuated for 1 h at 90 °C, then cooled to ~20 °C, and filled with dry argon. A sealed ampule with the known weighed sample of the complex (0.5—1.5 mg) was placed in the reactor under an argon flow and fixed in a special device. The autoclave was evacuated for 1 h at ~20 °C, and then the solvent (60 or 100 mL) and an organoaluminum compound in a certain Al/Zr ratio were introduced. For the copolymerization of ethylene with propylene, a mixture of comonomers with a specified mole ratio was fed to the reactor at a total pressure of 10 atm. In the copolymerization with hex-1-ene, the latter was introduced into the reactor in a necessary amount together with the solvent and the copolymerization process was carried out at an ethylene pressure of 10 atm. The autoclave was heated to a desired temperature. The solution was saturated with the monomer with vigorous stirring. After the monomer was completely dissolved (in 5—10 min) and the temperature equilibrium was established in the system, the ampule with complex was broken. This moment was accepted as the onset of polymerization, which was carried out at a constant pressure of the monomer in the autoclave. The monomer uptake in the reaction course was detected by the pressure drop in the volumetric cylinder. The reaction was terminated by the introduction of a 10% solution of HCl in ethanol. The polymer was filtered off, washed with an ethanol—water mixture, and dried at 60 °C until a constant weight was achieved.

Characterization of polymers. Gel chromatograms (hereinafter chromatograms) of the polymer samples were obtained on a Waters GPCV-2000 chromatograph using the column PLgel 5 μm MIXED-C in 1,2,4-trichlorobenzene at 135 °C. For the calculation of MW of the synthesized polymers, we used the universal calibration dependence taking into account constants K and α in the Mark—Houwink equation[33] obtained for polystyrene and polyethylene, respectively, in 1,2,4-trichlorobenzene.

Results and Discussion

Polymerization of ethylene using complex 1. After the treatment with commercial MAO, non-fluorinated complex **1** exhibits a high activity in ethylene polymerization (Table 1). The catalyst activity doubles with an increase in the Al_{MAO}/Zr ratio from 500 to 1500 mol mol^{-1} (entries *1*—*3* in Table 1). At the same time, the complex treated with "dry" MAO exhibits a very low activity (entry *4*).

There are few published experimental data on the activation of the FI complexes by conventional alkylaluminum compounds. The zirconium complex close in structure but, unlike complex **1**, containing no *tert*-butyl substituent in the *para*-position of the phenoxide moiety ex-

Table 1. Results of ethylene polymerization in the presence of complex **1** (30 °C, toluene, 20 mL, [Zr] = 0.6 μmol, ethylene pressure 1 atm)

Entry	Activator (A)	A/Zr/mol mol^{-1}	t/min	Y/g	A^a	M_w	M_n	M_w/M_n
1	MAO	500	5	0.35	7000	55400	7500	7.4
2	MAO	1000	5	0.56	11200	55350	7500	7.4
3	MAO	1500	5	0.63	12600	7900	3300	2.4
4	d-MAO[b]	1000	30	Traces	—	—	—	—
5	TMA	500	15	0.39	2600	53000	3000	17.7
6	TMA	700	15	0.18	1200	—[c]	—	—
7	TIBA	170	15	Traces	—	—	—	—
8	TIBA	300	15	0.29	1900	—[c]		—
9	TIBA	500	15	0.66	4400	75100	3550	21.2
10[d]	TIBA	500	15	0.69	4600	30000	1700	17.6

[a] A is activity in (kg of PE) (mole of $Zr)^{-1}$ h^{-1} atm^{-1}.

[b] d-MAO is "dry" MAO.

[c] M_w not determined.

[d] Before the introduction of the monomer, the catalytic system was stored for 0.5 h.

hibits a high activity in ethylene polymerization in hexane when activated by $AlEt_3$ and $AlMe_3$ taken in a cocatalyst/precatalyst ratio of 4000—20 000 mol mol^{-1}.[27] In terms of activity, this system is comparable with that where MAO was used as activator; however, after the treatment with TIBA it turned out to be inactive. On the contrary, according to the data obtained in this work, complex **1** is activated by both TMA (see entries *5*, *6*) and TIBA (entries *7*—*9*) in toluene when cocatalyst excess is not higher than 500 mol mol^{-1}. Measured activities account for approximately a fifth and a third of the activity of the **1**—MAO system (see entry *3*). The absence of activity in the system prepared by treating complex **1** with TMA-depleted MAO and a comparable order of activity observed for the system including trialkylaluminum and MAO containing TMA indicate that these are trialkylaluminum compounds that are the cocatalyst activating complex **1**.

The PE samples synthesized in the presence of complex **1** with all activators possess low MW and (in the most cases) high values of polydispersity indices. The exception is the samples obtained by the activation with MAO at the ratio Al_{MAO}/Zr = 1500 mol mol^{-1} (see entry *3*). An increase in the mole ratio Al_{MAO}/Zr from 500 to 1500 mol mol^{-1} results in a considerable decrease in MW (see entries *1*, *3*). As will be shown below in the analysis of microstructures of copolymers obtained on this catalytic system, the main reason for this behavior is the chain transfer to TMA which is contained in MAO. The chromatogram of the PE sample obtained at the ratio $Al_{MAO}/\mathbf{1}$ = 500 mol mol^{-1} contains the main peak with a maximum at $\log M_w \approx 4$ and small low-molecular- and high-molecular-weight components. The same three peaks but in other ratio appear in the GPC curves of the PE samples synthesized with TMA and TIBA (Fig. 1). For PE, which was synthesized[27,33] with the complex of similar structure and activated by trialkyls and MAO, the chromatograms are also polymodal. In addition to the main peak with a maximum near $\log M_w \approx 4$, these curves contain high-molecular-weight components, whose relative fraction increased with an increase in the polymerization duration. This phenomenon can be explained[33] by the formation in the system of active sites of several types, some of which (most active) form low-molecular-weight PE but are prone to fast deactivation, whereas other sites responsible for the formation of the high-molecular-weight fraction are less active but more stable. In our case, the formation of another low-molecular-weight peak with a maximum near $\log M_w \approx 3$ is observed, which is most pronounced when the complex is activated by TIBA. Its appearance can be related to the existence of an additional type of active sites. This suggestion is supported by the experiment in which the catalytic system was formed for 0.5 h prior to introducing the monomer (see Table 1, entry *10*). The activity of the considered system compared to that of the system synthesized by the "standard" procedure remained almost unchanged (*cf.* entries *9* and *10*), but the fraction of the low-molecular-weight fraction with a maximum near $\log M_w \approx 3$ increased considerably (Fig. 2). It can be concluded that the modification of the system leading to the formation of active sites, which are responsible for the formation of the low-molecular-weight fraction, is a slow process. Therefore, for the directed synthesis of low-molecular-weight PE using the catalytic system involving compound **1**, it is necessary to optimize the conditions of its aging in the absence of the monomer.

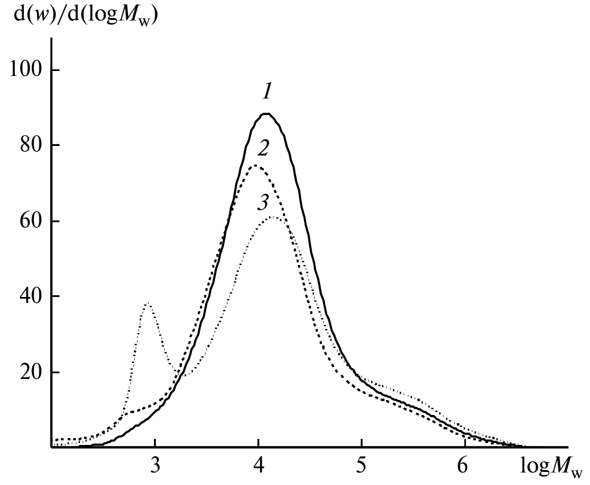

Fig. 1. Chromatograms of the PE samples prepared in the presence of complex **1**, activated by MAO (*1*), TMA (*2*), and TIBA (*3*) (see entries *1*, *5*, and *9* in Table 1, respectively).

Polymerization of ethylene using complex 2. Other conditions being equal, fluorinated complex **2** activated by MAO exhibits the activity compared to that of complex **1** (*cf.* entries *3* and *2* in Tables 2 and 1, respectively). How-

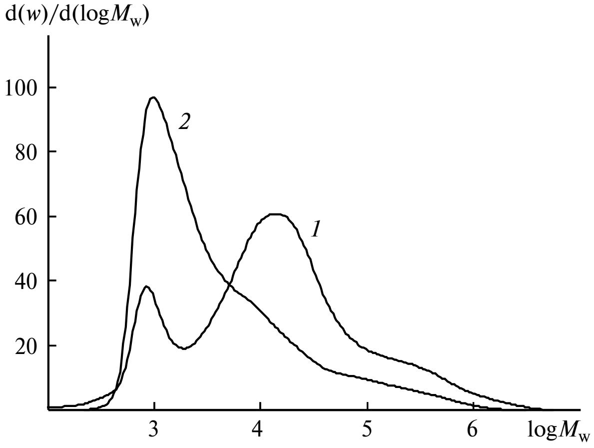

Fig. 2. Chromatograms of the PE samples prepared in the presence of complex **1** with TIBA as an activator at $Al_{TIBA}/\mathbf{1}$ = = 500 mol mol^{-1}: for catalytic system unstored (*1*) and stored (*2*) for 0.5 h before the introduction of ethylene (see entries *9* and *10* in Table 1).

Table 2. Results of ethylene polymerization in the presence of complex **2** (30 °C, toluene, 20 mL, [Zr] = 0.6 μmol, ethylene pressure 1 atm)

Entry	Activator (A)	A/Zr/mol mol^{-1}	t/min	Y/g	A	M_w	M_n	M_w/M_n
1	MAO	500	10	Traces	—	—	—	—
2	MAO	750	5	0.34	6800	460000	173000	2.66
3	MAO	1000	5	0.45	9000	220000	89000	2.47
4	MAO	1500	5	0.29	5800	249000	67000	3.70
5	d-MAO	750	5	0.04	800	608000	267000	2.27
6	d-MAO	1000	5	0.33	6600	497000	184000	2.70
7	d-MAO	2000	5	0.48	9600	155400	34400	4.52
8	TMA	500	10	Traces	—	—	—	—
9	TIBA	500	10	0.04	30	38000	6600	5.76

ever, its dependence on the mole ratio $Al_{MAO}/\mathbf{2}$, unlike that of complex **1**, is bell-shaped (see entries *1—4*, Table 2). At $Al_{MAO}/\mathbf{2}$ = 500 mol mol^{-1} only traces of the polymer were obtained and the maximum yield of the polymer was attained at the ratio $Al_{MAO}/\mathbf{2}$ = 1000 mol mol^{-1}.

Unlike complex **1**, the fluorinated analog is most efficient in ethylene polymerization under the activation with "dry" MAO. The activity of the system increases from 800 to 9600 (kg of PE) (mole of Zr)$^{-1}$ h^{-1} atm^{-1} with an increase in mole ratio $Al_{MAO}/\mathbf{2}$ from 750 to 2000 mol mol^{-1}. In addition, complex **2** manifests trace activity when treated with TMA (entry *8*), and this activity is 150 times lower than the activity of complex **1** after the treatment with TIBA (*cf.* entries *9* в in Tables 1 and 2).

The molecular weights of PE obtained in the presence of the system **2**/MAO considerably exceed the molecular weights of PE synthesized with **1**/MAO system with polydispersity indices close to those characteristic of single site system. An increase in $Al_{MAO}/\mathbf{2}$ mole ratio due to an increase in the MAO concentration is accompanied by a significant decrease in the MW of the formed PE: from M_n = 173 000 ($Al_{MAO}/\mathbf{2}$ = 750) to M_n = 67 000 ($Al_{MAO}/\mathbf{2}$ = 1500). The molecular weights of the PE formed by the activation of complex **2** with "dry" MAO are considerably higher but also decrease with an increase in the methylalumoxane concentration.

Complex **1**, unlike complex **2**, is not activated by "dry" MAO and with trialkylaluminum compounds exhibits the activity comparable to that of MAO. We may therefore assert that the main role in the formation of active sites in the systems with complex **1** belongs to trialkylaluminum and, as shown above, they are responsible, most likely, for the formation of the low-molecular-weight fractions of PE. When interacting with complex **1**, trialkylaluminum compounds are not only alkylating agents, but also efficient activators. The elucidation of the natures of the formed active sites and reactions leading to their formation in the highly active systems with complex **1** requires additional studies. For the systems **2**/MAO and **2**/"dry" MAO, the catalytic intermediates performing polymerization are, most likely, "classical" ion pairs $L_2Zr^+Pol...XMAO^-$ (X = Cl or Me, Pol is the growing polymer chain).[34]

Thus, when electron-withdrawing fluorine substituents that enhance the Lewis acidity of the central atom are introduced into the structure of the complex, the reactions with trialkylaluminum compounds leading to the formation of polycenter catalytic systems are considerably retarded. Indeed, other conditions being equal, the activity of complex **2** is ~150 times lower than that for complex **1**. The activation of the both complexes by TIBA forms low-molecular-weight PE. As can be seen from Fig. 3, the chromatograms of the both PE samples are similar and represented by the main peak with a maximum near $\log M_w \approx 4$ and a small high-molecular-weight peak with a maximum near $\log M_w \approx 5.5$. Similarity of the chromatograms indicates that the active sites formed from **1** and **2** under the action of this activator are also similar. The distinction is that the chromatogram of PE obtained in the presence of complex **2** contains no low-molecular-weight peak near $\log M_w \approx 3$. This suggests that in the

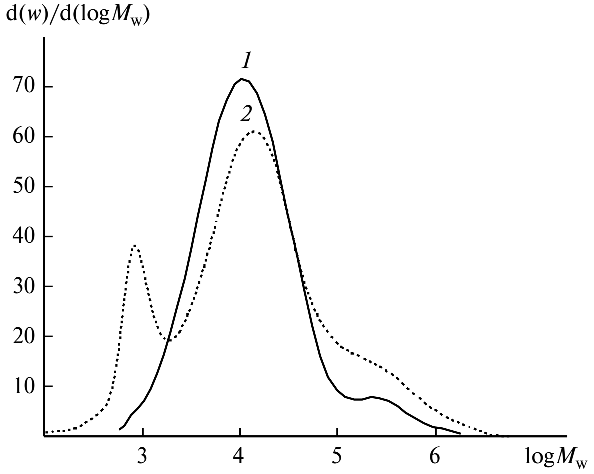

Fig. 3. Chromatograms of the PE samples prepared in the presence of complexes **2** (*1*) and **1** (*2*) activated with TIBA (see entries *9* in Tables 2 and 1, respectively).

reaction with TIBA the fluorinated analog of complex **1** produces no active sites responsible for the formation of PE with the lowest molecular weight, which are efficiently formed from complex **1**, especially in the absence of the monomer (see Fig. 2).

Copolymerization of ethylene with α-olefins using complex 1. Upon activation with MAO, complex **1** exhibits a high activity in the homopolymerization of ethylene and also in the ethylene uptake from a mixture of comonomers (ethylene/hex-1-ene (see Table 3, entries *1* and *2*) and ethylene/dec-1-ene (entry *3*)). The rates of ethylene uptake in ethylene homopolymerization (curve *1*) and copolymerization of ethylene with hex-1-ene (curves *2* and *3*) and ethylene with dec-1-ene (curve *4*) as a function of the reaction duration are compared in Fig. 4. The values of the rate are related to the concentration of the catalyst and the overall concentration of (co)monomers. Figure 4 shows that the presence of the comonomer in the reaction mixture substantially changes the kinetics of the ethylene uptake. The initial uptake rate is very high, but during the homopolymerization process it decreases 3 times within 4—5 min and then remains almost unchanged. In the presence of α-olefin at the equimolar ratio of the comonomers (curves *2* and *4*), the rate of ethylene uptake increases within 1 min to a constant value, which is ~1.3 times lower than that for homopolymerization. The twofold increase in the concentration of hex-1-ene in the reaction medium results in the approximately threefold decrease in the rate of ethylene uptake. The chromatograms of the homopolymer and polymers obtained in the presence of α-olefins are nearly identical to the chromatograms of PE, indicating an insignificant influence of the comonomer on the ratio of rates of chain growth and transfer during the ethylene uptake.

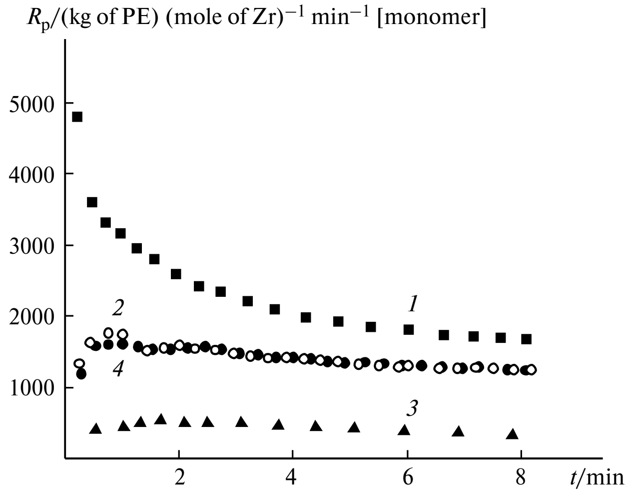

Fig. 4. Rate of ethylene uptake *vs* polymerization duration for the **1**/MAO system in the homopolymerization of ethylene (*1*), copolymerization of ethylene with hex-1-ene (*2*, *3*), and copolymerization of ethylene with dec-1-ene (*4*). Composition of the mixture of comonomers: ethylene/α-olefin ratio = 1 : 1 (*2*, *4*) and 1 : 2 mol mol^{-1} (*3*).

An analysis of the microstructure of the polymers obtained in the presence of α-olefins showed that the comonomer is inserted with a very low efficiency. The fragment of the ^{13}C NMR spectrum of the copolymer of ethylene with hex-1-ene formed at the equimolar ratio of the comonomers in the mixture is shown in Fig. 5. The signals in the spectrum of the comonomers were assigned

Table 3. Results of copolymerization of ethylene with α-olefins in the presence of complex **1** (30 °C, toluene, 20 mL, [Zr] = 0.6 μmol, ethylene pressure 1 atm)

Entry	Activator (A)	A/Zr /mol mol^{-1}	Comonomer* /mol mol^{-1}	t/min	Y/g	A	M_w	M_n	M_w/M_n
1	MAO	1000	C2/C6 (1/1)	8	1.21	15000	14400	4600	3.11
2	MAO	1000	C2/C6 (1/2)	8	0.47	5900	15800	4500	3.51
3	MAO	1000	C2/C10 (1/1)	8	1.24	15100	21150	3700	5.72
4	d-MAO	1000	C2/C6 (1/1)	10	Traces	—	—	—	—
5	TMA	500	C2/C6 (1/1)	23	0.14	600	—	—	—
6	TMA	500	C2/C6 (1/2)	23	Traces	—	—	—	—
7	TIBA	500	C2/C6 (1/1)	15	0.74	4900	—	—	—
8	TIBA	500	C2/C6 (1/2)	15	0.69	4600	—	—	—

* C2 is ethylene, C6 is hex-1-ene, and C10 is dec-1-ene.

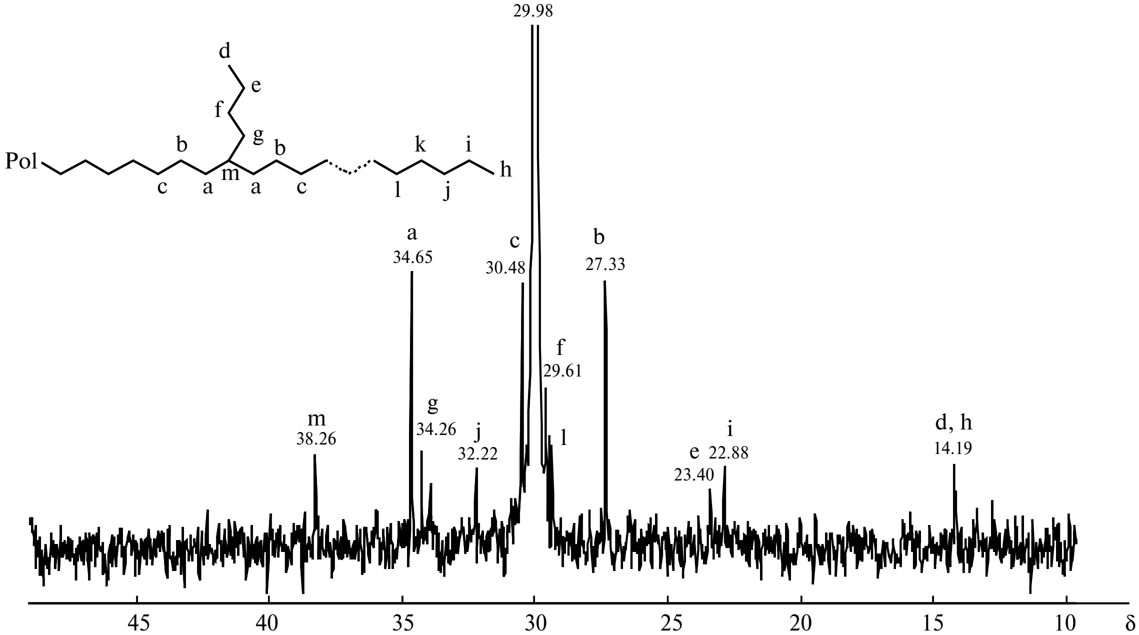

Fig. 5. Fragment of the ^{13}C NMR spectrum of a solution of the copolymer of ethylene with hex-1-ene in tetrachloroethane-d$_2$ (130 °C) obtained in the presence of the **1**/MAO system (see entry *2* in Table 3).

on the basis of the published data.[35,36] The content of the comonomer in the copolymer (signals a—g) is ~1 mol.%, which corresponds to the comonomer conversion at the level of several percents. Another group of low-intensity signals is attributed to the terminal propyl groups (h—l). The signals of the terminal unsaturated groups in the ^{13}C NMR spectrum were not detected. This indicates that the reaction of the β-hydride shift to the transition metal atom or coordinated monomer has insignificant contribution to the chain transfer. Thus, the main channel of chain transfer resulting in the formation of low-molecular-weight polymers in the presence of the catalytic system **1**/MAO is the transfer to TMA, which is contained in MAO. The number average MW (M_n) determined as the ratio of intensity of the terminal propyl group signals to those related to the main chain carbon atoms (see Table 3, entry *1*) is 4900, which agrees well with the value of M_n determined by GPC (M_n = 4600). Analogous conclusions were drawn from the analysis of the microstructure of the copolymer of ethylene with dec-1-ene.

Copolymerization of ethylene using complex 2. The results obtained in a study of the copolymerization of ethylene with propylene and hex-1-ene in the presence of complex **2** when it is activated by "dry" MAO and in the reaction of ethylene with propylene with the activation by TIBA are presented in Table 4. Experiments on copolymerization with the catalyst based on complex **2** were carried out for a mixture of comonomers of a certain composition at a pressure of 10 atm.

Under activation of complex **2** by "dry" MAO, the catalyst exhibits approximately the same activity in the copolymerization of ethylene with both propylene and hex-1-ene, which is ~3 times lower than its activity in ethylene homopolymerization (see Table 2, entry *6*). Copolymers

Table 4. Results of copolymerization of ethylene with α-olefins in the presence of complex **2** (30 °C, toluene, 60 mL, [Zr] = 5.4 μmol, pressure of a mixture of comonomers 10 atm)

Entry	Activator (A)	A/Zr /mol mol^{-1}	Comonomer /mol mol^{-1}	t/min	Y/g	A	M_w	M_n	M_w/M_n
1	d-MAO	1000	C2/C3* 0.7/1	4	7.9	2200	164400	42400	3.88
2	d-MAO	1000	C2/C6 0.7/1	4	6.6	1800	147436	20851	7.07
3	TIBA	500	C2/C3 0.7/1	20	2.4	130	31200	13220	2.36

* C3 is propylene.

of propylene with hex-1-ene have high values of M_w/M_n, and the copolymer of ethylene with propylene obtained with TIBA has the value of M_w/M_n characteristic of single site polymers. The chromatograms of the copolymers presented in Fig. 6 show (especially for the copolymer with hex-1-ene) that the polymers obtained with "dry" MAO are not unimodal (see curves *1* and *2*). This indicates the formation in the system of several catalytic sites, which can be formed either due to the action of both residual amounts of TMA in MAO and α-olefin or their combined participation in this process. The activation of complex **2** by TIBA in the presence of hex-1-ene results in the formation of active sites of the single type. It should be mentioned that they selectively insert ethylene. An analysis of the microstructure of this polymer indicates that the ^{13}C NMR spectrum of the sample contains only the signal with δ 29.98 corresponding to the carbon atoms in the sequences $—(CH_2)_n—$.

Complex **2** activated with "dry" MAO gives rise to copolymer with a very low content of the comonomer. At the same composition of comonomers feed and under other similar conditions, the comonomer content for the copolymer of ethylene with propylene is ~4 mol.%, whereas that for the copolymer of ethylene with hex-1-ene is ~1 mol.%. An analysis of the ^{13}C NMR spectra also showed that the insertion of the comonomer occurred mainly in the form of single units separated by long ethylene sequences and the relative intensity of signals of the carbon atoms of the sequences with the similar arrangement of propylene units, such as EPEPE, PEEP, and EPP, is at a noise level. No signals of the PPP sequences (δ 46.5) are observed in the spectrum.

Thus, we have investigated the catalytic properties of bis[*N*-(3,5-di-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1**) and its fluorinated analog bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]zirconium(IV) dichloride (**2**) in ethylene polymerization and copolymerization of ethylene with α-olefins upon the activation of complexes **1** and **2** with various organoaluminum compounds (OAC): commercial MAO containing ~35 mol.% TMA, MAO containing no TMA ("dry" MAO), TMA, and TIBA. It is shown that catalytic properties of the complexes are substantially different and the differences depend on the nature of the activator. Complex **1** is efficiently activated by MAO containing, TMA, and neat TMA and TIBA but is not activated by "dry" MAO. In terms of the activating ability the cocatalysts can be arranged in the series MAO > TIBA > TMA >> "dry" MAO. High values of polydispersity indices of the formed PE samples indicate the presence of multiple active sites in the catalytic systems studied. The aging of a toluene solution of the catalyst with TIBA before the introduction of the monomer results in the significant relative growth of the lowest-molecular-weight component of the polymer without activity loss of the system. These results indicate that the reactions of complex **1** with trialkylaluminum compounds proceed *via* several routes, which differ in rates and produce active sites different in composition and structure. Several questions arise because of the general character of the chromatograms of the PE samples obtained on structurally similar zirconium complexes in the present and previously published works. The determination of the degree (ideally, the mechanism) of participation of trialkylaluminum compounds in the formation of active sites and elucidation of catalytic intermediates, reaction rates, and the influence of the monomer on these process are among the stated problems. The solution of these problems facilitate the control the activity of the catalysts of this type and molecular weight characteristics of the polymers formed on them.

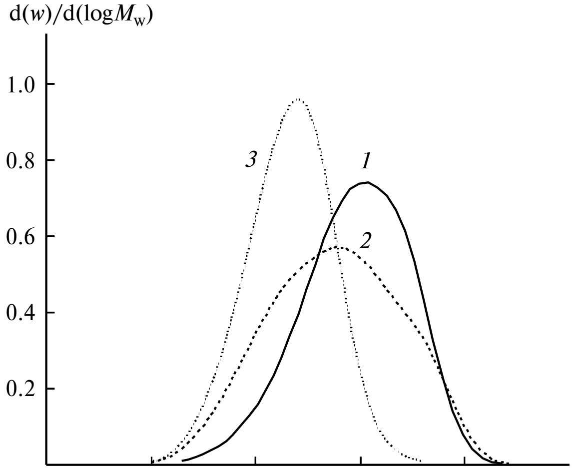

Fig. 6. Chromatograms of the samples of copolymers of ethylene with propylene (*1*) and hex-1-ene (*2, 3*) obtained for the catalytic system **2**/d-MAO (*1, 2*) and **2**/TIBA (*3*) (see entries *1—3* in Table 4).

Complex **2** is efficiently activated by both MAO and "dry" MAO but exhibits a very low activity when treated with TIBA. Its activity is almost zero after the treatment with TMA. In the two former cases, the catalyst forms (with approximately equal activity) high-molecular-weight PE with polydispersity indices close to those found for the polymers formed on single site catalytic systems. This means that fluorine substituents in the =N—Ph fragment suppress the reactions of complex **2** with trialkylaluminum compounds, which lead to the formation of multiple types of active sites in the case of complex **1**. Upon the activation with TIBA, complex **2**, as well as complex **1**, forms low-molecular-weight PE but shows a low activity. This indicates that the active sites formed by the action of TIBA on the complexes of both type are similar. At the same time, there are substantial differences in the rates of formation of these sites.

In the copolymerization of ethylene with α-olefins, the both complexes showed a low efficiency of insertion of the comonomer (1—4 mol.% at the approximately equimolar composition of a mixture of olefins). The same regularities of the influence of the activator type on the activity and molecular weight characteristics of the copolymers as in the homopolymerization of ethylene were observed for complex **1** when using various activators. An analysis of the microstructure of the copolymer of ethylene with hex-1-ene obtained in the presence of the **1**/MAO system suggested that the main channel of chain transfer is the transfer to TMA, which is present in MAO. Single insertions of the comonomer into the copolymer chain occur in the presence of the both catalysts.

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