Mechanochemical synthesis of zirconium and hafnium phenoxyimine complexes L_2MCl_2 (L = *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinate anion) and their catalytic properties in ethylene polymerization*

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A new method for preparation of zirconium and hafnium phenoxyimine complexes L_2MCl_2 (L is *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinate anion, M = Zr, Hf) by the solid state interaction of *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline, the corresponding metal chlorides, and sodium hydride under mechanical activation followed by heating of the activated mixture was developed. The obtained complexes have a high catalytic activity in the reaction of ethylene polymerization.

Key words: phenoxyimine complexes, zirconium, hafnium, mechanochemical synthesis, ^{1}H NMR spectra, catalysis, ethylene polymerization.

Complexes of 4 Group metals with phenoxyimine ligands play a special role in a series of post-metallocene catalysts of olefin polymerization based on coordination compounds of transition metals (precatalysts).[1—13] Attention to them is due to quite a number of unique properties of the catalytic systems involving these compounds (FI catalysts). For example, they are comparable or even surpass the most active metallocene catalysts in activity in ethylene polymerization. Various types of polyolefins were obtained with participation of FI catalysts: ultra-high-molecular-weight linear polyethylene (UHMWPE), low-molecular-weight PE with terminal vinyl groups, highly regular isotactic and syndiotactic polypropylene, high-molecular-weight atactic polypropylene, poly-α-olefins, ulta-high-molecular-weight random and block copolymers of ethylene with propylene, ethylene copolymers with nonbornene, and a series of other polyolefins. Among interesting properties of catalysts of this class are the ability to provide "living" ethylene and propylene polymerization even at high reaction temperatures[1] and the possibility to change the catalytic properties of the phenoxyimine complexes due to the variation of the electronic and steric characteristics of substituents in both the amine and phenol groups of the FI ligands ("tuning" to the synthesis of polyolefin with certain characteristics).[1—13] These properties of the phenoxyimine catalysts caused the choice of similar compounds as objects of the present study.

The FI complexes (as many other coordination compounds) are usually synthesized in solution in several steps.[14,15] Processes aimed at interacting of the solid initial substances in the absence of a solvent (solventless reactions) are of great interest at present.[16] Mechanical activation is used in many cases to accelerate the solid state reactions.[17,18] Using this method, we earlier obtained various types of coordination compounds: metal diketonates[19]; Ga and Cr acetylacetoneiminates[20]; cyclopentadienyl complexes of 3, 4, and 8 Group metals[21]; and Fe, Co, and Cr bis(dicarbollyl) complexes.[22] A convenient method was developed for the preparation of triphenylmethylium tetrakis(pentafluoro)borate $Ph_3C[B(C_6F_5)_4]$ widely used as an initiator in metallocene catalysis, and triphenylcyclopropenylium tetrakis(pentafluorophenyl)borate $Ph_3C_3[B(C_6F_5)_4]$.[23]

As for the reactions in solutions, in the case of solid state synthesis optimization is required for the goals of selecting optimal conditions (solvent, reactant ratio, duration, temperature of the process, *etc.*), for thorough stud-

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ies on the selection of the activating device with the corresponding energy potential, determination of the optimum ratio "activating filling/useful load (overall weight of activated compounds)," elucidation of the necessity and choosing the regime of the subsequent thermal treatment of an activated mixture, and optimization of other parameters. They are needed in each particular case for the solid state synthesis reactions using mechanochemical activation to establish the principal possibility of the synthesis, optimize the process, and prevent mechanical destruction of the starting compounds. The use of solid state methods allows one to exclude the application of solvents in the synthesis, obtain non-solvated products, reduce the amount of waste, and thus enhance ecological compatibility of the process.[17]

In this work, we describe a new method for the synthesis of zirconium and hafnium chloride complexes with *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinate ligands L_2MCl_2 by the solid state interaction of zirconium or hafnium tetrachlorides, ligand, and sodium hydride under the mechanochemical activation conditions. The results of studying the catalytic properties of the obtained compounds in ethylene polymerization reactions are presented. Neither synthesis, nor properties of the obtained hafnium complex were described earlier.

Results and Discussion

The influence of conditions of the mechanical action on LH—sodium hydride and LH—sodium hydride—zirconium (hafnium) tetrachloride mixtures (LH is (3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline) using a ball vibromill was studied to reveal the stability of the used substances under mechanical load and establish the principal possibility of the synthesis followed by the optimization of mechanical activation parameters. It was found, as a result, that the reaction is very sensitive to the purity and ratio of the initial reagents. Traces of the solvent (petroleum ether) in phenoxyimine, which is used for the recrystallization of LH, lead to the inhibition of the reaction. When using pure reagents for the treatment of an LH—sodium hydride mixture at a reagent ratio of 1 : 1, the color of the substance changes from white to yellow just after 10 min of activation. The diffraction pattern of the activated mixture shows a decrease in the reflection intensity of the initial reagents and the appearance of new reflections corresponding to the formation of (3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline sodium salt. After 1 h of mechanical treatment, the reflections of the starting substances almost completely disappear. Upon the addition of a zirconium or hafnium tetrachloride to the obtained reaction mixture followed by the mechanical action for 1—2 h, the reflections of the sodium salt of the ligand disappear from the diffraction pattern and easily identified reflections of sodium chloride appear. A similar result is observed for the interaction in an LH—sodium hydride—zirconium (hafnium) tetrachloride ternary system. Thus, it was found that the chemical reaction occurred upon the mechanical action on the reaction mixture.

To reveal the optimum conditions for the synthesis of target products, we studied the influence of the activation time, ratio of reagents (from 1 : 1 : 1 to 2 : 2 : 1), and parameters of heating of activated mixtures on their catalytic activity in ethylene polymerization.

Along with the reflections of sodium chloride, the diffraction patterns contain a broad hump at $2\theta \approx 20°$, indicating that the mixtures include an X-ray amorphous phase (Fig. 1). The nature of this phase remains unclear, but we tend to consider it as some intermediate substance rather than desired complex L_2MCl_2 (M = Zr, Hf). This viewpoint is substantiated by the fact that the mixture obtained by mechanical activation exhibits no catalytic activity in ethylene polymerization and dichloride complexes L_2MCl_2 cannot be isolated from this mixture by extraction with an organic solvent. To induce the catalytic activity, the obtained mixture should be heated to ~150 °C. However, no reflections from the expected complex L_2MCl_2 (M = Zr, Hf) or from any other substances, except for sodium chloride, appear before or after heating; *i.e.*, the reaction product still remains in the reaction mixture in the X-ray amor-

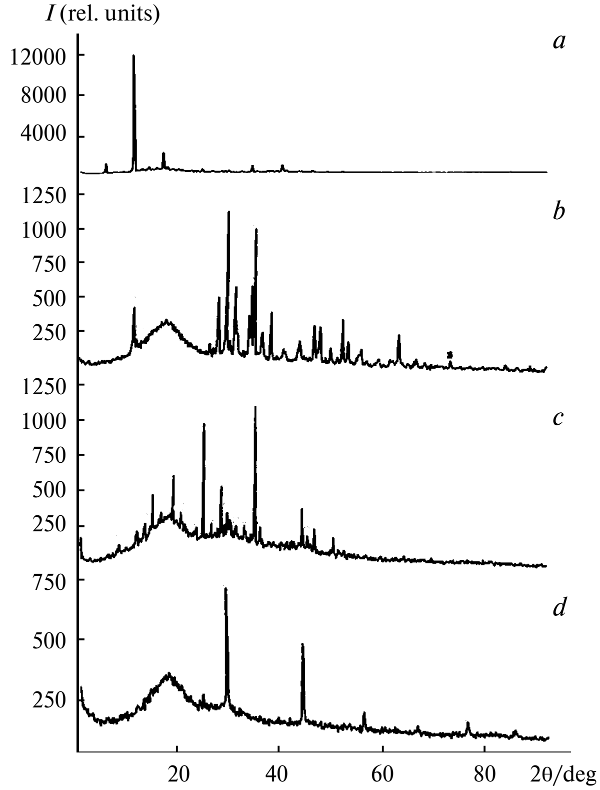
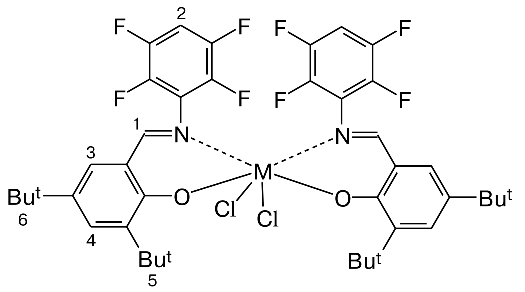


Fig. 1. Diffraction patterns of the initial substances and reaction mixtures: *a*, LH; *b*, NaH; *c*, mixture LH + NaH after mechanical activation for 1 h; *d*, mechanically activated mixture LH + NaH after $ZrCl_4$ addition and mechanical activation for 1 h.

phous state. Nevertheless, the fact of formation of phenoxyimine complexes L_2MCl_2 was reliably established when studying the NMR spectra of the solutions obtained after the extraction with hexane of the activated mixtures heated to 150 °C and was confirmed by the elemental analysis data for the products isolated from the solutions.

The IR spectra of the zirconium and hafnium complexes are nearly identical; *i.e.*, the nature of the metal in the studied frequency range weakly affects the shape of the spectra. The main distinctions of the IR spectra of the reaction products from the spectrum of the initial LH are that the intensity of the absorption band at 1619 cm^{-1} probably corresponding to vibrations of the C=N group of phenoxyimine[24] considerably decreases and the band shifts to 1604 cm^{-1}. Absorption bands at 545 and 470 cm^{-1} appear in the low-frequency spectral range and can be assigned to vibrations of M—O and M—N bonds. The diffraction patterns of the zirconium and hafnium complexes obtained after extraction with hexane indicate the crystalline state of the products. The positions of reflections in the diffraction patterns almost coincide for both complexes, indicating their isostructural character. Unfortunately, we failed yet to grow crystals for X-ray structure analysis.

It follows from the NMR spectral data that the purest complexes L_2MCl_2 are formed by the activation of LH—NaH—MCl_4 mixtures (M = Zr, Hf; LH is (3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline) with the ratio LH : MCl_4 = 1 : 1 rather than 2 : 1 as it is required by their stoichiometry. The same mixtures exhibit the highest catalytic activity in polymerization. The observed dependences of the run of the process and purity of the products on the reagent ratio and the necessity in the step of heating the activated mixture indicate a complicated mechanism of the solid state reaction, which needs further studies. As can be seen from the presented NMR spectra, the nature of the metal (Zr or Hf) exerts an insignificant effect on the electron density distribution in the proton-containing groups of the ligands in the considered complexes. The assignment of signals in the ^1H NMR spectra of the zirconium and hafnium complexes (Fig. 2, *c*, *d*) corresponds to the numeration of atoms presented in the formula of L_2MCl_2. The fragments of the ^1H NMR spectra of the initial phenoxyimine LH (spectrum *a*) and the corresponding titanium complex (spectrum *b*) described earlier[25] are presented in Fig. 2 for comparison. It should be mentioned that for all three complexes of the triad (Ti, Zr, Hf) the maximum upfield shifts compared to the starting LH are observed in the ^1H NMR spectra for protons of the groups arranged most closely to the complex-forming metal, namely, for the imine proton H(1) (shift 0.62 ppm (Ti, Zr) and 0.59 ppm (Hf)), and the protons of the *tert*-butyl substituent H(5) (0.13 ppm (Ti), 0.15 ppm (Zr), and 0.16 ppm (Hf)).



L_2MCl_2

M = Zr, Hf

As mentioned above, the mixtures obtained directly by mechanical activation exhibit no catalytic properties in ethylene polymerization, but after heating to 150 °C they demonstrate high activity (toluene, 30 °C, overall pressure of ethylene and toluene vapor 1 atm, polymerization time 20 min, MAO as an activator ($Al_{MAO}/M = 1000$ mol mol^{-1})). For example, for the mixture based on zirconium chloride the activity based on 1 mole of metal ion M (M = Zr, Hf) is 5500 (kg of PE) (mol h $atm)^{-1}$, whereas for the mixture based on hafnium chloride this value is 1100 (kg of PE) (mol h $atm)^{-1}$. The catalytic systems based on individual complexes L_2MCl_2 isolated by extraction from the heated mixtures showed a substantially higher activity: 10 200 and 2900 (kg of PE) (mol h $atm)^{-1}$ for the Zr and Hf complexes, respectively. Under analogous conditions, the activity of the titanium complex with the same ligand has an intermediate value of 7800 (kg of PE) (mol h $atm)^{-1}$. The decrease in the activity in the order Zr > Ti > Hf is typical of the most part of structural analogs of the metallocene catalysts.[1]

We have earlier shown[25] for the titanium and zirconium complexes with the same ligand that trimethylaluminum present in MAO favors the deactivation of the catalyst due to the exchange reaction of the ligands of the complexes with TMA. Probably, similar reactions occur in the course of polymerization involving the hafnium catalyst. Figure 3 compares the dependences of the specific activity of the hafnium complex when it is activated by MAO and "dry" MAO (from which TMA was removed by prolong evacuation). It is seen that ethylene polymerization with the activation of the catalyst by MAO is accompanied by the gradual deactivation of the catalyst (see Fig. 3, curve *1*), whereas the catalytic system with "dry" MAO performs the process with the stationary rate (curve *2*). An induction period (~3 min) is observed in experiment with "dry" MAO, which probably indicates a lower efficiency of methylation of L_2HfCl_2 under the action of "dry" MAO, and the step of alkylation of the dichloride complex is the necessary stage preceding the formation of cationic metal—alkyl complexes, the latter being active sites leading the polymerization process.

Thus, we developed the new (for this class of compounds) mechanochemical method of synthesis of the FI complexes of 4 Group metals by the direct interaction of

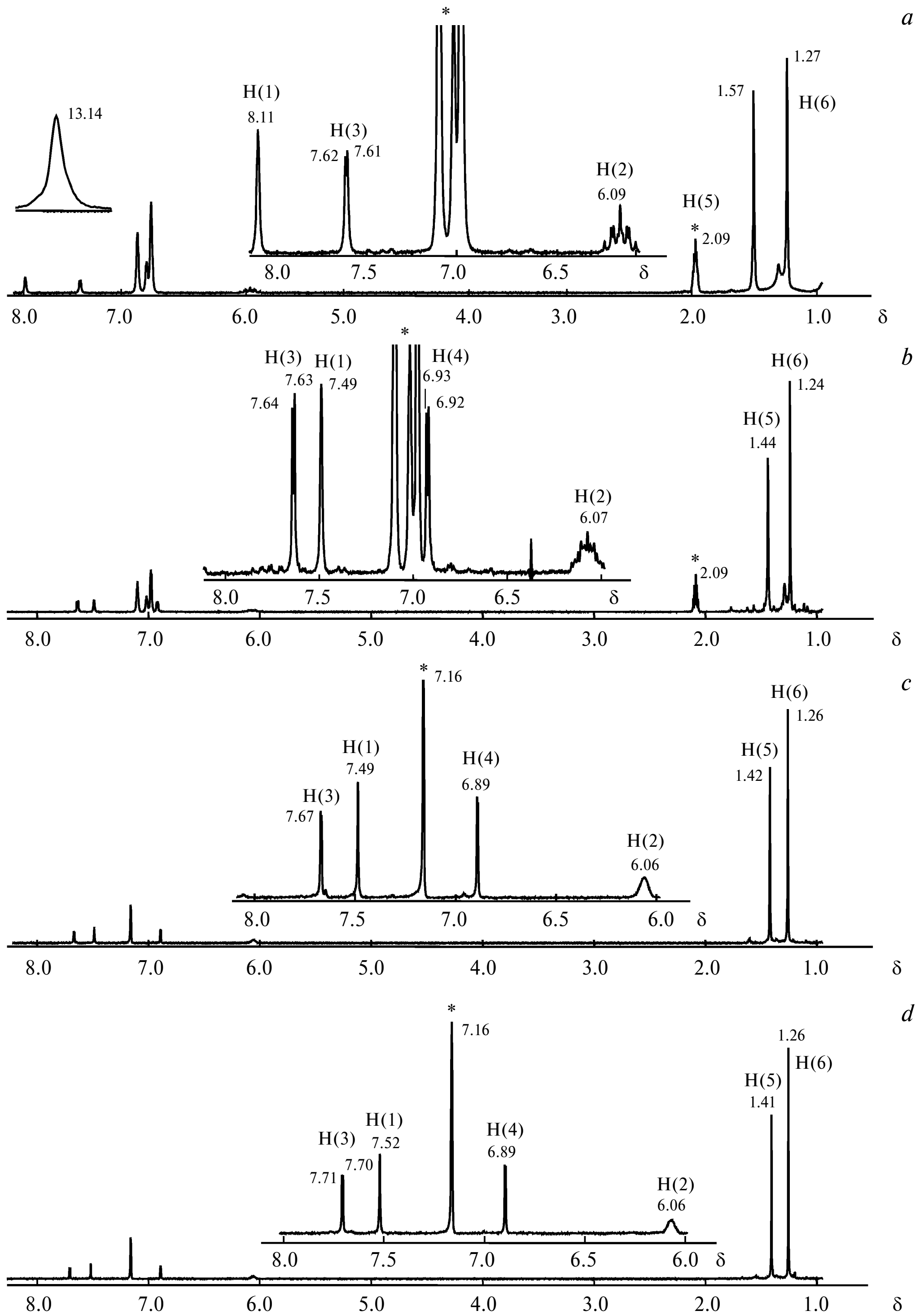


Fig. 2. Fragments of the ^{1}H NMR spectra of solutions of the initial LH (*a*) and titanium complex (*b*) in toluene-d$_8$ (see Ref. 16) and the zirconium (*c*) and hafnium (*d*) complexes in benzene-d$_6$.

anhydrous chlorides of these metals with *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline and sodium hydride followed by heating of the activated mixture and showed that the obtained complexes have a high catalytic activity of in ethylene polymerization.

Experimental

The starting commercial substances $ZrCl_4$, $HfCl_4$, and NaH were used without additional purification. *N*-(3,5-Di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline was synthesized according

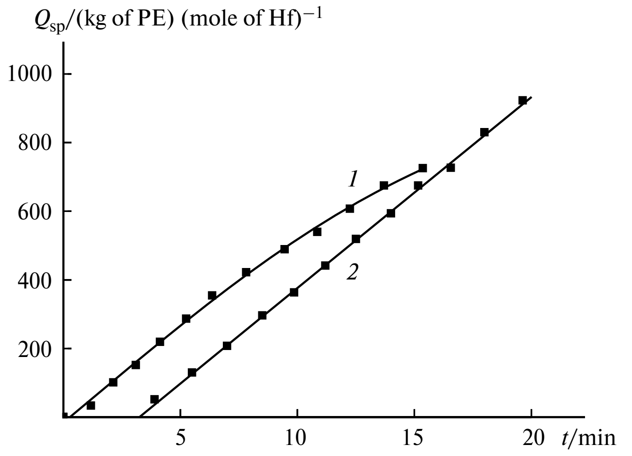


Fig. 3. Specific activity of hafnium complex L_2HfCl_2 *vs* time in ethylene polymerization for the activation of the catalyst by MAO (*1*) and "dry" MAO (*2*). Polymerization conditions: toluene, 30 °C, total pressure of ethylene and toluene vapors 1 atm, and Al/Hf mole ratio = 1000.

to a described procedure.[26] Hexane and benzene (reagent grade) were distilled over lithium alumohydride in the presence of cetyltrimethylammonium bromide. Toluene was doubly distilled over $LiAlH_4$ in an argon atmosphere. Methylaluminoxane (MAO) as a solution in toluene with a content of ~35 mol.% trimethylaluminum (TMA) (Aldrich) was used as received. Ethylene (polymerization purity) was additionally purified passing through columns packed with activated molecular sieves 4 Å and Al_2O_3. All procedures with compounds sensitive to the action of air and moisture were carried out in a helium box or using Schlenk technique.

The mechanical treatment of the reaction mixture was carried out using an eccentric vibromill (working frequency 12 Hz, amplitude 11 mm) in stainless steel reactors with a volume of ~85 cm^3. The activating filling was 20 steel balls with a diameter of 12.3 mm and a total weight of ~150 g.

The X-ray phase analysis of the samples was carried out on an ADN-2-01 diffractometer (Cu-Kα radiation, Ni filter) using the X-Ray program developed for the automation of the processes of obtaining, processing, and analysis of data on X-ray diffractometers (series DRON). The IR spectra of the initial substances, reaction mixtures, and reaction products were recorded on a UR-20 spectrophotometer in the range 400—4000 cm^{-1}. Samples for the studies were prepared as suspensions in Nujol (thin layer between KBr plates). The IR spectra of the initial phenoxyimine and obtained complexes were also detected on a PerkinElmer Spectrum 100 FT-IR spectrometer in the range 700—4000 cm^{-1}. ^{1}H NMR spectra were recorded at 20 °C in benzene-d$_6$ on a Bruker DPX-200 Fourier spectrometer.

Synthesis of bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]zirconium(IV) dichloride. A mixture of *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline (LH) (0.47 g, 1.2 mmol), NaH (0.08 g, 3.3 mmol), and $ZrCl_4$ (0.31 g, 1.3 mmol) was thoroughly triturated in an agate mortar, transferred into a reactor, and subjected to mechanical activation for 2 h. The activated mixture was heated *in vacuo* to 150 °C. The target product was isolated by extraction with hexane (3×25 mL) from 0.5 g of the activated mixture. The yield of the bright yellow finely crystalline substance L_2ZrCl_2 was 0.26 g. The yield with respect to the starting LH was 87% based on the amount of the reaction mixture taken for extraction. Found (%): C, 54.78; H, 4.97; Cl, 7.75; F, 15.05; N, 3.11; Zr, 9.28. $C_{42}H_{44}Cl_2F_8N_2O_2Zr$. Calculated (%): C, 54.65; H, 4.60; Cl 7.68; F, 16.5; N 3.03; Zr, 9.88. IR, ν/cm^{-1}: 2958 w, 2923 m, 2854 w, 1604 m, 1588 s, 1560 w, 1546 s, 1514 vs, 1469 m, 1435 w, 1391 br.m, 1364 w, 1274 m, 1253 m, 1177 m, 1041 s, 939 s, 851 s, 777 w, 757 w, 600 w, 550 s, 470 m. ^{1}H NMR (toluene-d$_8$), δ: 1.25 (s, Bu^t); 1.39 (s, Bu^t); 6.06 (m, $C_6F_4\underline{H}$); 6.90 (d, Ar, J = 2.43 Hz); 7.58 (s, $C\underline{H}$=N); 7.65 (d, Ar, J = 2.43 Hz). X-ray phase analysis, d/Å (I_{rel} (%)): 11.63 (66), 9.46 (21), 8.19 (88), 6.99 (19), 4.54 (100), 4.09 (55), 3.97 (55), 3.67 (43), 3.49 (35), 2.69 (19), 2.49 (20), 2.39 (17).

Synthesis of bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]hafnium(IV) dichloride. The reaction was carried out similarly to the previous example using LH (0.265 g, 0.695 mmol), NaH (0.035 g, 1.46 mmol), and $HfCl_4$ (0.225 g, 0.700 mmol). The target product was extracted with hexane (3×25 mL) from the heated mixture (0.34 g). The yield of the bright yellow finely crystalline substance L_2HfCl_2 was 0.17 g (75%). Found (%): C, 49.39; H, 4.96. $C_{42}H_{44}Cl_2F_8HfN_2O_2$. Calculated (%): C, 49.94; H, 4.39. IR, ν/cm^{-1}: 2958 w, 2923 m, 2854 w, 1604 m, 1588 s, 1560 w, 1546 s, 1514 vs, 1469 m, 1435 w, 1391 br.m, 1364 w, 1274 m, 1253 sh, 1177 m, 1041 s, 939 s, 851 s, 777 w, 757 w, 600 w, 545 s, 470 m. ^{1}H NMR (benzene-d$_6$), δ: 1.26 (s, Bu^t); 1.41 (s, Bu^t); 6.06 (m, $C_6F_4\underline{H}$); 6.89 (d, Ar, J = = 2.43 Hz); 7.52 (s, $C\underline{H}$=N); 7.71 (d, Ar, J = 2.43 Hz). X-ray phase analysis, d/Å (I_{rel} (%)): 11.56 (57), 9.40 (13), 8.15 (100), 6.99 (25), 5.16 (12), 4.53 (67), 4.09 (30), 3.96 (29), 3.65 (19), 3.48 (17), 2.69 (10), 2.49 (15), 2.42 (12), 2.38 (16).

Ethylene polymerization. Polymerization of ethylene was carried out using an earlier described procedure.[25]

The obtained products were identified by the data of chemical analysis and physicochemical methods of investigation. The chemical analysis, thermal studies, and detection of diffraction patterns and IR and NMR spectra were carried out at the Multiuser Analytical Center of the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

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