Complexes of titanium(IV) chloride with N-(3,5-R,R´-salicylidene)-2(3,4)-[bis(5-methyl-2-furyl)methyl]aniline, a novel type of phenoxyimine catalysts for olefin polymerization

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New representatives of chelate-type titanium(iv) salicylideneaniline complexes with bis(5-methyl-2-furyl)methyl substituents in the aniline fragment are synthesized. In the presence of poly(methylalumoxane), these complexes catalyze ethylene and propylene polymerization. The effect of the position of substituents in the ligands on the activities of the catalysts is studied. High-molecular-weight linear polyethylene ($M_w \approx 172200-300000$, $M_w/M_n \approx 2-3$) and high-molecular-weight atactic elastic polypropylene ($M_w \approx 1000000$, $M_w/M_n \ge 7.0$) are obtained.

Key words: titanium(IV) chlorides, oxoimine ligands, homogeneous catalysis, polymerization, olefins, polyethylene, polypropylene.

A new class of olefin polymerization catalysts based on the Group 4 transition metals and phenoxyimine ligands arouse steady interest since the first publications.¹⁻⁴ The attention to these catalytic systems is due to inherent unique properties. Thus various types of polyolefins, viz., superhigh-molecular-weight polyethylene (PE), low-molecular-weight PE with terminal vinyl groups, highly regular isotactic and syndiotactic polypropylene (PP), high-molecular-weight atactic PP, poly(α -olefins), superhigh-molecular-weight random and block-copolymers of ethylene with propylene, ethylene norbornene, and some others, have been prepared using these catalysts. $^{5-10}$ Some of them enable 'living' polymerization of ethylene and propylene even at high temperatures yielding PE and PP with very narrow molecularweight distribution $(M_w/M_n \approx 1)$; where M_w and M_n are weight-average and number-average molecular weights, respectively), which is one of their most interesting properties.

Currently, it is generally accepted that the active site of a Ziegler-type catalyst comprises a cation of a transi-

tion metal and an inorganic and/or organic ligand.11-13 Therefore, the concept of design of novel complexes belonging to post-metallocene catalysts is based on variations of the electron density in the ligand molecules together with the steric crowding of the active sites.¹⁴⁻¹⁶ Both these effects are reached upon introduction of diverse substituents into the ligands. On the other hand, the possibility of modification of a counter-ion, which can also control the catalytic activity of a system, is employed to a much lesser extent. Processes associated with the formation of contact ion pairs or zwitter-ions, which can be obtained, e.g., upon coordination of poly(methylalumoxane) (MAO) to precursor complexes through salicylideneaniline ligands, can be regarded as possible trends in this direction. Considering the ease of formation of aluminum donor-acceptor complexes with oxygen-containing ligands, one can regard bis(5-methyl-2-furyl)methyl substituents with two oxygen atoms that can be involved in the coordination as potential bridges between the transition metal sites and the counter-ions.

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In the present work, we describe synthesis of three groups of Schiff base derivatives containing *ortho-*, *meta-* and *para-*bis(5-methyl-2-furyl)methyl substituents in the aniline moieties of ligands as well as studies on catalytic properties of the respective Ti^{IV} complexes in homogeneous polymerization of ethylene and propylene.

Results and Discussion

2,2'-(2-Nitrophenyl)methylidenedi(5-methylfuran) (1a), 2,2'-(3-nitrophenyl)methylidenedi(5-methylfuran) (1b), and 2,2'-(4-nitrophenyl)methylidenedi(5-methylfuran) (1c) were obtained by reactions of the corresponding nitrobenzaldehydes with 2-methylfuran in the presence of chlorotrimethylsilane. Their reduction with sodium borohydride in the presence of Pd/C afforded bis(5-methyl-2-furyl)methylanilines 2a-c (Sheme 1). Signals for the aromatic protons in the ¹H NMR spectra of compounds 1a,b and 2a,b appear as multiplets.

Reactions of the aniline derivatives 2a-c with the corresponding salicylaldehyde derivatives yield the target N-(3,5-R,R'-salicylidene)-2(3,4)-[bis(5-methyl-2-furyl)methyl]anilines <math>3-17 (Scheme 2).

X-ray diffraction analysis of compound 6 gave additional information on the structures of the synthesized compounds (Fig. 1, Table 1).

In the crystal of compound **6**, the hydroxy group of the salicylaldehyde fragment is involved in intramolecular H-bonding N...H-O(N(1)...O(1), d2.600(2) Å) with closure of a planar six-membered ring. The phenyl ring of the amine is somewhat turned around with respect



Reagents and conditions: i. ClSiMe₃. ii. NaBH₄, Pd/C, MeOH.

to the salicylaldimine fragment with a torsion angle C(8)-N(1)-C(9)-C(14) of 34.1°. The bisector plane of the bis(5-methyl-2-furyl)methyl fragment is virtually coplanar with the phenyl ring. The corresponding bond lengths in the furan rings are the same and are close to those expected for this class of compounds. The bond angles C(21)-C(15)-C(16) and C(21)-C(15)-C(11) are somewhat enlarged (to 113.9(1)°) as compared with the standard values.



Scheme 1



Fig. 1. Structure of N-(5-methylsalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (6).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in structure **6**

Bond <i>d</i> /Å		Bond	d∕Å	Angle	ω/deg
O(1)-C(2)	1.358(2)	C(15)-C(16)	1.500(2)	C(16)-O(2)-	C(19) 106.43(15)
O(2) - C(16)	1.375(2)	C(16) - C(17)	1.340(3)	C(21) - O(3) -	C(24) 107.04(15)
O(2) - C(19)	1.381(2)	C(17) - C(18)	1.430(3)	C(8) - N(1) - C	(9) 121.01(15)
O(3) - C(21)	1.376(2)	C(18) - C(19)	1.334(3)	C(6) - C(1) - C	(2) 118.50(16)
O(3) - C(24)	1.383(2)	C(19) - C(20)	1.481(3)	N(1) - C(8) - C	(1) 121.87(16)
N(1) - C(8)	1.286(2)	C(21) - C(22)	1.346(3)	C(21) - C(15) -	-C(16) 113.90(14)
N(1) - C(9)	1.418(2)	C(22) - C(23)	1.420(3)	C(21)-C(15)-	-C(11) 113.94(14)
C(1) - C(2)	1.416(2)	C(23) - C(24)	1.337(3)	C(16) - C(15) -	-C(11) 109.64(15)
C(1) - C(8)	1.454(2)	C(24) - C(25)	1.479(3)		. , . ,
C(15)-C(21)	1.501(2)				

Despite *trans*-arrangement of the O(2) and O(3) atoms of the furan rings with a pseudotorsion angle O(2)-C(16)-C(21)-O(3) of 104.0° , the analysis of intramolecular contacts shows the lack of steric hindrance in the molecule for *cis*-arrangement of these atoms as well. Presumably, the conformation in the crystal **6** is determined by weak intermolecular contacts of the C-H...O type. Hence, one may suggest that the oxygen atoms are the more so prone to the coordination with MAO.

We prepared dichloride complexes of titanium(IV) with *N*-(3,5-R,R'-salicylidene)-2(3,4)-[bis(5-methyl-2-furyl)methyl]aniline by a known procedure¹⁷ from titanium dichloride diisopropoxide and the corresponding ligand in dry dichloromethane (Scheme 3). By analogy with the known data^{18,19} on the structures of oxoimine chloride complexes, we believe that compounds **18**–**32** prepared by us possess similar structures. Data from elemental analyses, ¹H NMR spectroscopy (compound **32**), and IR spectroscopy corroborate their structures. The IR spectra demonstrate a bathochromic shift of the band v(C=N) by 15–22 cm⁻¹ as compared with the spectrum

of the free ligand. In addition, new bands appear at 450– 570 cm⁻¹, which can be attributed to stretching vibrations of the Ti–N and Ti–O bonds. In the ¹H NMR spectrum, the characteristic signal for the aldimine protons is a singlet, which suggests their equivalence and C_2 -symmetry of the complex.

The catalytic properties of complexes **18–32** in ethylene polymerization were studied in reactions carried out at 30 °C and atmospheric pressure of the monomer with MAO as a co-catalyst at an Al_{MAO}/Ti ratio \approx 500.

The effect of the character and position of substituents in the ligands on the catalytic activities of the complexes is presented in Table 2.

As can be seen from Table 2, complexes **18–21**, poorly soluble in toluene, manifest very low catalytic activities. The introduction of two halogen atoms in the ligand increases the solubilities of complexes **22** and **23**. The yellow color of solutions of these complexes in toluene fades upon addition of MAO, which suggests their efficient alkylation (see Ref. 20); however, these complexes produce only trace amounts of PE in the catalytic reaction.



Simultaneous introduction of a bromine atom and a Me group in positions 3 and 5 of the salicylaldehyde fragment (complexes **24** and **25**) increases their integral activity to 1120 and 1733 kg PE (mol Ti h $[C_2H_4])^{-1}$, respectively. Complexes **29** and **31** with *o*- and *p*-bis(5-methyl-2-furyl)methyl substituents in the ligands are less active than complex **25** with the same substituent in the *meta*-position.

Of the compounds obtained, that with *tert*-butyl substituents (complex **32**) possessed the highest activity. As can be seen from Table 2, this is only 1.5-2-fold lower than that of the known record-holder among similar compounds, *viz.*, titanium bis(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinate.^{21,22} It is of note that complexes **30** and **28** with *o*- and *m*-bis(5-methyl-2furyl)methyl substituents in the ligand (the isomers of complex **32**) afford only trace amounts of PE. Presumably, this is related to steric crowding at the metal atom, which hampers approach of the monomer to the poly-



Fig. 2. Fragments of the IR spectra of PE obtained on catalysts 24 (1) and 32 (2).

meric chain that is growing (or is formed) at the active site.

Polyethylene specimens obtained on catalysts 24, 25, 31 and 32 have linear structures, which is supported by data from IR spectra of the polymers (Fig. 2) where no bands of the deformation vibrations of the methyl groups in branchings $(1378 \text{ cm}^{-1})^{23}$ were present. These PE specimens manifest virtually identical GPC patterns (Fig. 3).

Catalytic properties of a system **32**—MAO in propylene polymerization are given in Table 3. It can be seen that the reduced activity of the system in the liquid monomer medium at 50 °C (Table 3, entry 3) is 500 times lower than in ethylene polymerization. It should be mentioned that a much lesser decrease in reduced activity (*ca.* twofold) on going from ethylene polymerization to propylene polymerization has been observed²¹ for a series of structurally similar titanium phenoxyimine complexes.

The results of diffractometric and ¹³C NMR spectroscopic studies of polypropylene²⁴ obtained with the use of



Fig. 3. Molecular-mass distribution of PE obtained on catalysts **24** (*1*), **25** (*2*), **31** (*3*), and **32** (*4*).

Table 2. Structures of the starting ligands and catalytic activities of complexes **18–32** in polymerization of ethylene (MAO as a cocatalyst, $Al_{MAO}/Ti = 500 \text{ mol mol}^{-1}$, toluene, reaction temperature 30 °C, total pressure of ethylene and toluene vapor, 1 atm)

Li- gand	\mathbb{R}^1	R ²	Comp- lex	Ti∙10 ⁶ ∕mol	t /min	Y /g	A/kg PE (mol Ti h [C ₂ H ₄]) ⁻¹	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
3	Н	Н	18	3.6	30	0.01	44	_	_
4	Н	Cl	19	2.8	30	0.01	57	57 —	
5	Н	Ι	20	3.6	30	0.06	267	_	_
6	Н	Me	21	3.6	30	0.01	44	_	_
7	Cl	Cl	22	3.6	30	0.01	44	_	_
8	Br	Br	23	3.6	35	0.06	229	_	_
9	Br	Me	24	8.8	19	0.39	1120	199000	2.34
10	Me	Br	25	3.6	30	0.39	1733	172200	2.64
11	Br	OMe	26	3.6	29	0.01	44	_	_
12	NO_2	Н	27	8.7	16	0.01	44	_	_
13	Bu ^t	Bu ^t	28	2.6	60	0.01	44	_	_
14	Me	Br	29	3.6	30	0.01	44	_	_
15	Bu ^t	Bu ^t	30	2.9	30	0.02	110	_	_
16	Me	Br	31	2.6	30	0.10	615	180600	2.73
17	Bu ^t	Bu ^t	32	2.8	7	0.47	11510	306000	2.12
17	Bu ^t	Bu ^t	32	1.1	20	0.34	7418	_	_
17	Bu ^t	Bu ^t	32	0.14	50	0.06	4114	_	_

Note. Here and in Table 3, t is polymerization time, Y is yield of polymer, A is integral activity, M_w and M_n are weight-average and number-average molecular weights, respectively.

Table 3. Bulk polymerization of propylene on a catalytic system 32-MAO at 30 °C

Entry	[Ti] • 10 ⁵ /mol L ⁻¹	Al _{MAO} /Ti /mol mol ⁻¹	<i>t/</i> h	Y/g	A ^a	$M_{ m w}$	$M_{\rm w}$ $/M_{\rm n}$
1 ^b	2.31	1800	1.2	9.3	153	$1.2 \cdot 10^{6}$	7.6
2 ^c	2.26	600	1.2	6.4	105	$2.0 \cdot 10^{6}$	9.8
3 ^{c,d}	2.28	600	4.3	4.3	23	$2.0 \cdot 10^{6}$	9.8

^{*a*} Reduced activity in kg PP (mol Ti h $[C_3H_6])^{-1}$.

^b The catalyst was added as a solution in 10% solution of MAO in toluene.

^c The catalyst was added as a solid.

^{*d*} At 50 °C.

the system **32**—MAO suggest the formation of atactic (radioamorphous) polymer containing *ca.* 5 mol.% of regioerrors (*viz.*, 2,1-additions) ($\delta_{\rm C}$ 16—17). Moreover, the distribution of the methyl pentads in this polymer is similar to that in an 'ideal' atactic PP. Polypropylene with analogous properties has been obtained on other structurally similar catalysts studied by us earlier.^{25,26}

The atactic PP synthesized on the system **32**—MAO has high molecular mass (*ca.* 10⁷) and broad molecularmass distribution ($M_w/M_n = 7-10$). In addition, the polymer possessed properties of an elastomer: the residual elongation following stretching by 300% (ε_{300}) did not exceed 21%. In these parameters, the polypropylene obtained by us is analogous to elastomeric stereo-block polypropylene composed of short isotactic and syndiotactic blocks separated by atactic sequences.²⁷ Attention should be paid to the fact that no rupture of samples of high-molecular-mass atactic PP on their *ca*. 20-fold elongation was observed.

Thus, we have synthesized three groups of Schiff base derivatives containing the bis(5-methyl-2-furyl)methyl substituent in the *o*-, *m*-, and *p*-positions of the aniline moiety of the ligand. In the presence of polymethyl-alumoxane, titanium complexes with these ligands behave as catalysts of ethylene and propylene polymerization. The incorporation of the bis(5-methyl-2-furyl)methyl substituent enhances the catalytic activity as compared with conventional phenoxyimine catalysts.²⁸ The results obtained are in keeping with a suggestion that the enhancement of activities of complexes comprising bis(5-methyl-2-furyl)methyl substituents can be rationalized by coordination of the oxygen atoms of the furan rings to organoaluminum compounds resulting in, at the least, a contact ion pair.

Experimental

The complexes were synthesized in an atmosphere of argon. Tetrahydrofuran, dichloromethane, toluene, propan-2-ol, hexane, and ethyl acetate (chemically pure) were additionally purified according to known procedures.²⁹ Titanium(v) chloride (Fluka) was additionally distilled under argon. Commercial SiO₂, 2-, 3-, and 4-nitrobenzaldehydes, 2-methylfuran, and chlorotrimethylsilane (Fluka) were used. NMR spectra of the ligands in CDCl₃ were recorded on Bruker WP-200 and Bruker

AMX-400 spectrometers and IR spectra, on a Magna-IR 750 spectrophotometer. Elemental analyses were carried out on Carlo Erba-1106 and Carlo Erba-1108 instruments.

2,2'-(3-Nitrophenyl)methylenedi(5-methylfuran) (1b). Chlorotrimethylsilane (2 mL) was added to a solution of 3-nitrobenzaldehyde (15 g, 0.1 mol) and 2-methylfuran (18 g, 20 mL, 0.22 mol) in benzene (60 mL). After 2–3 h, water was added to the reaction mixture, the organic layer was washed with 3% NaHCO₃, concentrated and the residue recrystallized from hexane. The yield was 15.3 g (47%), m.p. 95–96 °C. Found (%): C, 68.57; H, 4.89; N, 4.58. C₁₇H₁₅NO₄. Calculated (%): C, 68.68; H, 5.09; N, 4.71. ¹H NMR, δ : 2.17 (s, 6 H, Me); 5.76 (m, 4 H, H_{fur}); 5.80 (s, 1 H, CH); 7.99, 8.00 (both m, 2 H each, 2 H_{Ar}).

Compounds **1a,c** were obtained analogously.

2,2'-(2-Nitrophenyl)methylenedi(5-methylfuran) (1a). The yield was 18.0 g (55%), m.p. 83–84 °C. Found (%): C, 68.46; H, 4.76; N, 4.60. $C_{17}H_{15}NO_4$. Calculated (%): C, 68.68; H, 5.09; N, 4.71. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.87 (m, 4 H, H_{fur}); 5.92 (s, 1 H, CH); 7.80, 8.10 (both m, 2 H each, H_{Ar}).

2,2'-(4-Nitrophenyl)methylenedi(5-methylfuran) (1c). The yield was 19.7 g (64%), m.p. 89–91 °C. Found (%): C, 68.50; H, 4.80; N, 4.65. $C_{17}H_{15}NO_4$. Calculated (%): C, 68.68; H, 5.09; N, 4.71. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.85 (s, 1 H, CH); 7.50, 8.00 (both d, 2 H each, H_{Ar}, J = 8.9 Hz).

3-[Bis(5-methyl-2-furyl)methyl]aniline (2b). To a solution of compound **1b** (3.00 g, 0.01 mol) in hot MeOH (70 mL), 10% Pd/C (0.50 g) was added followed by NaBH₄ (0.82 g, 0.02 mol), which was added in small portions with vigorous stirring. After 15 min, the mixture was filtered, the filtrate was concentrated *in vacuo*, the residue was triturated with ether and the extract was concentrated on a rotary evaporator. The oily residue was purified by column chromatography (hexane—AcOEt, 5 : 1) to give compound **2b** as yellow oil in a yield of 2.9 g (89.5%). Found (%): C, 76.19; H, 6.28; N, 5.18. C₁₇H₁₇NO₂. Calculated (%): C, 76.38; H, 6.41; N, 5.24. ¹H NMR, 8: 2.17 (s, 6 H, Me); 5.76 (m, 4 H, H_{fur}); 5.80 (s, 1 H, CH); 6.45, 6.89 (both m, 2 H each, H_{Ar}).

Compounds **2a**,**c** were obtained analogously.

2-[Bis(5-methyl-2-furyl)methyl]aniline (2a). The yield was 2.5 g (78%). Found (%): C, 76.03; H, 6.20; N, 5.07. $C_{17}H_{17}NO_2$. Calculated (%): C, 76.38; H, 6.41; N, 5.24. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.60 (m, 4 H, H_{fur}); 5.78 (s, 1 H, CH); 6.65, 6.98 (both m, 2 H each, H_{Ar}).

4-[Bis(5-methyl-2-furyl)methyl]aniline (2c). The yield was 3.0 g (92.6%). Found (%): C, 76.19; H, 6.14; N, 4.99. $C_{17}H_{17}NO_2$. Calculated (%): C, 76.38; H, 6.41; N, 5.24. ¹H NMR, δ : 2.25 (s, 6 H, Me); 5.66 (m, 4 H, H_{fur}); 5.85 (s, 1 H, CH); 6.78, 7.07 (both d, 2 H each, H_{Ar}).

N-(Salicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (3). Aniline 2b (0.23 g, 0.85 mmol) and TsOH (0.003 g, 0.02 mmol) were added to a solution of salicylaldehyde (0.10 g, 0.85 mmol), the mixture was refluxed with stirring for 20 h, filtered, the filtrate was concentrated and chromatographed on a column with silica gel (hexane—AcOEt, 5 : 1) to give compound 3 as yellow crystals in a yield of 0.26 g (87%). Found (%): C, 77.15; H, 5.81; N, 3.30. $C_{24}H_{21}NO_3$. Calculated (%): C, 77.61; H, 5.70; N, 3.77. ¹H NMR, δ : 2.30 (s, 6 H, Me); 5.60 (m, 4 H, H_{fur}); 5.87 (s, 1 H, CH); 7.10—7.45 (m, 8 H, H_{Ar}); 8.39 (s, 1 H, CH=N); 11.79 (s, 1 H, OH). Ligands 4–17 were obtained analogously.

N-(5-Chlorosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (4). The yield was 81%. Found (%): C, 70.85; H, 4.50; N, 2.97. $C_{24}H_{20}CINO_3$. Calculated (%): C, 71.02; H, 4.97; N, 3.45. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.90 (s, 1 H, CH); 6.90–7.40 (m, 7 H, H_{Ar}); 8.60 (s, 1 H, CH=N); 11.59 (s, 1 H, OH).

N-(5-Iodosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (5). The yield was 75%. Found (%): C, 57.70; H, 4.08; N, 2.70. $C_{24}H_{20}INO_3$. Calculated (%): C, 57.96; H, 4.50; N, 2.97. ¹H NMR, δ : 2.18 (s, 6 H, Me); 5.82 (m, 4 H, H_{fur}); 5.84 (s, 1 H, CH); 6.50–7.80 (m, 7 H, H_{Ar}); 8.46 (s, 1 H, CH=N); 11.50 (s, 1 H, OH).

N-(5-Methylsalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (6). The yield was 81%. Found (%): C, 70.85; H, 4.50; N, 2.97. $C_{25}H_{23}NO_3$. Calculated (%): C, 71.02; H, 4.97; N, 3.45. ¹H NMR, δ : 2.20 (s, 6 H, Me); 2.38 (s, 3 H, Me); 5.80 (m, 4 H, H_{fur}); 5.90 (s, 1 H, CH); 6.90–7.40 (m, 7 H, H_{Ar}); 8.60 (s, 1 H, CH=N); 11.59 (s, 1 H, OH).

N-(3,5-Dichlorosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (7). The yield was 76%. Found (%): C, 65.08; H, 4.18; N, 2.90. $C_{24}H_{19}Cl_2NO_3$. Calculated (%): C, 65.47; H, 4.35; N, 3.18. ¹H NMR, δ : 2.23 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.90 (s, 1 H, CH); 7.10–7.30 (m, 6 H, H_{Ar}); 8.60 (s, 1 H, CH=N); 11.59 (s, 1 H, OH).

N-(3,5-Dibromosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (8). The yield was 82%. Found (%): C, 54.12; H, 3.20; N, 2.50. $C_{24}H_{19}Br_2NO_3$. Calculated (%): C, 54.47; H, 3.62; N, 2.65. ¹H NMR, δ : 2.18 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.85 (s, 1 H, CH); 7.10–7.60 (m, 6 H, H_{Ar}); 8.40 (s, 1 H, CH=N); 11.60 (s, 1 H, OH).

N-(3-Bromo-5-methylsalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline (9). The yield was 81%. Found (%): C, 64.32; H, 4.26; N, 2.80. $C_{25}H_{22}BrNO_3$. Calculated (%): C, 64.66; H, 4.78; N, 3.02. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.83 (s, 1 H, CH); 7.10–7.20 (m, 6 H, H_{Ar}); 8.40 (s, 1 H, CH=N); 11.80 (s, 1 H, OH).

N-(5-Bromo-3-methylsalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline (10). The yield was 78%. Found (%): C, 64.32; H, 4.26; N, 2.80. $C_{25}H_{22}BrNO_3$. Calculated (%): C, 64.66; H, 4.78; N, 3.02. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.83 (s, 1 H, CH); 7.10–7.19 (m, 6 H, H_{Ar}); 8.36 (s, 1 H, CH=N); 11.90 (s, 1 H, OH).

N-(3-Bromo-5-methoxysalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline (11). The yield was 72%. Found (%): C, 62.02; H, 4.21; N, 2.65. $C_{25}H_{22}BrNO_4$. Calculated (%): C, 62.51; H, 4.62; N, 2.92. ¹H NMR, δ : 2.20 (s, 6 H, Me); 3.80 (s, 3 H, OMe); 5.80 (m, 4 H, H_{fur}); 5.83 (s, 1 H, CH); 6.90–7.13 (m, 6 H, H_{Ar}); 8.30 (s, 1 H, CH=N); 11.70 (s, 1 H, OH).

N-(3-Nitrosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline (12). The yield was 73%. Found (%): C, 69.60; H, 4.29; N, 6.50. $C_{24}H_{20}N_2O_5$. Calculated (%): C, 69.22; H, 4.84; N, 6.73. ¹H NMR, δ : 2.22 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.97 (s, 1 H, CH); 7.10–7.93 (m, 7 H, H_{Ar}); 8.39 (s, 1 H, CH=N); 11.97 (s, 1 H, OH).

N-(3,5-Di-*tert*-butylsalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline (13). The yield was 83%. Found (%): C, 79.52; H, 7.60; N, 2.70. $C_{32}H_{37}NO_3$. Calculated (%): C, 79.47; H, 7.71; N, 2.90. ¹H NMR, δ : 1.45 (s, 18 H, Me); 2.14 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.85 (s, 1 H, CH); 7.10–7.60 (m, 6 H, H_{Ar}); 8.40 (s, 1 H, CH=N); 11.70 (s, 1 H, OH). *N*-(5-Bromo-3-methylsalicylidene)-2-[bis(5-methyl-2-furyl)methyl]aniline (14). The yield was 72%. Found (%): C, 64.32; H, 4.26; N, 2.80. $C_{25}H_{22}BrNO_3$. Calculated (%): C, 64.66; H, 4.78; N, 3.02. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.83 (s, 1 H, CH); 7.10-7.19 (m, 6 H, H_{Ar}); 8.36 (s, 1 H, CH=N); 11.90 (s, 1 H, OH).

N-(3,5-Di-*tert*-butylsalicylidene)-2-[bis(5-methyl-2-furyl)methyl]aniline (15). The yield was 71%. Found (%): C, 79.52; H, 7.60; N, 2.70. $C_{32}H_{37}NO_3$. Calculated (%): C, 79.47; H, 7.71; N, 2.90. ¹H NMR, δ : 1.45 (s, 18 H, Me); 2.14 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.85 (s, 1 H, CH); 7.10–7.60 (m, 6 H, H_{Ar}); 8.40 (s, 1 H, CH=N); 11.70 (s, 1 H, OH).

N-(5-Bromo-3-methylsalicylidene)-4-[bis(5-methyl-2-furyl)methyl]aniline (16). The yield was 75%. Found (%): C, 64.32; H, 4.26; N, 2.80. $C_{25}H_{22}BrNO_3$. Calculated (%): C, 64.66; H, 4.78; N, 3.02. ¹H NMR, δ : 2.20 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.83 (s, 1 H, CH); 7.10–7.19 (m, 6 H, H_{Ar}); 8.36 (s, 1 H, CH=N); 11.90 (s, 1 H, OH).

N-(3,5-Di-*tert*-butylsalicylidene)-4-[bis(5-methyl-2-furyl)methyl]aniline (17). The yield was 85%. Found (%): C, 79.52; H, 7.60; N, 2.70. $C_{32}H_{37}NO_3$. Calculated (%): C, 79.47; H, 7.71; N, 2.90. ¹H NMR, δ : 1.45 (s, 18 H, Me); 2.14 (s, 6 H, Me); 5.80 (m, 4 H, H_{fur}); 5.85 (s, 1 H, CH); 7.10–7.60 (m, 6 H, H_{Ar}); 8.40 (s, 1 H, CH=N); 11.70 (s, 1 H, OH).

Synthesis of complex 18. To a solution of compound 3 (0.37 g, 0.10 mmol) in CH₂Cl₂ (10 mL), TiCl₂(OPrⁱ)₂ (0.12 g, 0.05 mmol) was added with stirring under argon. After 20 h, the red precipitate was filtered off and recrystallized from toluene. The yield was 0.73 g (85%). Found (%): C, 66.50; H, 4.60; Cl, 8.07; N, 3.15; Ti, 5.50. C₄₈H₄₀Cl₂N₂O₆Ti. Calculated (%): C, 67.08; H, 4.69; Cl, 8.25; N, 3.26; Ti, 5.57. IR, v/cm⁻¹: 1606 (C=N); 525 (Ti-O); 454 (Ti-N).

Bis{*N*-(5-chlorosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline}titanium(IV) dichloride (19). The yield was 68%. Found (%): C, 61.66; H, 4.00; Cl, 15.01; N, 2.50; Ti, 5.10. $C_{48}H_{38}Cl_4N_2O_6Ti$. Calculated (%): C, 62.09; H, 4.13; Cl, 15.31; N, 3.02; Ti, 5.16. IR, v/cm⁻¹: 1607 (C=N); 525 (Ti-O); 450 (Ti-N).

Bis{*N*-(5-iodosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline}titanium(IV) dichloride (20). The yield was 75%. Found (%): C, 51.36; H, 3.11; N, 2.27; Ti, 4.20. $C_{48}H_{38}Cl_2I_2N_2O_6Ti$. Calculated (%): C, 51.86; H, 3.42; N, 2.52; Ti, 4.30. IR, v/cm⁻¹: 1612 (C=N); 520 (Ti–O); 450 (Ti–N).

Bis{N-(5-methylsalicylidene)-3-[bis(5-methyl-2-fu-ryl)methyl]aniline}titanium(v) dichloride (21). The yield was 73%. Found (%): C, 67.25; H, 5.13; Cl, 7.43; N, 2.66; Ti, 5.12. $C_{50}H_{44}Cl_2N_2O_6$ Ti. Calculated (%): C, 67.65; H, 5.00; Cl, 7.99; N, 3.16; Ti, 5.39. IR, v/cm⁻¹: 1610 (C=N); 525 (Ti-O); 452 (Ti-N).

Bis{*N*-(3,5-dichlorosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline}titanium(*iv*) dichloride (22). The yield was 75%. Found (%): C, 57.30; H, 3.24; Cl, 21.03; N, 2.21; Ti, 4.30. $C_{48}H_{36}Cl_6N_2O_6Ti$. Calculated (%): C, 57.80; H, 3.64; Cl, 21.33; N, 2.81; Ti, 4.80. IR, v/cm⁻¹: 1614 (C=N); 515 (Ti-O); 455 (Ti-N).

Bis{*N*-(3,5-dibromosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline}titanium(*iv*) dichloride (23). The yield was 79%. Found (%): C, 48.76; H, 2.90; Cl, 5.80; N, 2.25; Ti, 3.87. $C_{48}H_{36}Br_4Cl_2N_2O_6Ti$. Calculated (%): C, 49.06; H, 3.09; Cl, 6.03; N, 2.38; Ti, 4.07. IR, v/cm⁻¹: 1617 (C=N); 522 (Ti-O); 446 (Ti-N). **Bis**{*N*-(3-bromo-5-methylsalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline}titanium(*iv*) dichloride (24). The yield was 74%. Found (%): C, 57.05; H, 3.75; Cl, 6.20; N, 2.40; Ti, 4.39. $C_{50}H_{42}Br_2Cl_2N_2O_6Ti$. Calculated (%): C, 57.44; H, 4.05; Cl, 6.78; N, 2.68; Ti, 4.58. IR, v/cm⁻¹: 1610 (C=N); 520 (Ti-O); 450 (Ti-N).

Bis{*N*-(5-bromo-3-methylsalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline}titanium(v) dichloride (25). The yield was 77%. Found (%): C, 57.09; H, 3.75; Cl, 6.50; N, 2.54; Ti, 4.30. C₅₀H₄₂Br₂Cl₂N₂O₆Ti. Calculated (%): C, 57.44; H, 4.05; Cl, 6.78; N, 2.68; Ti, 4.58. IR, v/cm⁻¹: 1610 (C=N); 527 (Ti-O); 453 (Ti-N).

Bis{*N*-(3-bromo-5-methoxysalicylidene)-3-[bis(5-methyl-2furyl)methyl]aniline}titanium(v) dichloride (26). The yield was 75%. Found (%): C, 55.40; H, 3.80; Cl, 6.49; N, 2.50; Ti, 4.12. C₅₀H₄₂Br₂Cl₂N₂O₈Ti. Calculated (%): C, 55.74; H, 3.93; Cl, 6.58; N, 2.60; Ti, 4.44. IR, v/cm⁻¹: 1615 (C=N); 528 (Ti-O); 443 (Ti-N).

Bis{*N*-(3-nitrosalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline}titanium(*iv*) dichloride (27). The yield was 65%. Found (%): C, 60.51; H, 3.83; Cl, 7.20; N, 2.40; Ti, 4.74. $C_{48}H_{38}Cl_2N_4O_{10}Ti$. Calculated (%): C, 60.71; H, 4.03; Cl, 7.47; N, 2.58; Ti, 5.04. IR, v/cm⁻¹: 1612 (C=N); 524 (Ti-O); 450 (Ti-N).

Bis{N-(3,5-di-*tert*-butylsalicylidene)-3-[bis(5-methyl-2-furyl)methyl]aniline}titanium(v) dichloride (28). The yield was 70%. Found (%): C, 70.76; H, 6.84; N, 2.40. C₆₄H₇₂Cl₂N₂O₂Ti. Calculated (%): C, 70.91; H, 6.69; N, 2.58. IR, v/cm⁻¹: 1616 (C=N); 519 (Ti-O); 454 (Ti-N).

Bis{*N*-(5-bromo-3-methylsalicylidene)-2-[bis(5-methyl-2-furyl)methyl]aniline}titanium(*iv*) dichloride (29). The yield was 75%. Found (%): C, 57.07; H, 3.70; Cl, 6.50; N, 2.52; Ti, 4.39. $C_{50}H_{42}Br_2Cl_2N_2O_6Ti$. Calculated (%): C, 57.44; H, 4.05; Cl, 6.78; N, 2.68; Ti, 4.58. IR, v/cm⁻¹: 1616 (C=N); 517 (Ti-O); 442 (Ti-N).

Bis{*N*-(3,5-di-*tert*-butylsalicylidene)-2-[bis(5-methyl-2-furyl)methyl]aniline}titanium(v) dichloride (30). The yield was 79%. Found (%): C, 70.70; H, 6.92; N, 2.50. C₆₄H₇₂Cl₂N₂O₂Ti. Calculated (%): C, 70.91; H, 6.69; N, 2.58. IR, v/cm⁻¹: 1610 (C=N); 517 (Ti-O); 444 (Ti-N).

Bis{*N*-(5-bromo-3-methylsalicylidene)-4-[bis(5-methyl-2furyl)methyl]aniline}titanium(v) dichloride (31). The yield was 68%. Found (%): C, 57.00; H, 4.00; Cl, 6.53; N, 2.50; Ti, 4.50. C₅₀H₄₂Br₂Cl₂N₂O₆Ti. Calculated (%): C, 57.44; H, 4.05; Cl, 6.78; N, 2.68; Ti, 4.58. IR, v/cm^{-1} : 1607 (C=N); 522 (Ti-O); 455 (Ti-N).

Bis{*N*-(3,5-di-*tert*-butylsalicylidene)-4-[bis(5-methyl-2-furyl)methyl]aniline}titanium(*v*) dichloride (32). The yield was 72%. Found (%): C, 70.83; H, 6.85; N, 2.50. $C_{64}H_{72}Cl_2N_2O_2Ti$. Calculated (%): C, 70.91; H, 6.69; N, 2.58. IR, v/cm⁻¹: 1610 (C=N); 517 (Ti–O); 447 (Ti–N). ¹H NMR (toluene-d₆), δ : 1.35 (s, 36 H, Me); 2.14 (s, 12 H, Me); 5.80 (m, 8 H, H_{Ar}); 5.85 (s, 2 H, CH); 7.10–7.60 (m, 12 H, H_{Ar}); 8.15 (s, 2 H, CH=N).

X-ray diffraction study of compound 6 ($C_{25}H_{23}NO_3$) was carried out on an automated Smart CCD 1000K three-circle diffractometer at 120 K (Mo-K α radiation, graphite monochromator, ω scan mode, $2\theta_{max} = 58^{\circ}$). The crystals are triclinic: a = 6.145(1) Å, b = 11.869(3) Å, c = 14.317(3) Å, $\alpha = 73.716(5)^{\circ}$, $\beta = 86.733(5)^{\circ}$, $\gamma = 83.066(5)^{\circ}$, V = 994.6(4) Å³, $d_{calc} = 1.287$ g cm⁻³, M = 385.44, F(000) = 408, $\mu = 0.84$ cm⁻¹, Z = 2 (Z' = 1), space group $P\overline{1}$. On the whole, 6705 reflections were

measured ($R_{int} = 0.0177$), 5105 of independent reflections were used in subsequent calculations and refinement. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation based on F_{hkl}^2 . The hydrogen atoms were localized from the difference Fourier syntheses of the electron densities and included in the final refinement in the isotropic approximation. The final divergence factors are: R = 0.0536 over 3151 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1164$ and goodness-of-fit 1.015 over all reflections. All calculations were performed using the SHELXTL PLUS program package.³⁰

Ethylene polymerization. In catalytic reactions on ethylene polymerization, 'special purity' grade toluene was used. The solvents were purified from possible admixtures according to known procedures.²⁵ Polymethylalumoxane (Witco) was used as a 10% solution in toluene. Argon and ethylene (high purity grade) were dried by passing the gases through columns filled with molecular sieves 5Å. All procedures for the assembly of the reactor and the protocol of the pretreatment and introduction of complexes and gaseous ethylene into the reactor, as well as the measurement of the polymerization kinetics were described earlier.²⁶ After complete dissolution of ethylene in a solution of the tested complex in toluene or hexane, polymerization was started by introducing a solution of the catalyst into the reactor and stopped by adding, to the reactor, 10% ethanolic hydrogen chloride. The polymeric product was filtered off, washed with ethanol and water, and dried in vacuo at 50-60 °C to a constant weight.

Propylene polymerization. Polymerization was carried out by complete filling the reactor with liquefied propylene ($P_{C_3H_6} \approx 40 \text{ atm}$) of the polymerization purity grade (99.7 vol.%), which was used without additional purification. The general procedure of conducting the experiments has been reported earlier.³¹ In the present study, two methods for the introduction of the catalyst were employed. According to one of them, MAO (~3/4 of the calculated amount of a 10% solution in toluene) was feeded to the reactor with liquid propylene. The mixture was stirred and then the tested complex dissolved in a solution of the rest of MAO was added. Alternatively, solid complex was introduced into the reactor following loading the calculated amount of MAO.

The ¹³C NMR spectra of PP in 1,1,2,2-tetrachloroethane- d_2 (7.5% wt/wt) were recorded on a Bruker AC-200 instrument at 110 °C. The X-ray diffraction analysis of PP specimens was carried out on a DRON-2 diffractometer. Mechanical tests were performed on a tensile-testing machine Instron-1122 according to a known procedure.³²

Molecular-mass characteristics $(M_w, M_n, M_w/M_n)$ of PE and PP were determined by gel permeation chromatography on a Waters 150-C instrument equipped with a linear column with HT- μ -Styragel in using solutions of the polymers in 1,2-dichlorobenzene at 135 °C.

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