
CATALYSIS

The Effect of Electron Deficiency of the *N*-aryl Fragment on the Catalytic Properties of Titanium Phenoxy-Imine Complexes in the Ethylene Polymerization

E. A. Fursov^a, A. Yu. Shabalin^{a,*}, and N. Yu. Adonin^a

^a*Boriskov Institute of Catalysis SB RAS, Novosibirsk, 630090 Russia*

**e-mail: shabalin@catalysis.ru*

Received February 2, 2024; revised March 24, 2024; accepted April 14, 2024

Abstract—A series of novel post-metallocene titanium complexes bearing polyfluorinated phenoxy-imines with para-substituents of varying electron-withdrawing ($-\text{NO}_2$, $-\text{F}$) or electron-donating ($-\text{OMe}$, $-\text{OEt}$, $-\text{O}^i\text{Pr}$, $-\text{OPh}$) properties in *N*-phenyl fragments were synthesized and used as ethylene polymerization catalysts. Upon activation with modified methylaluminoxane these complexes produce highly crystalline ultra-high molecular weight polyethylene. The resulting catalysts were investigated in terms of the impact of the mesomeric effect of the introduced substituent and the electron unsaturation of the *N*-aryl fragment on the catalytic activity and molecular weight of the polyethylene produced. A nonmonotonic character of the dependences of the activity of the catalyst and the molecular weight of the synthesized polymers on the electrophilicity of the titanium atom was found. An unexpected increase in polymerization activity was also found in the *OAlk* series upon the transition from *OMe* to larger groups. To explain these effects, possible reasons were considered clarifying the details of the studied process. The obtained results demonstrate that fine tuning of electronic features of the phenoxy-imine ligand by altering the para-substituents of *N*-aryl fragments is a powerful tool for control the activity of titanium catalysts as well as properties of the resulting polymers.

DOI: 10.1134/S1560090424600797

INTRODUCTION

One of the most important tasks of the chemical industry is to create new types of materials that should have outstanding characteristics and their production should tend to low cost and high environmental friendliness. From this point of view, polyolefins are one of the most promising materials. Although there is currently a large number of methods for the preparation of various types of polymers based on olefins, the problem of creating materials with predetermined characteristics remains relevant. The development of coordination polymerization methods opened up opportunities for controlling the structure of macromolecules (chain length, degree of branching, presence of functional groups) by varying the structure of the coordination sphere of the transition metal complex catalyzing reaction. Great strides have been made in this area but at present there is no consensus regarding the effect of ligands structure on the properties of the catalyst and characteristics of the synthesized polymer. Among the variety of known catalysts for coordination polymerization, complexes of titanium with fluorinated phenoxy-imine ligands (titanium FI catalysts) are of special interest [1–3]. Such complexes, in addition to high catalytic activity, have thermal stability and could initiate living polymerization

in which chain transfer and chain termination are practically absent [4]. These features of the titanium FI catalysts allow to produce the ultra-high molecular weight polyethylene (UHMWPE), possessing a number of specific properties: increased shock and wear resistance, frost resistance, resistance to radiation and aggressive media, biological inertia, as well as low coefficients of friction and water absorption. The combination of these properties allows the use of UHMWPE to replace materials designed to withstand high stresses such as steel or polyamides [5, 6]. An increase in strength indicators, following an increase in molecular weight, leads to difficulties associated with the processing of reactor powder into final products. The use of expensive gel technology is not environmentally friendly and requires the use of large quantities of organic solvents, which, combined with the high final cost of the functional material, are serious obstacles facing the widespread use of UHMWPE. The development of solid-phase processing technology for UHMWPE should in the future solve the problems mentioned above, but this method is sensitive to the method of obtaining the reactor powder. It has been shown that the use of fluorinated phenoxyimine titanium complexes, which ensure living polymerization, makes it possible to obtain a polymer with the

morphology necessary for solid-phase processing [7–10]. However, at present, the variety of fluorinated phenoxyimine complexes studied is limited solely by a small number of compounds containing different numbers of fluorine atoms. It is known that the living nature of the process is provided by fluorine atoms located in the ortho-position of the *N*-aryl fragment, i.e. in close proximity to the active center [11, 12]. Thus, the introduction of substituents having a mesomeric effect in positions other than ortho- would significantly expand the class of fluorinated FI catalysts while maintaining the ability to initiate living polymerization. Another important aspect of this study is to find an effective way to regulate catalytic activity at the molecular level. Due to the fact that ethylene polymerization is a highly exothermic process, the use of highly active catalysts makes the process sufficiently uncontrollable in a large-scale transition process. The production of UHMWPE processed to high strength materials having the necessary mechanical characteristics is highly dependent on the production conditions [8]. Too active catalysts lead to a significant reduction in synthesis time and, accordingly, high temperature gradients, which negatively affect the homogeneity of the properties of the final polymer material. Therefore, in order to achieve maximum efficiency and productivity, the development of advanced activity control methods is necessary.

In this work, phenoxy-imine Ti(IV) complexes containing electron-donating or electron-withdrawing groups in the polyfluorinated *N*-aryl fragment were used as ethylene polymerization catalysts. Our goal was to study the role of the electronic factor on the characteristics of the process and the properties of the resulting PE. So in order to exclude the contribution of the steric factor comparative studies were carried out with complexes differing in the nature of the most distant from the active center substituents, located in the para-position to the nitrogen atom. The complex containing hydrogen atom was chosen as the basis compound. The bulky 1-(4-*tert*-butylphenyl)ethyl group was chosen as a substituent located at the *ortho* position to the phenolic oxygen due to its optimal steric properties. Previously, Ivanchev [13] showed that this group effectively protects the oxygen atoms that bind the ligand to the central atom from interaction with methylalumoxane, which subsequently leads to the destruction of the titanium complex, and is not too bulky to create restrictions for ethylene molecules during the chain propagation.

EXPERIMENTAL

Materials

Methanol (J.T. Baker), *para*-toluenesulfonic acid monohydrate (Aldrich), silica gel 60 (60–200 μm , Acros), modified methylaluminoxane (MMAO-12, 7 wt % aluminum in toluene, Aldrich), decahy-

dronaphthalene (Acros), Irganox 1010 (Aldrich), isopropanol (Acros), 2,3,4,5,6-pentafluoroaniline **1a** (Acros), 2,3,5,6-tetrafluoroaniline **1b** (abcr) were used as supplied. Hexane and toluene were distilled and stored over the sodium. Dichloromethane was distilled over P_2O_5 . Ethylene (polymerization grade) and argon (polymerization grade) were dried using molecular sieves 3 Å (Aldrich) and Drierite desiccant (Aldrich), respectively. Toluene was degassed by bubbling argon for 0.5 h prior to the polymerization reaction.

2,3,5,6-Tetrafluoro-4-nitroaniline **1c** [14], 2,3,5,6-tetrafluoro-4-methoxy aniline **1d** [15], 2,3,5,6-tetrafluoro-4-ethoxyaniline **1e** [16], 3-[1-[4-(*tert*-butyl)phenyl]ethyl]-2-hydroxybenzaldehyde [17], 2-[1-[4-(*tert*-butyl)phenyl]ethyl]-6-[[2,3,4,5,6-pentafluorophenyl]imino]methyl]-phenol **2a** [13], [1-(4-(*tert*-butyl)phenyl)ethyl]-6-[[2,3,4,5,6-pentafluorophenyl]imino]methyl]-phenoxy]titanium(IV) dichloride **3a** [13], dichloro(di-*iso*-propoxy)titanium [18] were prepared as previously described.

Synthesis of Para-substituted Tetrafluoroaniline

2,3,5,6-Tetrafluoro-4-isopropoxyaniline (1f). The mixture of potassium hydroxide (185 mg, 3.29 mmol), isopropanol (10 mL), pentafluoronitrobenzene (500 mg, 2.35 mmol), and distilled water (5 mL) was stirred at 25°C for 0.5 h in a 100 mL flask equipped with a magnetic stirrer. The solvent was distilled off on a vacuum rotary evaporator. The residue was extracted with chloroform (3×5 mL). After evaporation under reduced pressure, 2,3,5,6-tetrafluoro-4-isopropoxynitrobenzene (487 mg, 82% yield) was obtained.

The synthesized product and glacial acetic acid (10 mL) were placed into 25 mL round bottom flask equipped with a magnetic stirrer, heating bath and reflux condenser. After heating to 60°C, preactivated with hydrochloric acid zinc dust (1 g, 15.4 mmol) was added in portions. The reaction mixture was refluxed for 3 h in an argon atmosphere. Insoluble substances were separated by filtration and the filtrate was diluted with distilled water. After neutralization of the acid with potassium carbonate, the product was extracted with diethyl ether (3×10 mL). Evaporation under reduced pressure gave 2,3,5,6-tetrafluoro-4-isopropoxyaniline (270 mg, 63%). ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.29 (J = 6.2, 3H, CH_3), 4.41 (q, J = 7.2, 2H, CH_2), 4.17 (c, 2H, NH_2) ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –159.21 (m, 2F), –164.01 (m, 2F)

2,3,5,6-Tetrafluoro-4-phenoxyaniline (1g). The mixture of potassium carbonate (415.0 mg, 3.00 mmol), phenol (238 mg, 3 mmol), pentafluoronitrobenzene (639 mg, 3 mmol), acetonitrile (50 mL) and distilled water (10 mL) was stirred at 25°C for 0.5 h in a 100 mL flask equipped with a magnetic stirrer. The solvent was distilled off on a vacuum rotary evaporator. The residue was extracted with chloroform (3×5 mL). After

evaporation under reduced pressure, 2,3,5,6-tetrafluoro-4-phenoxy-nitrobenzene (660 mg, 77% yield) was obtained. Similarly to procedure described above, the synthesized product reacted with preactivated zinc dust. After purification, the target product, 2,3,5,6-tetrafluoro-4-phenoxyaniline was obtained (396 mg, 67%). ^1H NMR (CDCl_3 , δ_{H} , ppm): 6.8–7.27 (m, 5H), ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –158.09 (m, 2F), –163.10 (m, 2F).

Phenoxy-Imine Ligand Synthesis (General Procedure)

The mixture of 3-[1-[4-(1,1-dimethyl-ethyl)phenyl]ethyl]-2-hydroxybenzaldehyde (1412.0 mg, 5.00 mmol), *para*-toluenesulfonic acid monohydrate (95.1 mg, 0.5 mmol), polyfluorinated aniline 1b (867.0 mg, 5.25 mmol) and 20 mL of toluene was refluxed under argon atmosphere for 18 h in a 50 mL flask equipped with a magnetic stirrer, a Dean-Stark nozzle and a reflux condenser. Progress of the reaction was monitored using TLC. The solvent was distilled off on a vacuum rotary evaporator. The residue was purified using flash chromatography (silica gel 60–200 μm , eluent toluene). Recrystallization of the residue from boiling methanol give the target phenoxy-imine 2b (681.0 mg, 32% yield).

2-[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluorophenyl]imino]methyl]phenol (2b). Yield 681.0 mg (32%), light yellow solid. ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.29 (s, 9H, ^tBu), 1.63 (d, $J = 7.4$, 3H, CH_3), 4.69 (q, $J = 7.2$, 1H, CH), 6.92–7.33 (m, 7H, H arom.; 1H, H arom._F), 8.80 (s, 1H, CHN), 12.67 (s, 1H, OH). ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –140.57 (m, 2F), –153.79 (m, 2F). Anal. calcd. for $\text{C}_{25}\text{H}_{23}\text{F}_4\text{NO}$ (429.46), %: C 69.92; H 5.40; N 3.26; F 17.70; found, %: C 69.78; H 5.32; N 3.18; F 17.63.

2-[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-nitrophenyl]imino]methyl]phenol (2c). Yield 759.1 mg (32%), light yellow solid. ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.28 (s, 9H, ^tBu), 1.61 (d, $J = 7.4$, 3H, CH_3), 4.66 (q, $J = 7.2$, 1H, CH), 6.95–7.4 (m, 7H, H arom.), 8.78 (s, 1H, CHN), 12.17 (s, 1H, OH). ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –144.11 (m, 2F), –147.02 (m, 2F). Anal. calcd. for $\text{C}_{25}\text{H}_{22}\text{F}_4\text{N}_2\text{O}_3$ (474.46), %: C 63.29; H 4.67; N 5.90; F 16.02; found, %: C 63.18; H 4.53; N 4.55; F 15.89.

2-[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-methoxyphenyl]imino]methyl]-phenol (2d). Yield 942.9 mg (41%), light yellow solid. ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.28 (s, 9H, ^tBu), 1.61 (d, 3H, CH_3), 4.08 (s, 3H, OCH_3), 4.69 (q, $J = 7.2$, 1H, CH), 6.9–7.4 (m, 7H, H arom.), 8.81 (s, 1H, CHN), 12.8 (s, 1H, OH). ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –152.14 (dd, $^3J = 21.2$, $^4J = 7.1$, 2F), –157.28 (dd, $^3J = 21$, $^4J = 7.2$, 2F). Anal. calcd. for $\text{C}_{26}\text{H}_{25}\text{F}_4\text{NO}_2$ (459.48), %: C

67.96; H 5.48; N 3.05; F 16.54; found, %: C 67.77; H 5.58; N 2.94; F 16.45.

2-[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-ethoxyphenyl]imino]methyl]-phenol (2e). Yield 1254.8 mg (53%), light yellow solid. ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.28 (s, 9H, ^tBu), 1.42 (t, $J = 6.4$, 3H), 1.63 (d, $J = 7.2$, 3H, CH_3), 4.29 (q, $J = 6.3$, 2H, OCH_2), 4.68 (q, $J = 7.2$, 1H, CH), 6.9–7.35 (m, 7H, H arom.), 8.8 (s, 1H, CHN), 12.8 (s, 1H, OH). ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –153.18 (dd, $^3J = 21.2$, $^4J = 7.1$, 2F), –157.45 (dd, $^3J = 21$, $^4J = 7.2$, 2F). Anal. calcd. for $\text{C}_{27}\text{H}_{27}\text{F}_4\text{NO}_2$ (473.51), %: C 68.49; H 5.75; N 2.96; F 16.05; found, %: C 68.17; H 5.61; N 2.83; F 15.94.

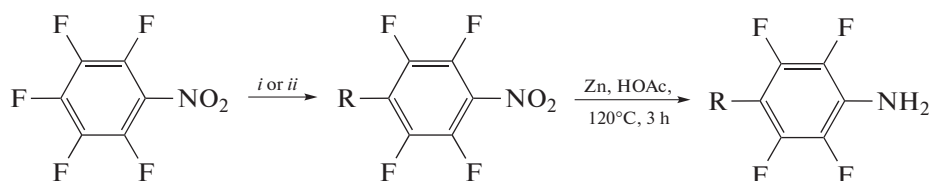
2-[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-isopropoxyphenyl]imino]-methyl]phenol (2f). Yield 1657.6 mg (68%), light yellow solid. ^1H NMR (CDCl_3 , δ_{H} , ppm): ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.28 (s, 9H, ^tBu), 1.38 (d, $J = 6.4$, 6H, $\text{OCH}(\text{CH}_3)_2$), 1.65 (d, 3H, CH_3), 4.53 (m, 1H, $\text{O}(\text{CH})$), 4.72 (q, $J = 7.2$, 1H, CH), 6.9–7.31 (m, 7H, H arom.), 8.82 (s, 1H, CHN), 12.82 (s, 1H, OH). ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –152.4 (dd, $^3J = 21.2$, $^4J = 7.1$, 2F), –155.5 (dd, $^3J = 21$, $^4J = 7.2$, 2F). Anal. calcd. for $\text{C}_{28}\text{H}_{29}\text{F}_4\text{NO}_2$ (487.54), %: C 68.98; H 6.00; N 2.87; F 15.59; found, %: C 69.05; H 5.85; N 2.71; F 15.42.

2-[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-phenoxyphenyl]imino]-methyl]phenol (2g). Yield 1121.3 mg (43%), light yellow solid. ^1H NMR (CDCl_3 , δ_{H} , ppm): 1.3 (s, 9H, ^tBu), 1.65 (d, 3H, CH_3), 4.72 (q, $J = 7.2$, 1H, CH), 6.9–7.31 (m, 12H, H arom.), 8.85 (s, 1H, CHN), 12.71 (s, 1H, OH). ^{19}F NMR (CDCl_3 , δ_{F} , ppm): –153.5 (dd, $^3J = 21.2$, $^4J = 7.1$, 2F), –155.91 (dd, $^3J = 21$, $^4J = 7.2$, 2F). Anal. calcd. for $\text{C}_{31}\text{H}_{27}\text{F}_4\text{NO}_2$ (521.56), %: C 71.39; H 5.22; N 2.69; F 14.57; found, %: C 71.20; H 5.47; N 2.70; F 14.41.

Titanium Dichloride Complex Synthesis (General Procedure)

Dichloro(di-*iso*-propoxy)titanium (100.0 mg, 0.42 mmol) and phenoxy-imine 2b (362.5 mg, 0.84 mmol) were weighed inside a glove box into a 50 mL flask equipped with a magnetic stirrer. After adding of 10 mL of dichloromethane the reaction mixture was stirred at 25°C under argon for 20 h. The solvent was distilled off in vacuum and the solid residue was washed on a Schlenk filter with 5 mL of *n*-hexane. The residue was dried in vacuum to constant weight to give the target titanium complex 3b (319.6 mg, 78% yield).

[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro phenyl]imino]methyl]phenoxy]-titanium(IV) dichloride (3b). Yield 319.6 mg (78%), brick red solid.



i: R = PrⁱO; KOH, PrⁱOH, H₂O, 25°C, 0.5 h

ii: R = PhO; K₂CO₃, PhOH, H₂O–CH₃CN, 25°C, 0.5 h

Scheme 1.

Anal. calcd. for C₅₀H₄₄Cl₂F₈N₂O₂Ti (975.67), %: C 61.55; H 4.55; F 15.58; N, 2.87; found, %: 61.37; H 4.28; F 15.51; N, 2.74.

[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-nitrophenyl]imino]methyl]-phenoxy]-titanium(IV) dichloride (3c). Yield 340.1 mg (76%), brick red solid. Anal. calcd. for C₅₀H₄₂Cl₂F₈N₄O₆Ti (1065.66), %: C 56.35; H 3.97; F 14.26; N, 5.26; found, %: C 56.13; H 3.76; F 14.21; N, 5.11.

[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-methoxy phenyl]imino]methyl]-phenoxy]titanium(IV) dichloride (3d). Yield 308.9 mg (71%), brick red solid. Anal. calcd. for C₅₂H₄₈Cl₂F₈N₂O₄Ti (1035.72), %: C 60.30; H 4.67; F 14.67; N, 2.70; found, %: C 59.93; H 4.41; F 14.61; N, 2.58.

[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-ethoxy phenyl]imino]methyl]-phenoxy]titanium(IV) dichloride (3e). Yield 344.0 mg (77%), brick red solid. Anal. calcd. for C₅₄H₅₂Cl₂F₈N₂O₄Ti (1063.77), %: C 60.97; H 4.93; F 14.29; N, 2.63; found, %: C 60.78; H 4.84; F 14.17; N, 2.52.

[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-isopropoxy phenyl]imino]-methyl]phenoxy]titanium(IV) dichloride (3f). Yield 247.6 mg (54%), brick red solid. Anal. calcd. for C₅₆H₅₆Cl₂F₈N₂O₄Ti (1091.83), %: C 61.60; H 5.17; F 13.92; N, 2.57; found, %: C 61.24; H 5.03; F 13.65; N, 2.31.

[1-[4-(*tert*-Butyl)phenyl]ethyl]-6-[[2,3,5,6-tetrafluoro-4-phenoxy phenyl]imino]methyl]-phenoxy]titanium(IV) dichloride (3g). Yield 248.4 mg (51%), brick red solid. Anal. calcd. for C₆₂H₅₂Cl₂F₈N₂O₄Ti (1159.86), %: C 64.20; H 4.52; F 13.10; N, 2.42; found, %: C 63.89; H 4.33; F 12.96; N, 2.21.

Polymerization Procedure

Toluene (78 mL) and MMAO-12 (0.8 mL of solution in toluene, 0.8 mmol) were placed into an autoclave and thermostatted at 30°C with stirring. A solution of complex 3b (0.78 mg, 0.8 μmol) in toluene (1.2 mL) was transferred to the autoclave and the reaction mixture was saturated with ethylene. After 1 h, ethylene gas feed was stopped and isopropyl alcohol (15 mL) was added to terminate the polymerization

reaction. The polymer was isolated by filtration and dried in air to constant weight. Other polymerizations were conducted similarly.

Characterization

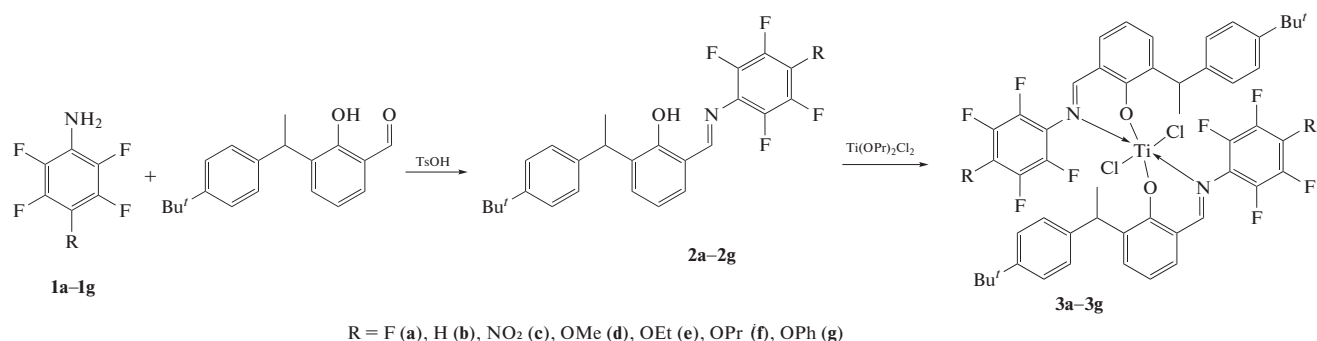
The NMR spectra were acquired using a Bruker AVANCE 300 (¹⁹F 282.40 MHz, ¹H 300.13 MHz) spectrometer in multi-access Chemical Service Center (CSC, Novosibirsk). The chemical shifts are assigned to TMS (¹H), CCl₃F (¹⁹F, with C₆F₆ as internal standard, –162.9 ppm). The viscosity-average molecular weight M_v of the obtained polymer samples were determined from intrinsic viscosity $[\eta]$ measured in decahydronaphthalene at 135°C in accordance with standard ASTM D4020 using Ubbelohde type capillary glass viscometer. Calculation was carried out using formula $M_v = 53700 \times [\eta]^{1.37}$. The degree of crystallinity (X) was determined using differential scanning calorimetry (DSC) according to the ISO 11357-3 standard on a Netzsch STA 409 instrument at a heating rate of 10 K/min in a helium flow and calculated by the formula $X = \Delta H \times 100\% / \Delta H_{100\%PE}$, where ΔH is the measured heat of fusion, $\Delta H_{100\%PE}$ is the heat of fusion of 100% crystalline PE (288 J/g). The melting temperature and the degree of crystallinity for each sample were determined from the data of the first and the second melting data.

RESULTS AND DISCUSSION

Synthesis of the Titanium Complexes

Previously undescribed anilines 1f, 1g were obtained by two-step syntheses involving alkoxy- or aryloxydefluorination of pentafluoronitrobenzene and reduction of nitro group of the corresponding products (Scheme 1).

New Schiff bases 2b–2g were synthesized by condensation reaction of 4-substituted tetrafluoroanilines 1b–1g with derivative of salicylaldehyde in analogy with imines containing polyfluorinated aryl fragments (Scheme 2) [19]. A series of bis(phenoxy-imine) titanium dichloride complexes 3a–3g was prepared in good preparative yields (51–78%) by a one-step



Scheme 2.

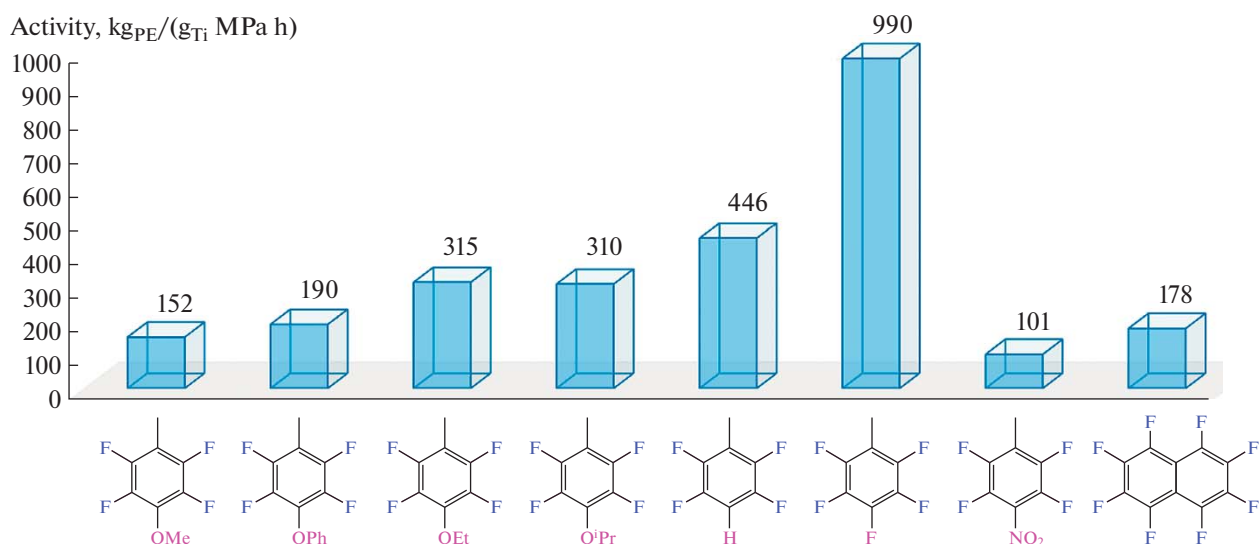


Fig. 1. Polymerization activities of the phenoxy-imine complexes 3a–3g.

method based on the direct interaction of $\text{Ti}(\text{O}^i\text{Pr})_2\text{Cl}_2$ with N,O-chelating proligands 2a–2g.

Qualitative Analysis of Electronic Influence of Substituents

Upon activation with MMAO-12, complexes 3a–3g showed activities in range 101–990 $\text{kg}_{\text{PE}}/(\text{g}_{\text{Ti}} \text{ MPa h})$ for ethylene polymerization (Fig. 1). It was found that the replacement of a hydrogen atoms with other groups has an ambiguous effect on the observed catalytic activity. The replacement by a fluorine atom led to a twofold increase in activity (Table 1, entry 1), which can be explained by a general increase in the electron deficiency of the N-aryl fragments and the associated electrophilicity of the titanium atom. A similar increase in the activity of FI catalysts upon the replacement of hydrogen atoms by fluorine in the N-aryl fragment of the ligand was previously reported by Fujita [20].

Taking into account the positive effect of an increase in the number of electronegative atoms in N-aryl fragments on the catalytic activity, it turned out to be unexpected that the introduction of a strong electron-withdrawing NO_2 group instead of a hydrogen atom leads to an almost five times decrease in the catalyst activity (Table 1, entry 3). A similar effect we observed earlier during the study of the influence of the number and mutual arrangement of fluorine atoms in the polyfluorinated arylimine fragments on catalytic activity of FI catalysts. Replacement of pentafluorophenyl group with more electron-withdrawing heptafluoronaphtyl group (F-Np) led to a sharp decrease in catalytic activity instead of the expected increase [19, 21]. In this regard, we assumed that this could be due to the peculiarities of the polymerization mechanism. According to the mechanism proposed by Cossee-Arlman, the growth of the polymer chain takes place in two stages: coordination of ethylene to form a π -complex and the insertion of an ethylene molecule via the Ti–C bond [22]. The introduction of electro-

Table 1. Catalytic activity of phenoxy-imine complexes 3a–3g in ethylene polymerization and characteristics of PE powders

Entry	Complex	R	Yield, g ^a	Activity ^b	T_m , °C		Crystallinity, %		$M_v \times 10^{-6}$
					T_1^c	T_2^d	X_1^c	X_2^d	
1	3a	F	9.37	990	144.1	135.1	72.7	38.9	16.1
2	3b	H	4.38	446	143.1	134.3	90.7	46.5	>20 ^e
3	3c	NO ₂	1.02	101	142.9	134.5	79.1	39.2	>17 ^e
4	3d	MeO	1.40	152	143.0	134.8	66.2	33.1	10.7
5	3e	EtO	3.19	315	142.5	134.6	76.3	37.1	2.5
6	3f	Pr ⁱ O	2.72	310	143.5	135.3	66.4	33.3	6.7
7	3g	PhO	1.75	190	142.7	136.4	65.3	33.2	5.4
8	F-Np ^f	C ₁₀ F ₇	1.44	178	143.3	135.3	71.6	37.9	>21

^aReaction conditions: Toluene, 1 h, 30°C, ethylene pressure 0.25 MPa, Al/Ti = 1000, C(Al) = 10⁻⁵ mol/ml; ^bkg_{PE}/(g_{Ti} MPa h); ^cfirst melting; ^dsecond melting; ^eincomplete dissolution of PE; ^fdata from [17].

negative atoms or strong electron-withdrawing groups leads to an increase in the effective positive charge of the titanium atom, which leads to stronger binding of the ethylene molecule into the π -complex and makes its formation more energetically favorable. However, at the same time increase in electrophilicity of the cationic center can lead to a significant increase in the energy barrier of the second stage due to stronger bonding of the polymer chain to the titanium atom and high stability of intermediate π -complex complicating the intramolecular rearrangement leading to the insertion of monomer. The replacement of the hydrogen atom with electron-donating alkoxy or phenoxy group led to the expected decrease in catalytic activity (Table 1, entries 4–7). For a series of OMe-OEt-OⁱPr substituents we expected to see approximately the same reaction rate, but for the complex 3d containing the methoxy group the activity was significantly lower. Compared to alkoxy groups, the OPh group has a stronger positive mesomeric effect due to the presence of a bound conjugated system, which is a donor of the fluorinated ring, which in our case is confirmed experimentally. The reason for this low activity of complex 3d, which is even lower than that of complex 3g, remains unclear. It can be assumed that the reasons lie in the smaller spatial volume of the methyl group compared to ethyl, *iso*-propyl, and phenyl, which leads to unexpected interactions with methylalumoxane or “free” trimethylaluminum (residual trimethylaluminum included in substantial amounts in commercial alumoxanes).

Quantitative Analysis of Electron Influence of Substituents Using Hammett Equations

In order to quantify the electronic effects of the substituents R in 4-RC₆F₄ groups on the rate of polymerization reaction, we carried out a correlation analysis using the Hammett equation (Eq. (1)) [23].

$$\log \frac{k}{k_0} = \rho \times \sigma, \quad (1)$$

where k —reaction rate constant of the unsubstituted reactant, k_0 —reference reaction rate constant, ρ —sensitivity constant, σ —substituent constant. The required σ values were calculated using previously described in the paper [24] values of the inductive constants σ_I and resonance constants σ_R° according to Eq. (2) [25, 26].

$$\sigma = \sigma_I + \sigma_R^\circ \quad (2)$$

Since the values of the electronic parameters for the 4-NO₂C₆F₄ group have not been determined, as far as we know, it was excluded from consideration. The logarithm of the ratio of the reaction rate constants was plotted as a function of substituent constant of 4-RC₆F₄ groups (Fig. 2).

As Fig. 3 shows there is a positive relationship of the logarithm of the ratio of the reaction rate constants and substituent constant of 4-RC₆F₄ groups. The resulting Hammett plot is discrete and is divided into two parts. The occurrence of nonlinear Hammett's plots is usually interpreted as a consequence of a change in reaction mechanism or in rate determine step [27, 28]. It seems unlikely that in our case these factors are the cause of the observed dependence. It can be suggested that, in contrast to the rest of the investigated titanium complexes, compounds 3d and 3g are modified as a result of Lewis acid–base interactions between the oxygen atoms of the methoxy or phenoxy groups and MMAO-12. Apparently, the methyl group does not provide sufficient steric hindrance compared to ethyl or isopropyl. The phenyl group, which has a planar structure, probably has similar properties. Therefore, the catalysts formed from compounds 3d and 3g should apparently be considered as a separate reaction series. The unique role of

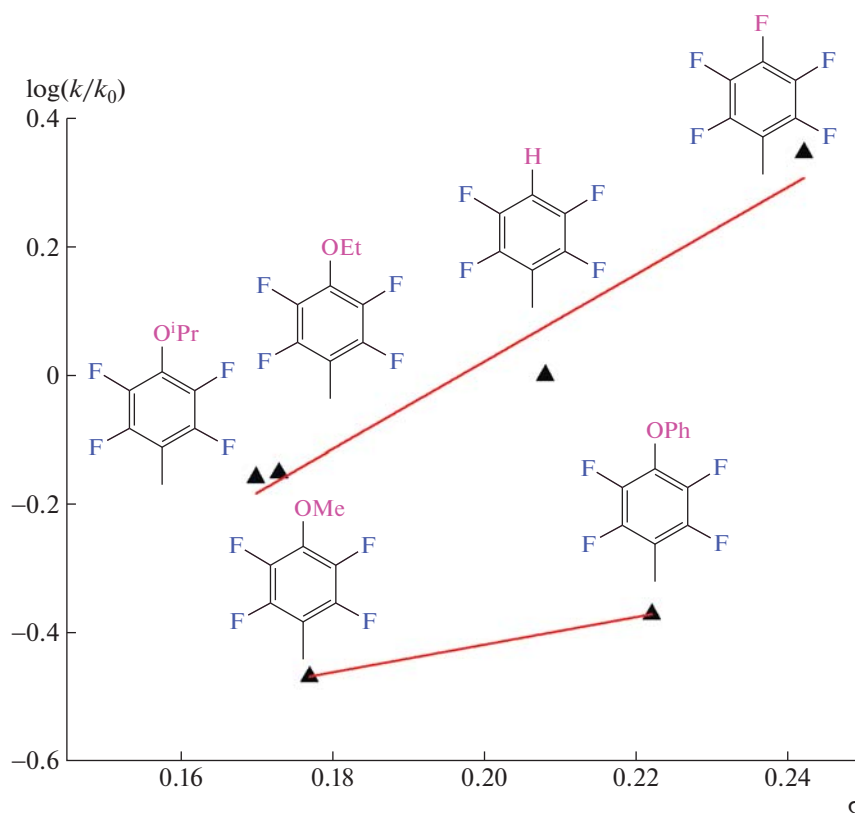


Fig. 2. Relationship between the logarithm of the ratio of reaction rate constants and substituent constant σ of 4-RC₆F₄ group.

MAO in generating of catalysts with specific properties due to the modification of the basic Lewis centers of the ligands during activation was demonstrated earlier for a number of Zr metallocene complexes catalyzing ethylene or propylene polymerization reactions [29, 30]. It is worth noting that the introduction of even one methoxy group into the phenyl fragment of the ligand is sufficient to change drastically the stereoselectivity of the catalyst generated in situ from zirconocene and MAO [31–33].

Discussion

Characteristics of the synthesized polymers are given in Table 1. The viscosity average molecular weight of all polymers is significantly higher than 10^6 . It is distinctive that complex 3c forms one of the highest molecular weight products in the series despite the low activity, as well as the heptafluoronaphthyl group-containing complex discussed above, while the introduction of donor substituents into the *N*-aryl fragment opposite leads to a noticeable drop thereof. Such a strong influence of the electron factor on the molecular weight of the product, which under living polymerization conditions is a function of only the chain growth constant and reaction time, leads us to an alternative hypothesis of the mechanism of influence of the electrophilicity of the central atom on the process.

It is known that the activation of a similar titanium phenoxyimine complex by methylalumoxane is not quantitative and that the use of an excess amount of MAO leads to an increase in activity at an Al/Ti ratio up to 35000. In our case, it can be assumed that the reason for the decrease in the activity observed for complex 3c is an increase in the activation potential caused by a stronger binding of titanium and chlorine atoms, leading to a decrease in the number of active centers. The introduction of donor substituents into *N*-aryl fragments led to a significant decrease in the molecular weight of PE's (Table 1, entries 4–7). According to DSC data, all UHMWPE powders have high melting temperatures in the range of 142.5–144.1°C. More significant differences are observed in the crystallinity of polymers, the values of which vary in the range 65–91%. The morphology of the reactor powders was investigated by scanning electron microscopy (Fig. 3). Despite the significant difference in the observed catalytic activity, all samples have a similar structure in which clusters of submicron particles having relatively regular shapes are joined together by filaments of different thicknesses into uniform granular layers, or into larger filaments.

The tendency to this or that type of agglomeration leads to noticeable differences at the macroscopic level, leading to the formation of rarely interconnected granular particles or larger spindle-shaped particles

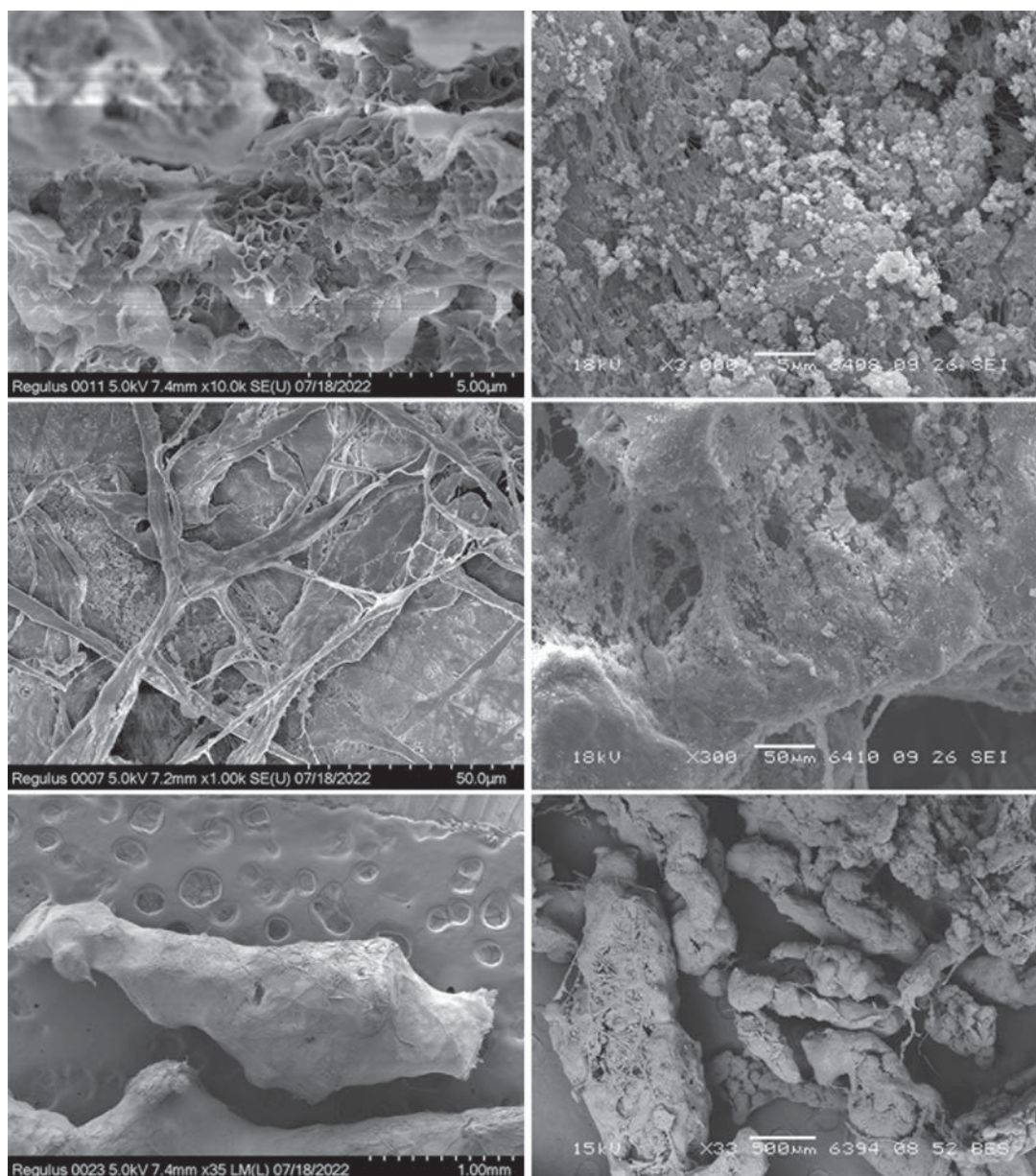


Fig. 3. SEM images of UHMPE powders obtained using catalysts 3c (left) and 3g (right).

with a uniform surface. The tendency to preferentially form fibrillar structures or spherulite formations certainly cannot be determined solely by the chemical structure of the active site but quite unequivocally this is influenced by the concentration of nucleation centers, which clearly depends on the activation potential of the titanium complex, as well as on the amount of enthalpy, transferred in the form of oscillatory energy, a growing polymer chain, which depends on the transition state energy corresponding to the ethylene insertion stage. Reactor powders of UHMPE shown in Fig. 3 are obtained on complexes 3c and 3g containing substituents that are most strongly different from each other in terms of electronic influence. Other samples

are similar in structure to the polymer obtained using the 3g complex.

CONCLUSIONS

In this work six new fluorinated bis(phenoxy-imine) titanium complexes containing substituents of various electron nature in *N*-aryl fragments were synthesized. It was shown that the electronic influence exerted by the introduction of electron-withdrawing or electron-donating groups largely determine both the catalytic properties of titanium complexes. It was found that an increase in the electron deficiency of the *N*-aryl fragment does not lead to a monotonic increase

in activity. Despite a sharp decrease in the activity observed for complex containing NO₂ groups the molecular weight of the polymer remains high. The obtained results made it possible to put forward two hypotheses about the mechanism of the electronic influence of substituents on the kinetics of the process. On the example of a series of complexes containing alkoxy groups of similar structure, it was found that the complex bearing methoxy groups demonstrates behavior uncharacteristic for the rest of the elements of the series, which can presumably be associated with the interaction of the methylaluminoxane molecule with an unprotected oxygen atom. In conclusion, these results demonstrate that control of the electronic features of the phenoxy-imine ligand could be used as promising tool for the rational design of new titanium FI catalysts.

FUNDING

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (FWUR-2024-0035).

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.* **103**, 283 (2003).
2. H. Makio and T. Fujita, *Acc. Chem. Res.* **42**, 1532 (2009).
3. R. S. Birajdar, D. Bodkhe, P. Gupta, M. H. Shaikh, R. Ramekar, and S. H. Chikkali, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2023**, 1 (2023).
4. A. Sakuma, M.-S. Weiser, and T. Fujita, *Polym. J.* **39**, 193 (2007).
5. S. M. Kurtz, *UHMWPE Biomaterials Handbook: Ultra High Molecular Weight Polyethylene in Total Joint Replacement and Medical Devices* (Academic Press, 2009).
6. K. Patel, S. H. Chikkali, and S. Sivaram, *Prog. Polym. Sci.* **109**, 101290 (2020).
7. S. Rastogi, Y. Yao, S. Ronca, J. Bos, and J. Van Der Eem, *Macromolecules* **44**, 5558 (2011).
8. A. N. Ozerin, E. K. Golubev, S. S. Ivanchev, V. A. Aulov, A. S. Kechev'yan, T. S. Kurkin, E. M. Ivan'kova, and N. Yu. Adonin, *Polym. Sci., Ser. A* **64**, 73 (2022).
9. E. Golubev, T. Kurkin, and A. Ozerin, *Russ. Chem. Bull.* **72**, 749 (2023).
10. H. Yang, S. Lolage, J. van der Eem, S. Rastogi, and D. Romano, *Mol. Catal.* **552**, 113668 (2024).
11. M. C. Chan, S. C. Kui, J. M. Cole, G. J. McIntyre, S. Matsui, N. Zhu, and K. H. Tam, *Chem. Eur. J.* **12**, 2607 (2006).
12. S. C. Kui, N. Zhu, and M. C. Chan, *Angew. Chem.* **115**, 1666 (2003).
13. S. S. Ivanchev, E. I. Ruppel', and A. N. Ozerin, *Dokl. Phys. Chem.* **468**, 89 (2016).
14. K. A. Chehade and H. P. Spielmann, *J. Org. Chem.* **65**, 4949 (2000).
15. J. Marquet, Z. Jiang, I. Gallardo, A. Batlle, and E. Cayón, *Tetrahedron Lett.* **34**, 2801 (1993).
16. M. Castle and R. Plevy, *J. Fluorine Chem.* **2**, 431 (1973).
17. A. Kochnev, I. Oleynik, I. Oleynik, S. Ivanchev, and G. Tolstikov, *Russ. Chem. Bull.* **56**, 1125 (2007).
18. K. Mikami, M. Terada, and T. Nakai, *J. Am. Chem. Soc.* **112** (1990).
19. E. Fursov, A. Yu. Shabalin, A. Potapov, Yu. A. Chesalov, S. Prikhod'ko, and N. Yu. Adonin, *Polym. Sci., Ser. B* **64**, 779–790 (2022).
20. H. Makio, H. Terao, A. Iwashita, and T. Fujita, *Chem. Rev.* **111**, 2363 (2011).
21. A. Yu. Shabalin and E. A. Fursov, *Polzunov. Vestn.* **4**, 73 (2019).
22. P. Cossee, *J. Catal.* **3**, 80 (1964).
23. L. P. Hammett, *J. Am. Chem. Soc.* **59**, 96 (1937).
24. V. V. Bardin, A. Yu. Shabalin, and N. Yu. Adonin, *Beilstein J. Org. Chem.* **11**, 608 (2015).
25. R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.* **85**, 3146 (1963).
26. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.* **91**, 165 (1991).
27. F. A. Carroll and W. J. I. Noble, *J. Chem. Educ.* **75**, 417 (1998).
28. S. Hoz and M. Ben-Zion, *J. Chem. Soc., Chem. Commun.* **10**, 453 (1980).
29. S. K. Kim, H. K. Kim, M. H. Lee, S. W. Yoon, and Y. Do, *Angew. Chem., Int. Ed.* **45**, 6163 (2006).
30. Y. Han, H. Kim, M. H. Lee, Y. Kim, J. Lee, Y. S. Lee, and Y. Do, *J. Organomet. Chem.* **694**, 4216 (2009).
31. S. W. Yoon, H. K. Kim, S.-K. Kim, T. Kim, M. H. Lee, and Y. Do, *Bull. Korean Chem. Soc.* **35**, 236 (2014).
32. H. K. Kim, S. K. Kim, J. H. Park, S. W. Yoon, M. H. Lee, and Y. Do, *Chem. Asian J.* **3**, 1912 (2008).
33. S. K. Kim, H. K. Kim, M. H. Lee, S. W. Yoon, and Y. Do, *Chem. Eur. J.* **13**, 9107 (2007).

Publisher's Note. Pleiades Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.