Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(1):39–51 ISSN 2686-7575 (Online)

Chemistry and technology of organic substances
Химия и технология органических веществ

UDC 54.057+547.791+544.478+66.095.261.4
https://doi.org/10.32362/2410-6593-2024-19-1-39-51

RESEARCH ARTICLE

Synthesis and application of chromium complexes based on 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazole ligands to obtain higher C_{10}–C_{18} olefins

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Abstract

Objectives. To synthesize 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazole ligands and new chromium complexes based on them, in order to obtain a fraction of higher C_{10}–C_{18} alpha-olefins from ethylene.

Methods. The Schlenk technique was used to obtain the target chromium complexes. Diphenylphosphanyl triazole ligands can be characterized by nuclear magnetic resonance spectroscopy. The composition of the final products was confirmed by elemental analysis. The liquid phase of the oligomerization reaction was studied by gas chromatography.

Results. **L1**–**L9** ligands were obtained, and **K1**–**K9** chromium complexes were synthesized based on the correspondent ligands using commercially available chromium (III) trichloride tris(tetrahydrofuran). The **K1**–**K9** complexes thus obtained were tested in the process of ethylene oligomerization.

Conclusions. Chromium complexes based on 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazoles **K1**–**K9** were produced in high yields using the Schlenk technique. It was found that systems based on the **K4**–**K7** and **K9** complexes enable the ethylene oligomerization process to be carried out with a sufficiently high level of productivity. It was shown that the introduction of a dialkyl zinc derivative increases the performance and selectivity of the catalytic system for the target fraction.

Keywords

chromium complexes, 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazoles, olefins, catalytic system, ethylene oligomerization

Submitted: 28.07.2023
Revised: 06.12.2023
Accepted: 25.01.2024

For citation

Senin A.A., Polyanskii K.B., Sheloumov A.M., Afanasiev V.V., Yumasheva T.M., Rudyak K.B., Vorobyev S.V. Synthesis and application of chromium complexes based on 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazole ligands to obtain higher C_{10}–C_{18} olefins. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2024;19(1):39–51. https://doi.org/10.32362/2410-6593-2024-19-1-39-51

НАУЧНАЯ СТАТЬЯ

Синтез комплексных соединений хрома на основе 4,5-бис(дифенилфосфанил)-*H*-1,2,3-триазольных лигандов и их применение для получения высших олефинов C_{10}–C_{18}

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Аннотация

Цели. Синтезировать 4,5-бис(дифенилфосфанил)-*H*-1,2,3-триазольные лиганды и на их основе новые комплексы хрома для получения фракции высших альфа-олефинов C_{10}–C_{18} из этилена.

Методы. Для получения целевых комплексов хрома использовали методы работы в инертной атмосфере (техника Шленка). Дифенилфосфанил триазольные лиганды охарактеризованы методами спектроскопии ядерного магнитного резонанса. Состав конечных продуктов подтвержден с помощью элементного анализа. Жидкая фаза реакции олигомеризации охарактеризована методом газовой хроматографии.

Результаты. Получены лиганды **L1**–**L9** и из них с помощью коммерчески доступного трихлоридтрис(тетрагидрофуран) хрома(III) синтезированы комплексы хрома **К1**–**К9**. Полученные комплексы **К1**–**К9** испытаны в процессе олигомеризации этилена.

Выводы. С высокими выходами получены новые комплексы хрома на основе 4,5-бис(дифенилфосфанил)-*H*-1,2,3-триазолов **К1**–**К9**. Обнаружено, что системы на основе комплексов **К4**–**К7** и **К9** позволяют проводить процесс олигомеризации этилена с достаточно высокой производительностью. Показано, что введение диалкильного производного цинка повышает производительность и селективность каталитической системы по целевой фракции.

Ключевые слова

4,5-бис(дифенилфосфанил)-Н-1,2,3-триазолы, комплексы хрома, олефины, каталитическая система, олигомеризация этилена, метилалюмоксан

Поступила: 28.07.2023
Доработана: 06.12.2023
Принята в печать: 25.01.2024

Для цитирования

Сенин А.А., Полянский К.Б., Шелоумов А.М., Афанасьев В.В., Юмашева Т.М., Рудяк К.Б., Воробьев С.В. Синтез комплексных соединений хрома на основе 4,5-бис(дифенилфосфанил)-*H*-1,2,3-триазольных лигандов и их применение для получения высших олефинов C_{10}–C_{18}. *Тонкие химические технологии*. 2024;19(1):39–51. https://doi.org/10.32362/2410-6593-2024-19-1-39-51

INTRODUCTION

Higher alpha-olefins are valuable multipurpose raw materials for a range of applications. In particular, C_{10}–C_{18} fractions are used to produce poly alpha-olefins and additives for lubricants, alcohols for detergents, amines, amine oxides, nonionic surfactants, hydraulic fluids, and are also used as components of drilling fluids. C_{20+} olefins can be raw materials for the production of synthetic oils and cutting fluids, and can also be used in oilfield chemistry. As a rule, the use of individual olefins is not required in these areas, but the entire fraction of heavy linear terminal alkenes is [1, 2].

In contrast to the existing highly selective processes for the di-, tri- and tetramerization of ethylene, to date selective processes for the production of individual high-molecular-weight alpha-olefins have not been developed. According to the generally accepted mechanism [3], this can be explained by the impossibility of sequential coordination and cyclization of more than three to four ethylene molecules during the catalytic cycle. This is due to steric hindrances and thermodynamic limitations of the ethylene oligomerization process.

In modern scientific and patent literature, there are few descriptions of ethylene oligomerization processes in which the reaction products contain significant amounts of heavy olefin fractions [4–7]. Fe(II), Fe(III) complexes, as well as Cr(III) complexes containing a tridentate ligand with benzimidazole and pyridyl

fragments, activated with methylaluminoxane (MAO) or with modified MAO (MMAO), can catalyze the oligomerization of ethylene to form fractions C_{8+} and C_{10+} olefins under mild conditions [8–10]. Catalytic systems based on chromium complexes with diphosphine ligands exhibit a high level of activity in the process of trimerization of ethylene to 1-hexene [11].

The objective of our work was to synthesize 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazole ligands and the chromium complexes based on them, in order to obtain a higher alpha-olefin fraction C_{10}–C_{18} from ethylene.

EXPERIMENTAL

The synthesis of compounds and the preparation of catalytic systems were carried out in an inert atmosphere using the Schlenk technique. The initial solvents (tetrahydrofuran (THF) (reagent grade, *Chimmed*, Russia), toluene (special purity grade, *Chimmed*), and hexane (reagent grade, *Chimmed*)) used for the synthesis were purified by boiling and distillation over sodium with benzophenone ketyl at atmospheric pressure in an argon flow. Diphenyl(chloro)phosphine (95%, *Acros Organics*, Belgium) was distilled in a vacuum (boiling point T_b = 124–126°C at 3 mm Hg). Acetone (special purity grade, *Chimmed*), chloroform (reagent grade, stabilized with 0.6–1.0% EtOH, *Chimmed*), ethyl acetate (reagent grade, *Chimmed*), methanol (Labscan, HPLC-grade), and methylene chloride (reagent grade, *Chimmed*) were used without additional purification. Chromium(III) trichloride tris(tetrahydrofuran) ($Cr(THF)_3Cl_3$) (98%, *Acros Organics*, Belgium), MAO (10% solution in toluene, *Sigma-Aldrich*, USA), diethylzinc ($ZnEt_2$) (1.5 M solution in toluene, *Sigma-Aldrich*), *n*-pentadecane (99%, *Sigma-Aldrich*), copper(I) iodide (98%, *Acros Organics*), aqueous hydrogen peroxide (35%, *Acros Organics*), sodium azide (special purity grade, *Chimmed*), trichlorosilane (99%, *Acros Organics*), methyl iodide (99%, *Sigma-Aldrich*), *n*-butyl chloride (99%, *Sigma-Aldrich*), sodium iodide (special purity grade, *Chimmed*), *n*-hexyl iodide (98%), *n*-octyl chloride (99%), silica gel (60 A, *Sigma-Aldrich*), pyridine (97%, *Acros Organics*), calcium carbide (98%, *Acros Organics*), and triethylamine (99%, *Acros Organics*) were used without any additional purification. Dibromobis(triphenylphosphine)nickel(II) ($NiBr_2(PPh_3)_2$) was obtained from nickel(II) bromide (98%, *Acros Organics*) and triphenylphosphine (99+%, *Acros Organics*) according to the published procedure [12]. Alkyl azides were obtained from the corresponding commercially available alkyl halides (*Sigma-Aldrich*). Ethylene (*Mostekhgaz*, Russia) was passed through three series-connected columns filled with activated carbon (*Chimmed*) and zeolites (3A and 13X, *Chimmed*). High-purity argon (*Moscow Gas Processing Plant*, Russia) was further purified by being passed through three series-connected columns filled with zeolites (3A and 13X), copper oxide (CuO reduced to Cu, *Chimmed*), and a CE35KF polisher (*Entegris*, USA). This ensured the residual content of oxygen, water, CO, etc. at the 1 ppb level. The purity of the resulting compounds was determined by ^1H and $^{31}P\{^1H\}$ nuclear magnetic resonance (NMR) spectroscopy.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded by means of a Bruker AVANCE 400 NMR spectrometer (*Bruker Corporation*, USA) at the A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, using tetramethylsilane as an internal standard and 85% H_3PO_4 as an external standard. Elemental analysis was performed using a FLASH 2000 CHNS/O analyzer (*Thermo Fisher Scientific*, United Kingdom). The melting points were measured by the capillary method with an Electrothermal IA 9000 Series (*Thermo Fisher Scientific*) digital melting point apparatus. The studies were carried out at the Analytical Laboratory, *United Research and Development Center*, Moscow, Russia.

The liquid phase of the reaction mixture containing ethylene oligomerization products was analyzed using a Focus GC gas chromatograph (*ThermoFinnigan*, USA) with a flame ionization detector and a DB5 MS capillary column (length 50 m, diameter 0.2 mm) at a maximum operating temperature of 340°C. The contents of individual components in the mixture of ethylene oligomerization products were determined by the internal standard method using *n*-decane as an internal standard. A 0.2–0.3-μL sample was introduced using a *Hamilton* microsyringe (USA).

The column thermostat was programmed as follows: initial temperature 75°C; isothermal holding at 75°C, 12 min; heating from 75 to 290°C at a rate of 7 deg/min; isothermal holding at 290°C, 95 min. The vaporizer was programmed as follows: temperature 280°C; total carrier gas (helium) flow rate 35 mL/min; split ratio 50 : 1; constant gas flow rate through the column, 0.7 mL/min.

The general methodology for testing catalytic systems in the process of ethylene oligomerization was described earlier [13].

Synthesis of ligands

Method for the synthesis of 1,2-bis(diphenylphosphanyl)acetylene (**1**)

A solution of 50.0 g (0.23 mol) of diphenyl(chloro)-phosphine, 1.30 g (6.81 mmol) of copper(I) iodide, 57.4 g (0.568 mol) of triethylamine, and 4.0 g (5.68 mmol) of $NiBr_2(PPh_3)_2$ in 100 mL of toluene was stirred at 60°C for 18 h in an atmosphere of dry and purified acetylene obtained from 73.0 g (1.135 mol) calcium carbide. Next, the solvent was evaporated, and 1,2-bis(diphenylphosphanyl)acetylene was isolated from the residue by chromatography (silica gel; eluent: chloroform–hexane (1 : 10)).

Yield: 32.0 g (71%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 7.34–7.46 (13H, m, H_{Ar}), 7.60–7.73 (8H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) −32.13 (1P, s). ^{13}C NMR spectrum (101 MHz, $CDCl_3$): δ (ppm) 106.9, 128.7, 129.2, 132.6 132.8, 135.7. $C_{26}H_{20}P_2$. Calculated (%): C, 79.18; H ,5.11. Found (%): C, 79.13; H, 5.19.

Method for the synthesis of acetylene-1,2-diylbis(diphenylphosphine oxide) (**2**)

A 35% aqueous solution of hydrogen peroxide (6.51 mL (76.1 mmol)) was added dropwise with stirring to a solution (cooled to 5°C) of 10.0 g (25.4 mmol) of compound **1** in 100 mL of THF, and the obtained mixture was then stirred for 30 min. Next, 50 mL of a saturated aqueous solution of sodium thiosulfate was added and left to stir for 30 min, after which the obtained mixture was extracted 3 times with 50 mL of chloroform. The organic layer was dried over sodium sulfate, the solvent was evaporated, and acetylene-1,2-diylbis(diphenylphosphine oxide) was obtained in the form of a light yellow powder.

Yield: 9.30 g (86%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 7.45–7.55 (8H, m, H_{Ar}), 7.57–7.64 (4H, m, HAr), 7.73–7.85 (8H, m, HAr). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) 9.78 (1P, s). ^{13}C NMR spectrum (101 MHz, $CDCl_3$): δ (ppm) 99.9, 129.2, 129.7, 131.0, 131.1, 132.2, 133.3. $C_{26}H_{20}P_2O_2$. Calculated (%): C, 73.24; H, 4.73. Found (%): C, 73.18; H, 4.75.

Method for the synthesis of (2*H*-1,2,3-triazole-4,5-diyl)bis(diphenylphosphine oxide) (**3**)

To a solution of 9.30 g (21.8 mmol) of compound **2** in 75 mL of THF, 1.84 g (28.3 mmol) of sodium azide was added, and the obtained mixture was stirred at a temperature of 50°C for 10 h. Then the reaction mass was evaporated to dryness, and the residue was dissolved in 100 mL of water and acidified to pH 5. The formed precipitate was filtered off, washed on the filter with water 3 times, 30 mL each, and dried in a vacuum.

Yield: 7.80 g (76%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 7.45–7.55 (8H, m, H_{Ar}), 7.57–7.66 (84H, m, H_{Ar}), 7.83 (8H, dd, J = 13.83, 8.11 Hz, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) 9.18 (1P, s). $C_{26}H_{21}N_3P_2O_2$. Calculated (%): C, 66.53; H, 4.51; N, 8.95. Found (%): C, 66.37; H, 4.49; N, 8.74.

General procedure for the synthesis of (1-R-1*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxides)

To a solution of 9.30 g (21.8 mmol) of compound **2** in 75 mL of THF, 28.3 mmol of azide was added, and the obtained mixture was stirred at a temperature of 50°C for 10 h. Then the reaction mass was cooled to room temperature (20°C), the solvent was evaporated, and the residue was chromatographed (silica gel; eluent: ethyl acetate–hexane (3 : 1)).

(1-hexyl-1*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**4**)

Yield: 8.80 g (73%). ^{1}H NMR spectrum (400 MHz, dimethyl sulfoxide-d_6 (DMSO-d_6)): δ (ppm) 0.74–0.84 (3H, m, CH_3), 1.09–1.19 (6H, m, 3 x CH_2), 1.75 (2H, q, J = 7.23 Hz, CH_2), 5.05 (2H, t, J = 7.31 Hz, CH_2), 7.21–7.59 (16H, m, H_{Ar}), 7.85–7.91 (4H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) 18.05 (1P, s), 21.22 (1P, s). $C_{32}H_{33}N_3P_2O_2$. Calculated (%): C, 69.43; H, 6.01; N, 7.59. Found (%): C, 69.50; H, 6.39; N, 7.44.

(1-(2-octylthioethyl)-1*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**5**)

Yield: 10.80 g (77%). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 0.92 (3H, t, J = 6.83 Hz, CH_3), 1.19–1.61 (12H, m, 6 x CH_2), 2.41–2.57 (2H, m, CH_2), 2.87–3.01 (2H, m, CH_2), 2.88–3.02 (2H, m, CH_2), 5.25 (2H, t, J = 7.31 Hz, CH_2), 7.27–7.58 (16H, m, H_{Ar}), 7.83–8.00 (4H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, CD_2Cl_2): δ (ppm) 17.00 (1P, s), 20.88 (1P, s). $C_{36}H_{41}N_3P_2O_2S$. Calculated (%): C, 67.38; H, 6.44; N, 6.55. Found (%): C, 67.57; H, 6.39; N, 6.45.

General procedure for the synthesis of (2-(alkyl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxides)

To a solution of 9.30 g (21.8 mmol) of compound **2** in 75 mL of THF, 1.84 g (28.3 mmol) of sodium azide was added, and the mixture was stirred at a temperature of 50°C for 10 h. Then the reaction mass was cooled to room temperature (20°C), and the formed precipitate was filtered off. To the filtrate, 21.8 mmol of alkyl iodide was added, and the mixture was heated at 70°C with reflux and stirring for 8 h. Then the reaction mass was cooled to room temperature, the precipitate was filtered off, the filtrate was evaporated, and the residue was chromatographed (silica gel; eluent: ethyl acetate–hexane (3 : 1)). As a result, compounds **6**–**11** were obtained.

(2-(methyl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**6**)

Yield: 6.50 g (62%). ^{1}H NMR spectrum (400 MHz, C_6D_6): δ (ppm) 4.31 (3H, s, CH_3), 7.31–7.75 (20H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, C_6D_6): δ (ppm) 18.65 (1P, s). $C_{27}H_{23}N_3P_2O_2$. Calculated (%): C, 67.08; H, 4.80; N, 8.69. Found (%): C, 67.00; H, 4.79; N, 8.64.

(2-(butyl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**7**)

Yield: 7.60 g (66%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 0.91 (3H, t, J = 7.31 Hz, CH_3), 1.28–1.34 (2H, m, CH_2), 1.93 (2H, q, J = 7.15 Hz, CH_2), 4.50 (2H, t, J = 7.15 Hz, CH_2), 7.31–7.36 (8H, m, H_{Ar}), 7.43–7.50 (4H, m, H_{Ar}), 7.67–7.73 (8H, m, H_{Ar}). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) 21.81 (1P, s). $C_{30}H_{29}N_3P_2O_2$. Calculated (%): C, 68.56; H, 5.56; N, 8.00. Found (%): C, 68.47; H, 5.60; N, 7.95.

(2-(hexyl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**8**)

Yield: 8.60 g (71%). ^{1}H NMR spectrum (400 MHz, DMSO-d_6): δ (ppm) 0.93 (3H, t, J = 6.83 Hz, CH_3), 1.31–1.38 (4H, m, 2 x CH_2), 1.77–1.87 (2H, m, CH_2), 3.17–3.30 (2H, m, CH_2), 4.53 (2H, t, J = 6.83 Hz, CH_2), 7.33–7.46 (8H, m, H_{Ar}), 7.51–7.58 (4H, m, H_{Ar}), 7.62–7.66 (8H, m, H_{Ar}). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, DMSO-d_6): δ (ppm) 17.90 (1P, s). $C_{32}H_{33}N_3P_2O_2$. Calculated (%): C, 69.43; H, 6.01; N, 7.59. Found (%): C, 69.40; H, 6.09; N, 7.57.

(2-(octyl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**9**)

Yield: 8.50 g (67%). ^{1}H NMR spectrum (400 MHz, DMSO-d_6): δ (ppm) 0.79–0.92 (3H, m, CH_3), 1.10–1.35 (4H, m, 2 x CH_2), 1.68–1.91 (6H, m, 3 x CH_2), 3.12–3.26 (2H, m, CH_2), 4.50 (2H, t, J = 6.99 Hz, CH_2), 7.34–7.47 (8H, m, H_{Ar}), 7.45–7.55 (4H, m, H_{Ar}), 7.65–7.78 (8H, m, H_{Ar}). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, DMSO-d_6): δ (ppm) 17.62 (1P, s). $C_{34}H_{37}N_3P_2O_2$. Calculated (%): C, 70.21; H, 6.41; N, 7.22. Found (%): C, 70.21; H, 6.45; N, 7.19.

(2-(allyl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**10**)

Yield: 8.30 g (75%). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 5.40 (2H, d, J = 6.36 Hz, CH_2), 5.22–5.35 (2H, m, =CH_2), 6.0–6.13 (1H, m, =CH), 7.35–7.38 (8H, m, H_{Ar}), 7.48–7.58 (4H, m, H_{Ar}), 7.61–7.74 (12H, m, H_{Ar}). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, CD_2Cl_2): δ (ppm) 18.37 (1P, s). $C_{29}H_{25}N_3P_2O_2$. Calculated (%): C, 68.37; H, 4.95; N, 8.25. Found (%): C, 68.29; H, 4.91; N, 8.23.

(2-(hex-5-en-1-yl)-2*H*-1,2,3-triazol-4,5-diyl)-bis(diphenylphosphine oxide) (**11**)

Yield: 7.85 g (65%). ^{1}H NMR spectrum (400 MHz, DMSO-d_6): δ (ppm) 1.07–1.30 (2H, m, CH_2), 1.77–1.85 (2H, m, CH_2), 1.87–1.95 (2H, m, CH_2), 4.54 (2H, t, J = 6.68 Hz, $CH_2CH{=}CH_2$), 4.89–4.96 (2H, m, $CH{=}CH_2$), 5.63–5.75 (1H, m, $CH{=}CH_2$), 7.39–7.48 (8H, m, H_{Ar}) 7.55 (12H, d, J = 11.44 Hz). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, DMSO-d_6): δ (ppm) 15.82 (1P, s). $C_{32}H_{31}N_3P_2O_2$. Calculated (%): C, 69.68; H, 5.67; N, 7.62. Found (%): C, 69.67; H, 5.59; N, 7.57.

General procedure for the reduction of diphenylphosphine oxides to obtain ligands L1–L9

A 250-mL magnetically stirred three-neck round-bottom flask with an inert gas supply line and a dropping funnel was charged with 0.014 mol of one of compounds **3**–**11** and 75 mL of absolute toluene. To the obtained solution, 11.5 g (0.085 mol) of trichlorosilane and then 20.1 g (0.255 mol) of pyridine were added dropwise in an argon atmosphere. The reaction mixture was stirred at 90°C for 2 h and next filtered, the filtrate was evaporated, and the residue was chromatographed (silica gel; eluent: ethyl acetate–hexane (1:10)). As a result, **L1**–**L9** ligands were obtained.

4,5-bis(diphenylphosphanyl)-2*H*-1,2,3-triazole (**L1**)

Yield: 2.50 g (41%). Retention factor R_f = 0.22 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (300 MHz, $CDCl_3$): δ (ppm) 7.21–7.56 (20H, m, H_{Ar}), 12.42 (1H, br. s, NH). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) −36.26 (1P, s), −2.49 (1P, s). $C_{26}H_{21}N_3P_2$. Calculated (%): C, 71.39; H, 4.84; N, 9.61. Found (%): C, 71.37; H, 4.79; N, 9.64.

4,5-bis(diphenylphosphanyl)-1-hexyl-1*H*-1,2,3-triazole (**L2**)

Yield: 5.46 g (74%). R_f = 0.37 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 0.80–0.87 (3H, m, CH_3), 1.10–1.23 (6H, m, 3 x CH_2), 1.65–1.69 (2H, m, CH_2), 4.40 (2H, t, J = 7.63 Hz, CH_2), 7.19–7.36 (20H, m, H_{Ar}). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) –36.09 (1P, m). $C_{32}H_{33}N_3P_2$. Calculated (%): C, 73.69; H, 6.38; N, 8.06. Found (%): C, 73.87; H, 6.49; N, 7.94.

4,5-bis(diphenylphosphanyl)-1-((2-octylthio)-ethyl)-1*H*-1,2,3-triazole (**L3**)

Yield: 6.50 g (76%). R_f = 0.41 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 0.84–0.97 (3H, m, CH_3), 1.23–1.55 (12H, m, 6 x CH_2), 2.38–2.47 (2H, m, CH_2), 2.76–2.85 (2H, m, CH_2), 4.66 (2H, t, J = 7.63 Hz, CH_2), 7.27–7.41 (20H, m, H_{Ar}). ^{31}P{^{1}H} NMR spectrum (161.98 MHz, $CDCl_3$): δ (ppm) −36.09 (1P, s). $C_{36}H_{41}N_3P_2S$. Calculated (%): C, 70.91; H, 6.78; N, 6.89. Found (%): C, 70.87; H, 6.79; N, 6.82.

4,5-bis(diphenylphosphanyl)-2-(methyl)-2*H*-1,2,3-triazole (**L4**)

Yield: 4.30 g (68%). R_f = 0.33 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (500 MHz, $CDCl_3$): δ (ppm) 4.23 (3H, m, CH_3), 7.24–7.31 (12H, m, H_{Ar}), 7.36–7.44 (8H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (202 MHz, $CDCl_3$): δ (ppm) −34.29 (1P, s). $C_{27}H_{23}N_3P_2$. Calculated (%): C, 71.83; H, 5.14; N, 9.31. Found (%): C, 71.85; H, 5.29; N, 9.34.

4,5-bis(diphenylphosphanyl)-2-(butyl)-2*H*-1,2,3-triazole (**L5**)

Yield: 4.40 g (64%). R_f = 0.35 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 0.90–0.96 (3H, m, CH_3), 1.25–1.35 (2H, m, CH_2), 1.88–1.96 (2H, m, CH_2), 4.47 (2H, t, J = 7.13 Hz, CH_2), 7.24–7.30 (12H, m, H_{Ar}), 7.37–7.44 (8H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (202 MHz, $CDCl_3$): δ (ppm) −34.10 (1P, s). $C_{30}H_{29}N_3P_2$. Calculated (%): C, 73.01; H, 5.92; N, 8.51. Found (%): C, 73.07; H, 5.84; N, 8.50.

4,5-bis(diphenylphosphanyl)-2-(hexyl)-2*H*-1,2,3-triazole (**L6**)

Yield: 5.53 g (75%). R_f = 0.37 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 0.89–0.97 (3H, m, CH_3), 1.25–1.36 (6H, m, 3 x CH_2), 1.90–2.03 (2H, m, CH_2), 4.50 (2H, t, J = 6.99 Hz, CH_2), 7.28–7.46 (20H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, CD_2Cl_2): δ (ppm) −34.02 (1P, s). $C_{32}H_{33}N_3P_2$. Calculated (%): C, 73.69; H, 6.38; N, 8.06. Found (%): C, 73.70; H, 6.39; N, 7.97.

4,5-bis(diphenylphosphanyl)-2-(octyl)-2*H*-1,2,3-triazole (**L7**)

Yield: 5.23 (68%). R_f = 0.40 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 0.88–0.98 (3H, m, CH_3), 1.18–1.31 (10H, m, 5 x CH_2), 1.87–1.99 (2H, m, CH_2), 4.47 (2H, t, J = 6.99 Hz, CH_2), 7.25–7.43 (20H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, CD_2Cl_2): δ (ppm) −34.14 (1P, s). $C_{34}H_{37}N_3P_2$. Calculated (%): C, 74.30; H, 6.79; N, 7.65. Found (%): C, 74.37; H, 6.89; N, 7.54.

4,5-bis(diphenylphosphanyl)-2-(allyl)-2*H*-1,2,3-triazole (**L8**)

Yield: 5.00 g (75%). R_f = 0.34 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 5.08–5.35 (4H, m, 2 x CH_2), 6.04–6.22 (1H, m, CH), 7.24–7.31 (12H, m, H_{Ar}), 7.28–7.69 (20H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, CD_2Cl_2): δ (ppm) −33.69 (1P, s). $C_{29}H_{25}N_3P_2$. Calculated (%): C, 72.95; H, 5.28; N, 8.80. Found (%): C, 72.94; H, 5.21; N, 8.74.

4,5-bis(diphenylphosphanyl)-2-(hex-5-en-1-yl)-2*H*-1,2,3-triazole (**L9**)

Yield: 5.24 g (71%). R_f = 0.37 (Sorbfil); eluent: ethyl acetate–hexane (1 : 2). ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): δ (ppm) 1.18–1.48 (3H, m, CH_3), 1.90–2.17 (4H, m, CH_2), 4.51 (2H, t, J = 6.99 Hz, =$CHCH_2$), 4.87–5.17 (2H, m, CH_2=CH), 5.79 (1H, ddt, J = 17.05, 10.29, 6.68, 6.68 Hz, CH_2=CH), 7.24–7.53 (20H, m, H_{Ar}). $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, CD_2Cl_2): δ (ppm) −34.00 (1P, s). $C_{32}H_{31}N_3P_2$. Calculated (%): C, 73.98; H, 6.01; N, 8.09. Found (%): C, 73.97; H, 5.99; N, 8.07.

General procedure for the synthesis of chromium complexes

In a 100-mL magnetically stirred Schlenk flask, 3.39 g (9.1 mmol) of the $Cr(THF)_3Cl_3$ complex and 10.1 mmol of the corresponding **L1**–**L9** ligand were placed. The flask was evacuated and filled with argon. In a stream of argon, 50 mL of absolute THF was added, the obtained suspension was degassed and stirred at room temperature (20°C) for 18 h. The solvent was evaporated, and the residue was washed with hexane and dried in vacuum. As a result, **K1**–**K9** complexes were obtained.

(4,5-bis(diphenylphosphanyl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K1**)

Yield of the final **K1** chromium complex in the form of a blue-violet powder: 4.30 g (71%). Melting point T_{melt} > 250°C. $C_{30}H_{29}Cl_3CrN_3OP_2$. Calculated (%): C, 53.97; H, 4.35; N, 6.29. Found (%): C, 53.66; H, 4.26; N, 6.44.

(4,5-bis(diphenylphosphanyl)-1-hexyl-1*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K2**)

Yield of the final **K2** chromium complex, in the form of a blue-violet powder: 5.60 g (82%). T_{melt} > 250°C. $C_{36}H_{41}Cl_3CrN_3OP_2$. Calculated (%): C, 57.52; H, 5.46; N, 5.59. Found (%): C, 56.37; H, 5.29; N, 5.94.

(4,5-bis(diphenylphosphanyl)-1-(2-octylthio)ethyl)-1*H*-1,2,3-triazole-P,P)-tetrahydrofurantrichlorochrome(III) (**K3**)

Yield of the final **K3** chromium complex in the form of a blue-violet powder: 5.90 g (77%). T_{melt} > 250°C. $C_{40}H_{47}Cl_3CrN_3OP_2S$. Calculated (%): C, 57.34; H, 5.61; N, 5.02. Found (%): C, 56.88; H, 5.91; N, 5.18.

(4,5-bis(diphenylphosphanyl)-2-(methyl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K4**)

Yield of the final **K4** chromium complex in the form of a dark blue powder: 4.35 g (70%). T_{melt} > 250°C. $C_{31}H_{31}Cl_3CrN_3OP_2$. Calculated (%): C, 54.62; H, 4.55; N, 6.16. Found (%): C, 53.79; H, 4.24; N, 6.12.

(4,5-bis(diphenylphosphanyl)-2-(butyl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K5**)

Yield of the final **K5** chromium complex in the form of a blue powder: 4.50 g (68%). T_{melt} > 250°C. $C_{34}H_{37}Cl_3CrN_3OP_2$. Calculated (%): C, 56.43; H, 5.12; N, 5.81. Found (%): C, 55.89; H, 5.04; N, 5.88.

(4,5-bis(diphenylphosphanyl)-2-(hexyl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K6**)

Yield of the final **K6** chromium complex in the form of a blue powder: 5.82 g (85%). T_{melt} > 250°C. $C_{36}H_{41}Cl_3CrN_3OP_2$. Calculated (%): C, 57.52; H, 5.46; N, 5.59. Found (%): C, 57.37; H, 5.29; N, 5.44.

(4,5-bis(diphenylphosphanyl)-2-(octyl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K7**)

Yield of the final **K7** chromium complex in the form of a blue-violet powder: 5.34 g (75%). T_{melt} > 250°C. $C_{38}H_{45}Cl_3CrN_3OP_2$. Calculated (%): C, 58.53; H, 5.78; N, 5.39. Found (%): C, 58.31; H, 5.56; N, 5.54.

(4,5-bis(diphenylphosphanyl)-2-(allyl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K8**)

Yield of the final **K8** chromium complex in the form of a blue powder: 5.89 g (76%). T_{melt} > 250°C. $C_{33}H_{33}Cl_3CrN_3OP_2$. Calculated (%): C, 56.01; H, 4.67; N, 5.94. Found (%): C, 56.20; H, 4.51; N, 5.98.

(4,5-bis(diphenylphosphanyl)-2-(hex-5-en-1-yl)-2*H*-1,2,3-triazole)-P,P)-tetrahydrofurantrichlorochrome(III) (**K9**)

Yield of the final **K9** chromium complex in the form of a blue-violet powder: 4.93 g (72%). T_{melt} > 250°C. $C_{36}H_{39}Cl_3CrN_3OP_2$. Calculated (%): C, 57.67; H, 5.21; N, 5.60. Found (%): C, 57.29; H, 5.16; N, 5.54.

RESULTS AND DISCUSSION

L1–**L9** ligands were synthesized according to Schemes 1 and 2. 4,5-Disubstituted 1,2,3-triazoles were obtained by reacting activated alkynes with various azides [13, 14]. Acetylene-1,2-diylbis(diphenylphosphine oxide) (**2**), a key compound for the synthesis of a whole series of ligands, was produced by reacting diphenylchlorophosphine with acetylene in the presence of copper and nickel salts. This was followed by oxidation of diphenylphosphanylacetylene with an aqueous solution of hydrogen peroxide.

To synthesize NH-triazole **L1**, the corresponding diphenylphosphine oxide was obtained from acetylene-1,2-diylbis(diphenylphosphine oxide) and sodium azide. It was then reduced in the trichlorosilane–pyridine system.

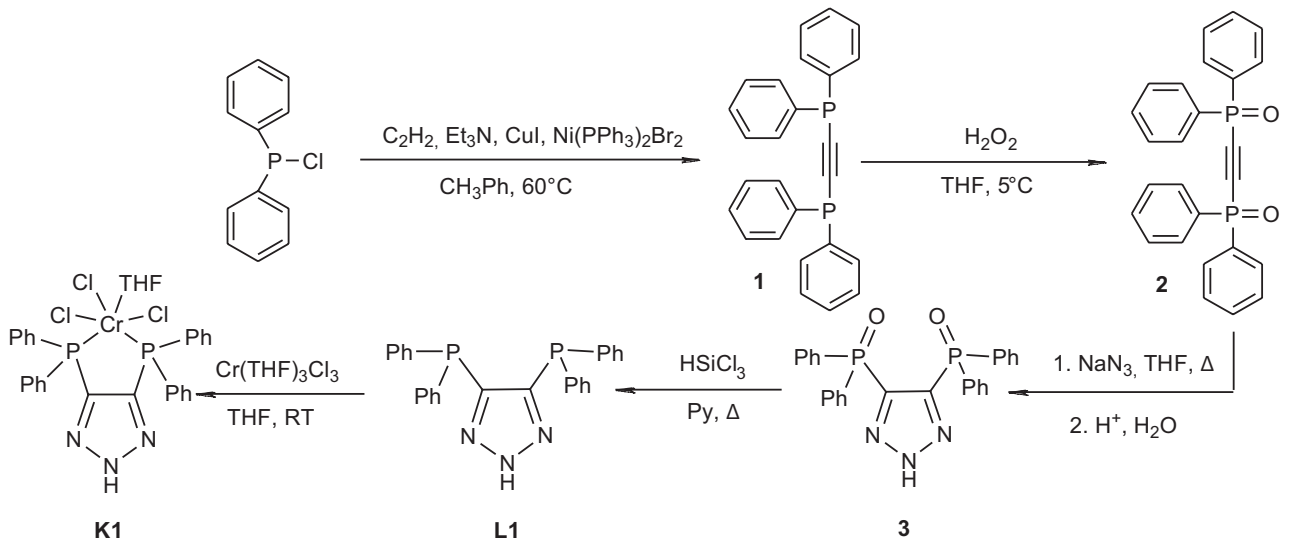
In order to obtain **L2** and **L3**, acetylene-1,2-diylbis(diphenylphosphine oxide) was reacted with alkyl azides, and then the intermediate dioxo derivative thus formed was reduced in the trichlorosilane–pyridine system.

In the synthesis of **L4**–**L9** ligands, the sodium triazole salt obtained was treated with the corresponding alkyl halide. As a result, after chromatographic separation, the resulting diphenylphosphine oxides were reduced. 4,5-disubstituted triazoles easily form complexes with various metals [14–17], due to which the reaction can occur under mild conditions.

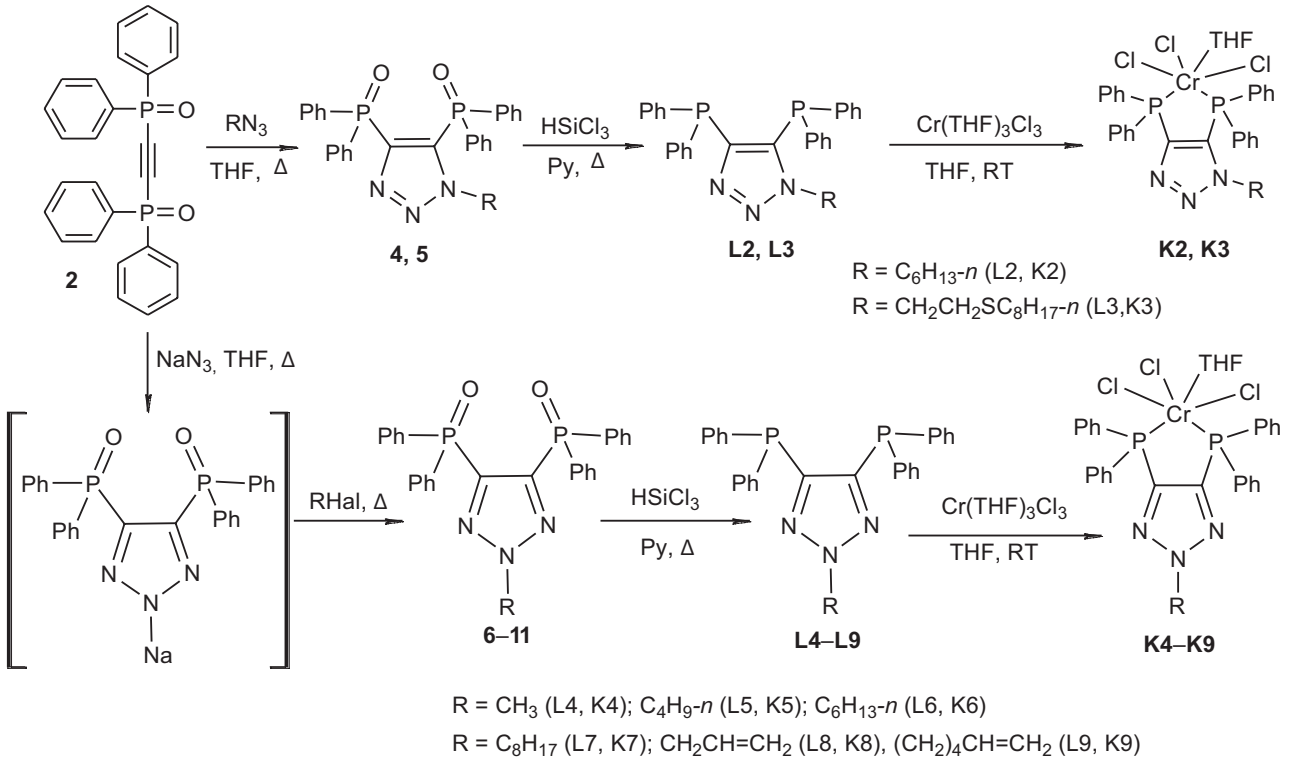
K1–**K9** complexes were synthesized from the corresponding **L1**–**L9** ligands and a commercially available chromium source $Cr(THF)_3Cl_3$ with yields of up to 85% (Schemes 1 and 2).

K1–**K9** chromium complexes are paramagnetic compounds and NMR spectroscopy cannot directly confirm their structure. However, NMR spectroscopy data on their precursors, diphosphine ligands **L1**–**L9**, as well as elemental analysis data on **K1**–**K9** make it possible for their structure and composition to be unambiguously determined.

Chromium complexes based on polydentate heteroatomic ligands in combination with organoaluminum compounds as activators are highly efficient catalytic systems for ethylene oligomerization [18, 19]. The resulting **K1**–**K9** complexes were tested for activity in the process of ethylene oligomerization using methylaluminoxane as an initiator. Table 1 presents the characteristics of the process of oligomerization in toluene at an operating temperature of 95°C and a pressure of 2.0 MPa. It was previously shown that chromium complexes with polydentate organic ligands demonstrate the highest performance under these conditions [11]. The process of ethylene oligomerization using **K1**–**K9** complexes is nonselective. The productivity ranges from 2.0 to 51.0 kg/g_{Cr}·h, depending on the compounds



Scheme 1. Synthesis of **L1** ligand and **K1** complex



Scheme 2. Synthesis of **L2**–**L9** ligands and **K2**–**K9** complexes

used. The amount of the polymer by-product also varies significantly (Table 1). For all the systems being studied, the main olefin fraction is the C_{10}–C_{18} fraction (from 27.0 to 47.0 wt %). The content of the C_{20}–C_{30} heavy olefin fraction in the oligomerization products ranges from 4.4 to 13.0 wt %. The selectivity of the process for the final product (individual higher alpha-olefin or alpha-olefin fraction) is determined both by the process conditions and, to a large extent, by the structure and electronic properties of the organic ligands included in the metal complex catalysts. In this regard, three groups can be distinguished among the tested catalytic systems: based on **K1**–**K3**, **K4**–**K8**, and **K9** complexes. The process of ethylene oligomerization with the participation of the first group is characterized by low productivity and selectivity for C_{10}–C_{18} fractions, as

well as high polymer content, making it inefficient. Systems based on **K4**–**K8** enable the process to be carried out with a fairly high productivity from 11.0 to 43.0 kg/g_{Cr}·h and a moderate content of the polymer product (no more than 3.1 wt %). The best performance of the process is demonstrated by the system based on the **K9** complex with the ligand 4,5-bis(diphenylphosphanyl)-2-(hex-5-en-1-yl)-2*H*-1,2,3-triazole. This ensures selectivities for the C_{10}–C_{18} and C_{20}–C_{30} olefin fractions in products of 47.4 and 13.0 wt %, respectively, with a productivity of more than 50 kg/g_{Cr}·h.

The literature shows that the use of additives of organozinc compounds to the catalytic system for ethylene oligomerization, Cr(PNP)Cl_3/MAO (PNP = = $Ph_2PN(i\text{-}Pr)PPh_2$), helps to increase the productivity and selectivity of the process for the fraction of C_{10}–C_{22} oligomers (35–60 wt %). It also reduces the amount of the polyethylene by-product and its molecular weight [5]. In view of this, we used a diethylzinc solution as a coactivator for the catalytic system based on the **K7** complex and MAO (Table 2) at a temperature of 95°C and a pressure of 2.0 MPa, in order to increase the productivity of the process and reduce the yield of the polymer product. As a result, it was shown that increasing the ratio of diethylzinc in the composition of the catalytic system to the molar ratio [Cr] : [MAO] : [$ZnEt_2$] = = 1 : 850 : 300 leads to a decrease in the content of the polymer product to 0.2 wt %, and to an increase in selectivity for the C_{10}–C_{18} fraction to 49.1 wt % with an increase in productivity to 57.9 kg/g_{Cr}·h.

We studied the effect of temperature on the oligomerization process for the catalytic system with the component ratio [Cr] : [MAO] : [$ZnEt_2$] = = 1 : 850 : 300 (Table 3). As a result, it was shown that reducing the temperature to 45°C leads to an increase in the yield of the polymer by-product, as well as a decrease in selectivity for the C_{10}–C_{18} fraction to 46.3 wt %, and a drop in process productivity by a factor of 2.5. An increase in temperature to 110°C also leads to a decrease in the selectivity of the process for C_{10}–C_{18} fractions, whereas the productivity decreases to 14.4 kg/g_{Cr}·h. This shows that the optimal temperature regime for the oligomerization process using the **K7** complex activated by methylaluminoxane and diethylzinc is 95°C.

Table 1. Results of testing of catalytic systems based on **K1**–**K9** complexes activated by methylaluminoxane in the reaction of oligomerization of ethylene

Complex	Productivity, kg/g_{Cr}·h	Selectivity, wt %						
		Polymer	C_4	C_6	C_8	C_{10}–C_{18}	C_{20}–C_{30}	C_{30+}
K1	5.0	5.3	16.7	13.4	14.3	40.2	9.1	1.0
K2	2.0	10.5	28.5	13.3	13.9	29.4	4.4	–
K3	3.0	18.9	15.2	10.0	18.5	27.0	10.5	–
K4	43.0	1.4	10.4	16.6	15.5	46.8	8.8	0.5
K5	17.0	3.1	9.3	14.9	14.2	46.4	11.2	0.9
K6	28.0	1.9	10.8	17.2	16.0	46.9	6.8	0.4
K7	21.0	1.7	9.5	14.9	14.8	46.7	11.7	0.7
K8	11.0	1.6	11.4	13.9	14.6	44.7	12.2	1.6
K9	51.0	1.9	8.5	14.6	14.6	47.4	13.0	–

Experimental conditions: 75-mL autoclave with magnetic stirrer; solvent: toluene (25.0 mL); loading of chromium complexes **K1**–**K9**, 0.85 μmol; activator, MAO; molar ratio [Cr] : [MAO] = 1 : 850; temperature, 95°C; pressure, 2.0 MPa; duration of the experiment, 0.5 h.

Table 2. Effect of diethylzinc as a coactivator of the catalytic system of ethylene oligomerization based on the **K7** complex

Molar ratio [Cr] : [MAO] : [$ZnEt_2$]	Productivity, $kg/g_{Cr}·h$	Selectivity, wt %						
		Polymer	C_4	C_6	C_8	C_{10}–C_{18}	C_{20}–C_{30}	C_{30+}
1 : 850 : 0	21.0	1.7	9.5	14.9	14.8	46.7	11.7	0.7
1 : 850 : 100	54.7	1.3	9.0	16.4	15.4	50.5	7.1	0.3
1 : 850 : 300	57.9	0.2	10.0	16.7	14.7	49.1	8.8	0.5
1 : 850 : 600	44.5	–	11.5	18.2	15.1	47.5	7.3	0.4

Experimental conditions: 75-mL autoclave with magnetic stirrer; solvent, toluene (25.0 mL); loading of chromium complexes **K7**, 0.85 μmol; activator, MAO; coactivator, $ZnEt_2$; temperature, 95°C; pressure, 2.0 MPa; duration of the experiment, 0.5 h.

Table 3. Parameters of the process of ethylene oligomerization based on the **K7** complex activated by a mixture of methylaluminoxane and diethylzinc at various temperatures

Temperature, °C	Productivity, $kg/g_{Cr}·h$	Selectivity, wt %						
		Polymer	C_4	C_6	C_8	C_{10}–C_{18}	C_{20}–C_{30}	C_{30+}
45	20.9	0.7	12.8	19.1	15.5	46.3	5.5	0.1
75	44.3	0.5	11.3	17,3	15.0	48.4	7.2	0.3
95	57.9	0.2	10.0	16.7	14.7	49.1	8.8	0.5
110	14.4	–	12.8	18.8	14.3	47.1	6.8	0.2

Experimental conditions: 75-mL autoclave with magnetic stirrer; solvent, toluene (25.0 mL); loading of chromium complex **K7**, 0.85 μmol, activator, MAO; molar ratio [Cr] : [MAO] : [$ZnEt_2$] = 1 : 850 : 300; pressure, 2.0 MPa; the duration of the experiment, 0.5 h.

CONCLUSIONS

The study proposed a method for the preparation of **L1**–**L9** bis(diphenylphosphanyl)triazole ligands from commercially available compounds. This allows the introduction of alkyl and alkenyl substituents with different carbon chain lengths into the triazole fragment. This also improves the solubility of chromium complexes in the reaction medium, and affects the steric and electronic properties of ligands which control the catalytic activity and selectivity of the ethylene oligomerization process. New chromium complexes **K1**–**K9** based on 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazoles were synthesized (with yields of 69–85%). The process of ethylene oligomerization using catalytic systems based on them was also studied. It was determined that systems based on the **K4**–**K7** and **K9** complexes enable the process of ethylene oligomerization to be carried out with a fairly high level of productivity (up to 51.0 kg/g_{Cr} h). The maximum selectivity for C_{10}–C_{18} and C_{20}–C_{30} olefins was observed for the catalytic system based on the **K9** complex with a hexenyltriazole ligand. It was shown that the introduction of diethylzinc as a coactivator of the catalytic system based on the **K7** complex leads to an increase in the productivity of the system and an increase in selectivity for the heavy olefin fraction. Further study of catalytic systems based on 4,5-bis(diphenylphosphanyl)-*H*-1,2,3-triazoles is promising with regard to determining the characteristics of the oligomerization process, as well as in creating catalysts for the production of linear alpha-olefins with a high level of selectivity for the fraction of higher alpha-olefins intended for the synthesis of synthetic oils and fuel additives.

Authors' contributions

A.A. Senin – conducting experiments on the synthesis complex compounds and oligomerization of ethylene, systematization and processing of the results obtained, and writing the text of the article.

K.B. Polyanskii – conducting experiments on the synthesis of ligands and complex compounds, systematization and processing of the results obtained, and writing the text of the article.

A.M. Sheloumov – review of publications on the topic of the article, writing the text of the article.

V.V. Afanasiev – development of the research concept and systematization of the results obtained, and preparation of materials for publication.

T.M. Yumasheva – development of the research concept and scientific guidance at all stages of the study.

K.B. Rudyak – guidance at all stages of the study.

S.V. Vorobyev – critical revision with the introduction of valuable intellectual content in the article and preparation of materials for publication.

The authors declare no conflicts of interest.

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Translated from Russian into English by V. Glyanchenko
Edited for English language and spelling by Dr. David Mossop