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Catalytic Systems for Production of 1-Hexene by Selective Ethylene Trimerization

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Abstract—New chromium complexes with diphosphine ligands have been obtained by the reaction of chromium(III) hexahydrate and diphosphines in acetone. The structure of chromium(III) complex **4** containing water molecule and 1,2-bis(diphenylphosphino)benzene as ligands and that of two chromium(III) complexes (**12** and **13**) with 1,2-bis(diphenylphosphino)benzene ligands containing alkenyl substituents in the *ortho*-position of one of the phenyl groups at the phosphorous atom have been determined using X-ray diffraction analysis. The catalytic properties of the obtained complexes in the composition of catalytic systems for ethylene trimerization have been studied. It has been shown that the obtained series of catalytic systems manifests high activity in the process of ethylene trimerization to 1-hexene, with the process selectivity exceeding 94%. The highest value of productivity amongst known selective catalytic systems for trimerization was achieved using a chromium complex **13** bearing the 2-methylprop-1-enyl group at the *ortho*-position of one of the phenyl groups. The influence of temperature, pressure, the nature of the solvent and the composition of the catalytic system on the parameters of the process of ethylene trimerization to form 1-hexene has been determined.

Keywords: selective ethylene trimerization, 1-hexene, diphosphine chromium complexes
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Selective production processes of 1-hexene and heavier olefins hold a special position among the developed processes of ethylene oligomerization to linear alpha-olefins. Despite considerable progress in this field, there are few examples of catalytic systems providing significant productivity of the process and a low amount of the byproduct polymer along with high selectivity for the desired product [1–3].

We have shown earlier that the use of structurally modified diphosphine ligands in the composition of the catalytic system for ethylene oligomerization makes it possible to obtain 1-hexene [4, 5] selectively. The formulas of the modified diphosphine ligands in the catalytic systems are given below as they are mentioned.

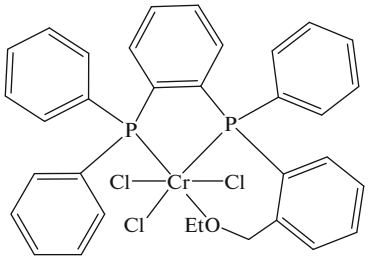

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Fig. 1. Chromium complex **1** with a diphosphine ligand which forms a catalytic system for selective ethylene oligomerization [4, 5].

For example, a solution of chromium complex **1** with the CH_2OEt functional group at the *ortho*-position of one of the phenyl substituents at the phosphorous atom activated by a mixture of methylaluminoxane (MAO) and trialkylaluminum effectively catalyzes the ethylene trimerization process. In that case, the 1-hexene selectivity of 92.0 wt % is achieved at the productivity of the process of 33.5 kg $\cdot$ g_{Cr}^{-1} $\cdot$ h^{-1} [4] and it is possible to achieve the 1-hexene selectivity of 96.4 wt % at the productivity of 57.9 kg $\cdot$ g_{Cr}^{-1} $\cdot$ h^{-1} by optimizing the process conditions [5] (Fig. 1).

The achieved value of selectivity for the desired product is high enough; however, the productivity index is lower by more than an order of magnitude in comparison with a known process developed by BP Chemicals in 2002, which utilizes PNP-type ligands in the catalytic system (1033 kg $\cdot$ g_{Cr}^{-1} $\cdot$ h^{-1} [6, 7]).

In this study, we expanded the range of chromium complexes used for the purpose and studied the influ-

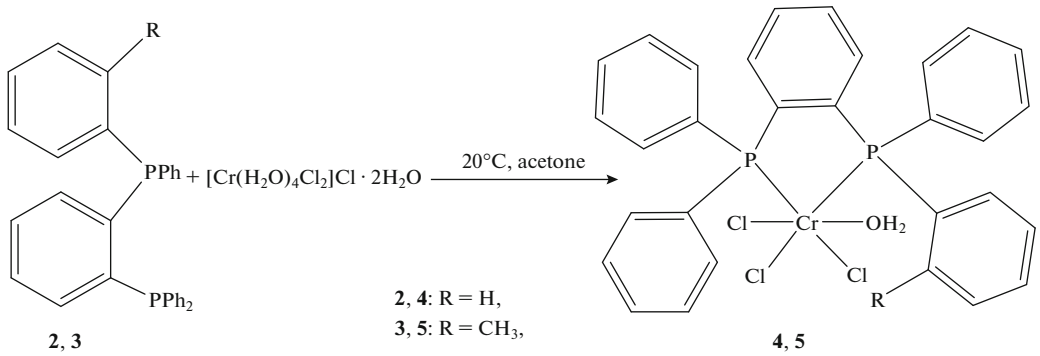

Fig. 2. Scheme of preparation of complexes **4** and **5**.

ence of their structural features on the catalytic activity of the system to increase the process productivity of ethylene trimerization to form 1-hexene. The optimization of the oligomerization process conditions was performed for the most active catalytic systems. The optimum operating temperature and pressure were selected and the influence of the solvent nature on the parameters of the selective ethylene oligomerization process was studied. The procedures for synthesis of precursors, ligands, and chromium complexes are presented after the Results and Discussion section.

RESULTS AND DISCUSSION

In the present work, the synthesis method of diphosphine chromium complexes was substantially simplified. Earlier the chromium complexes were synthesized using the reaction of tris(tetrahydrofuran)chromium(III) trichloride $CrCl_3(THF)_3$ with the corresponding diphosphine ligands [8, 9]. The starting metallating agent, $CrCl_3(THF)_3$, is expensive and unstable upon long-term storage. We developed a procedure that makes it possible to use an available reagent, chromium(III) chloride hexahydrate $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, as a source of chromium in the synthesis of diphosphine complexes. The interaction of diphosphine ligands with chromium(III) chloride hexahydrate in acetone (stirring of the reaction mixture for 24 h at room temperature) leads to the formation of diphosphine chromium complexes with a yield above 90%. The chromium complexes formed are slightly soluble in acetone and precipitate as a blue fine-crystalline solid during the reaction, thereby simplifying their separation and purification. The procedure was optimized during the preparation of complexes **4** and **5** based on 1,2-bis(diphenylphosphino)benzene(dppb) (**2**) and [(2-diphenylphosphino)phenyl][2-(methyl)phenyl]phenylphosphine (**3**) (Fig. 2).

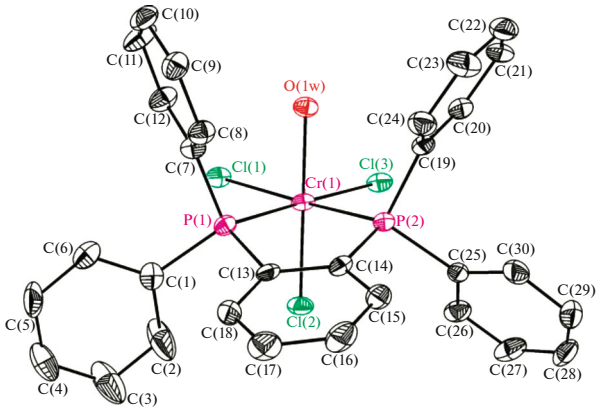

Fig. 3. Molecular structure of complex $[2\text{-}(C_6H_5)_2\text{-}P(C_6H_4)P(C_6H_5)_2]CrCl_3(H_2O)$ (**4**). The hydrogen atoms have been omitted for clarity.

The structure of compound **4** was determined by X-ray diffraction study of a single crystal (Fig. 3). Complex **4** has a distorted octahedral configuration. The complex contains a coordinated H_2O molecule that is in the *trans*-position to one of the chlorine atoms. The source of coordinated water is chromium(III) chloride hexahydrate $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ used in the reaction to prepare **4**.

The ligand environment of the chromium atom in complex **4**, (**2**)$CrCl_3(H_2O)$, differs from that established earlier for (dppb)$CrCl_3(THF)$ (**6**) [9] obtained via the reaction of 1,2-bis(diphenylphosphino)benzene with $CrCl_3(THF)_3$. The coordination sphere of the chromium atom in the (dppb)$CrCl_3(THF)$ complex contains a tetrahydrofuran (THF) molecule as a labile ligand, the source of which is the starting complex $CrCl_3(THF)_3$. As it was shown by the investigation of the catalytic properties of the ethylene oligomerization catalytic system based on complex **4**, this structural modification does not affect the productivity and selectivity of the process. The results of testing the catalytic properties of the systems based on complexes **4** and **5**, as well as the (dppb)$CrCl_3(THF)$ complex, are presented in Table 1.

The obtained results show that the exchange of the labile ligand in the coordination sphere of the chromium atom (in this case, THF for H_2O) has no sub-

Table 1. Results of testing the catalytic systems based on chromium complexes **4**, **5** and **6** in the ethylene oligomerization reaction

Complex	Productivity, $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$	Selectivity, wt %					
		polymer	C_4	C_6	C_8	C_{10+}	1-C_6 in C_6 fr.
4	210	3.8	0.4	52.8	27.3	15.7	88.1
5	450	0.5	0.4	84.8	6.9	7.4	98.7
6	220	0.4	6.3	50.3	29.7	13.3	86.9

Conditions: the load of chromium complexes is 1.9×10^{-3} mmol (the concentration in the solution is 7.4×10^{-5} mol/L), solvent is methylcyclohexane (25.0 mL), concentration of the activator (a 10% solution of methylaluminoxane in toluene) is 4.7×10^{-2} mol/L (the load is 1.2 mmol), molar ratio [Cr] : [MAO] is 1 : 630, temperature is 85°C, pressure is 20 bar, and experiment duration is 0.5 h.

stantial influence on the catalytic activity of the systems based on complexes with the 1,2-bis(diphenylphosphino)benzene ligand. It appears that the treatment of both complexes (**4** and **6**) with a methylaluminoxane solution leads to the formation of the same activated complex. It was shown earlier [4–6] that the addition of a functional group capable of coordination with a chromium atom at the *ortho*-position of one of the phenyl substituents at the phosphorous atom in the diphosphine ligand facilitates the process of ethylene trimerization into 1-hexene. In the case of complex **5**, the methyl group introduced is not coordinated to the metal atom; nevertheless, the use of a catalytic system including this chromium complex makes it possible to achieve enhanced selectivity of the ethylene oligomerization process with a simultaneous increase in productivity. At an operating pressure of 40 bar, it turns out to be possible to achieve an even more significant increase in the productivity of the ethylene oligomerization process up to 726 $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$ in the case of using the catalytic system based on complex **5**, with the 1-hexene selectivity remaining almost unchanged to be 84.5 wt %.

Based on the data about using of complex **5** in the ethylene trimerization to 1-hexene it was suggested that the introduction of alkenyl substituents into the *ortho*-position of one of the phenyl substituents at the phosphorous atom of the diphosphine ligand would make it possible to approach to the creation of highly active and selective catalytic systems. Alkenyl groups have potential capacity for the coordination of the unsaturated C=C moiety to the chromium atom as a catalytic center in the process of catalysis, which can promote the increase in the selectivity of the catalytic system. For this purpose, a number of diphosphine ligands **7**–**11** with different alkenyl substituents in the *ortho*-position of the phenyl ring were synthesized. Diphosphine ligands **7**–**11** were characterized using ^1H and ^{31}P NMR spectroscopy. The formation of geometrical *cis*- and *trans*-isomers was found for ligands **9** and **10** with different substituents R_1 and R_2 at the carbon–carbon double bond. Then complexes **12**–**16** were synthesized according to the developed procedure by the reaction of **7**–**11** with chromium(III) chloride hexahydrate (Fig. 4).

Complex **16**, bearing long-chain $C_{10}H_{21}$ alkyl groups on its aromatic ring, has good solubility in saturated hydrocarbons including methylcyclohexane. According to published data, improvement in solubility of the catalytic precursor can promote an increase in the activity of the resulting catalytic system. Thus the productivity of the ethylene trimerization process with the participation of a chromium complex based on a PNP-ligand with the C_{18} alkyl substituent at the

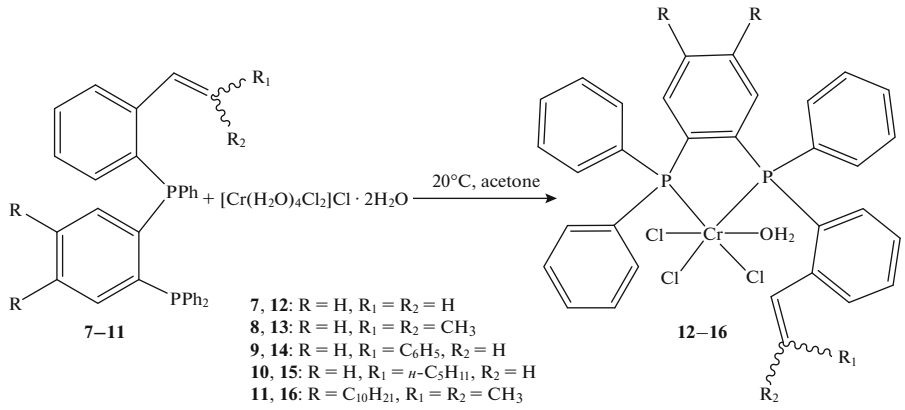

Fig. 4. Scheme of preparation of complexes **12**–**16**.

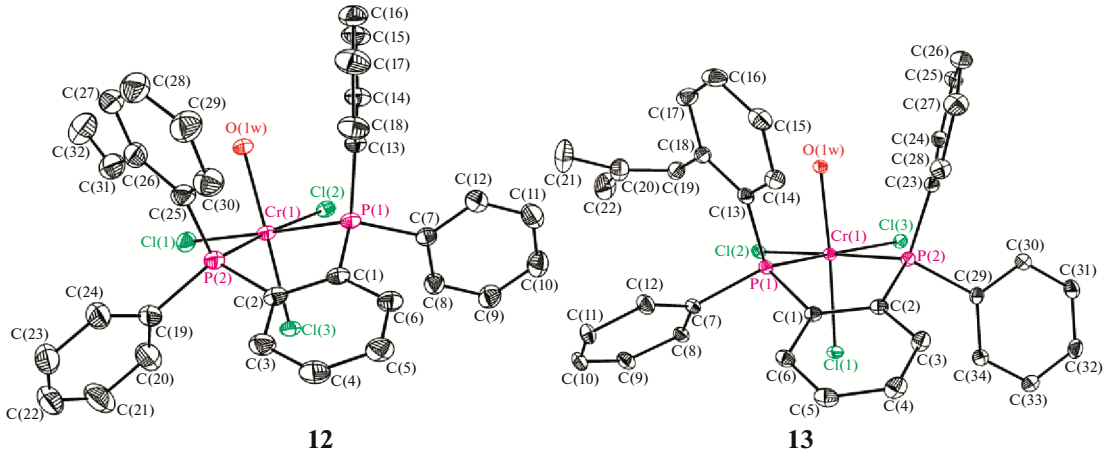

Fig. 5. Molecular structure of complexes $[2\text{-}(C_6H_5)_2P(C_6H_4)(2\text{-}(CH_2{=}CH)C_6H_4)(C_6H_5)P]CrCl_3(H_2O)$ (**12**) and $[2\text{-}(C_6H_5)_2P(C_6H_4)(2\text{-}(CH_2{=}C(CH_3)_2)C_6H_4)(C_6H_5)P]CrCl_3(H_2O)$ (**13**). The hydrogen atoms have been omitted for clarity.

nitrogen atom is 6.5-fold higher than in the case of the unsubstituted ligand under the same conditions [10].

The structure of compounds **12** and **13** was unambiguously confirmed by X-ray diffraction analysis data (Fig. 5). The X-ray diffraction study has shown that complexes **12** and **13** have a distorted octahedral configuration. The orientation of the alkenyl groups of the complexes in the crystal rules out their interaction with the chromium atom, thus, the alkenyl groups are oriented away from the metal atom relative to the phenyl ring. As in the case of **4**, the chromium atom coordinates an H_2O molecule that is located in the *trans*-position to one of the chlorine atoms.

The absence of coordination of the introduced functional group to the chromium atom gave grounds to suppose that the use of complexes of this type in the composition of a catalytic system for ethylene trimerization would not ensure high selectivity of the process. However, the performed experiments on ethylene oligomerization with the use of complexes **12**–**16** did not confirm this assumption. The experimental data are presented in Table 2.

The activation of the complexes was performed using a mixture of solutions of methylaluminoxane and trimethylaluminum (TMA). It was shown earlier for model systems based on diphosphine complexes that using a mixture of methylaluminoxane and trimethylaluminum with predefined ratio instead of a solution of methylaluminoxane alone can increase the productivity of the process [11]. A similar molar ratio of chromium complexes and activators was used during the preparation of the catalytic systems based on complexes **12**–**16**. All the obtained catalytic systems make it possible to obtain 1-hexene from ethylene with a high selectivity. The purity of the obtained C_6 fraction with respect to 1-hexene is also high, 99.0–99.7%. Other important criteria of the efficiency of a catalytic system for ethylene trimerization into 1-hexene are the productivity of the process and amount of the byproduct polymer. Systems based on complexes **12** and **13** stand out with respect to these two parameters; thus, the process of trimerization with their use proceeds with the selectivity above 90%. The catalytic system based on complex **16** has increased solubility in the reaction solution; however, it is just an insignifi-

Table 2. Results of testing the catalytic systems based on chromium complexes **12**–**16** in the ethylene oligomerization reaction

Complex	T, °C	Pressure, bar	Productivity, $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$	Selectivity, wt %					
				polymer	C_4	C_6	C_8	C_{10+}	1-C_6 in C_6 fr.
12	85	40	640	0.2	0.3	91.7	5.6	2.2	99.5
13	85	40	1890	<0.1	0.1	94.0	3.2	2.7	99.7
14	85	40	280	2.5	0.9	89.4	4.5	2.7	99.0
15	60	30	510	0.4	2.8	87.8	7.0	2.0	99.0
16	70	30	650	2.3	1.2	79.7	5.7	11.1	99.7

Conditions: the load of chromium complexes is 9×10^{-5} mmol (the concentration in the solution is 3.6×10^{-6} mol/L), solvent is methylcyclohexane (25.0 mL), activators are TMA (a 1.0 M solution in methylcyclohexane) and MAO (a 0.085 M solution in toluene), molar ratio [Cr] : [MAO] : [TMA] is 1 : 300 : 1100, and experiment duration is 0.5 h.

Table 3. Influence of temperature on the parameters of the ethylene trimerization process for the catalytic systems based on complexes **12** and **13**

T, °C	Productivity, $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$	Selectivity, wt %					
		polymer	C_4	C_6	C_8	C_{10+}	1-C_6 in C_6 fr.
Catalytic system based on complex **12**							
41	690	1.0	0.2	72.9	21.7	4.2	98.6
50	1080	0.7	0.3	80.7	15.0	3.4	98.7
60	1630	0.2	0.1	86.0	10.4	3.3	98.8
70	1110	0.3	0.5	88.7	7.7	2.7	98.9
80	890	0.1	0.2	90.9	6.6	2.3	99.1
90	400	0.2	0.4	92.5	4.7	2.2	99.6
100	370	0.2	0.5	92.3	5.2	1.8	99.0
115	100	5.3	0.7	78.6	5.6	9.9	97.7
140	50	25.4	4.2	33.2	4.1	33.2	96.3
Catalytic system based on complex **13**							
30	1750	0.1	0.2	74.0	21.2	4.5	98.9
50	2130	0.1	0.1	87.2	9.6	3.0	99.5
60	2510	0.1	0.1	89.8	7.0	3.0	99.7
70	2830	<0.1	0.1	92.2	4.5	3.2	99.6
80	2360	<0.1	0.1	93.3	3.7	2.9	99.7
90	1410	<0.1	0.1	94.8	2.8	2.3	99.5
100	720	0.2	0.2	94.4	2.7	2.5	99.4
110	320	22.8	0.2	70.9	2.7	3.4	99.5

Conditions: the loading of chromium complexes is 9×10^{-5} mmol (the concentration in the solution is 3.6×10^{-6} mol/L), solvent is methylcyclohexane (25.0 mL), activators are TMA (a 1.0 M solution in methylcyclohexane) and MAO (a 0.085 M solution in toluene), molar ratio [Cr] : TMA : MAO is 1 : 1100 : 300, pressure is 40 bar, and experiment duration is 0.5 h.

cant technical advantage regarding introduction of a chromium complex solution. In the case of using this system, the selectivity of the process is the lowest to be 79.7% in the series of complexes under study. It can be noted that steric factors are pivotal in the case of formation of highly selective catalytic systems for ethylene trimerization with the participation of the series of diphosphine chromium complexes under study. The spatial arrangement of the substituents at the double bond is pivotal since it is responsible for shielding the catalytic site and hindering the approach of substrate molecules. Substituents that are more remote from the chromium atom also have a spatial effect, like $C_{10}H_{21}$ alkyl groups in the central aromatic ring in complex **16**. Nevertheless, it cannot be ruled out that there is interaction of the unsaturated moiety with the metal atom in the activated catalytically active complex in the solution is possible. So it can affects the selectivity of the process of trimerization together with the steric factors of the substituents.

For the obtained highly selective catalytic systems for ethylene trimerization to 1-hexene based on **12** and **13**, the optimum process parameters such as temperature, pressure, and solvent effect on catalytic activity, were selected. The reaction temperature is the main factor determining the stability of the catalytic system and its performance. We studied the character of changes in the process parameters of ethylene trimerization upon varying the temperature in a range from 30 to 140°C at a constant ethylene pressure of 40 bar. The obtained experimental data are presented in Table 3.

The testing of the catalytic systems based on complexes **12** and **13** at different temperatures demonstrated that the highest productivity in the processes of selective ethylene trimerization to 1-hexene was achieved in the range of operating temperatures of 50–80°C. The temperature range of the maximum 1-hexene selectivity of the process is shifted to higher tem-

Table 4. Influence of the ethylene pressure on the process parameters of selective ethylene trimerization to 1-hexene over the catalytic systems based on complexes **12** and **13**

Pressure, bar	Productivity, $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$	Selectivity, wt %					
		polymer	C_4	C_6	C_8	C_{10+}	1-C_6 in C_6 fr.
Catalytic system based on complex **12**							
10	40	1.0	1.8	89.7	2.4	5.0	97.9
20	210	0.4	0.5	92.4	2.9	3.8	98.4
30	290	0.8	0.9	91.0	3.9	3.4	99.0
40	400	0.2	0.4	92.5	4.7	2.2	99.6
50	580	0.3	0.3	90.3	6.6	2.5	99.4
60	850	9.0	0.6	80.0	4.6	5.8	99.3
Catalytic system based on complex **13**							
10	130	<0.1	0.5	94.3	2.8	2.4	99.2
20	400	<0.1	0.3	94.8	2.7	2.2	99.4
30	1020	<0.1	0.2	94.8	2.5	2.5	99.5
40	1410	<0.1	0.1	94.8	2.8	2.3	99.5
60	1810	3.4	0.5	89.8	3.9	2.4	99.1

Conditions: the loading of chromium complexes is 9×10^{-5} mmol (the concentration in the solution is 3.6×10^{-6} mol/L), solvent is methylcyclohexane (25.0 mL), activators are TMA (a 1.0 M solution in methylcyclohexane) and MAO (a 0.085 M solution in toluene), molar ratio [Cr] : TMA : MAO is 1 : 1100 : 300, temperature is 90°C, and experiment duration is 0.5 h.

peratures of 80–100°C. Further increase in the temperature to 140°C leads to a noticeable decrease in the productivity of the catalysts and process selectivity, since the harsher thermal conditions promote the occurrence of the side reactions of formation of higher C_{10+} olefins and a polymer. It should be noted that decreasing the process temperature to 30–40°C leads to a growth in 1-octene, the ethylene tetramerization product, the concentration of which reaches 21%. Note that these catalytic systems are capable of carrying out the oligomerization process with a sufficiently high productivity.

The character of changes in the process parameters of ethylene trimerization to 1-hexene in the pressure range of 10 to 60 bar can be comprehended from the experimental data in Table 4, which presents an example of the use of the catalytic systems based on complexes **12** and **13**.

The productivity of the ethylene trimerization process monotonically increases with pressure growth. The selectivity for the C_6 fraction remains almost unchanged up to 40 bar and substantial decreases at a pressure above. Unlike temperature, pressure insignificantly affects the selectivity of the process. It is also seen that there is no clear pressure dependence of the amount of the polymer formed; at the same time, the amount of C_8 olefins increases with pressure. At a pressure of 60 bar and above, polymerization processes become noticeable.

The influence of the solvent nature on the parameters of the trimerization process was studied using, as an example, the catalytic system based on complex **12**. For this purpose, the process of selective trimerization was run in five different solvents, namely, methylcyclohexane, isooctane, toluene, *o*-xylene, and decahydronaphthalene (decalin). The results of the experiments are presented in Table 5.

The obtained data give evidence for the exceptionally effective ethylene trimerization reaction to give 1-hexene in methylcyclohexane in comparison with the reactions in toluene and *o*-xylene. The possible reason for the drop in the productivity and selectivity of the process in aromatic solvents is the interaction of the activated complex with the aromatic hydrocarbons to form new chromium complexes with the η^6-coordinated aromatic ring of the solvent molecule that are not capable of catalyzing the selective process of 1-hexene synthesis [3]. The main products formed in the case of toluene or *o*-xylene are a number of lin-

Table 5. Solvent effect on the parameters of the trimerization process over the catalytic system based on complex **12**

Solvent	Productivity, $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$	Selectivity, wt %					
		polymer	C_4	C_6	C_8	C_{10+}	1-C_6 in C_6 fr.
Methylcyclohexane	430	<0.1	0.5	94.0	3.4	2.1	99.2
Isooctane	100	0.2	2.0	86.9	8.0	2.9	97.3
Decalin	20	19.1	13.0	53.9	10.9	3.1	95.6
Toluene	10	0.1	38.3	11.1	0.1	50.4	35.0
o-Xylene	10	1.3	28.4	14.0	0.5	55.8	53.1

Conditions: the loading of chromium complex **12** is 9×10^{-5} mmol (the concentration in the solution is 3.6×10^{-6} mol/L), solvent (25.0 mL), activators are TMA (a 1.0 M solution in methylcyclohexane) and MAO (a 0.085 M solution in a methylcyclohexane–toluene mixture), molar ratio [Cr] : TMA : MAO is 1 : 1100 : 300, temperature is 90°C, pressure of ethylene is 40 bar, and experiment duration is 0.5 h.

Table 6. Influence of 1-hexene concentration in the reaction medium on the parameters of the process of ethylene trimerization to 1-hexene (by the example of the catalytic system based on complex **13**)

Initial 1-hexene concentration, wt %	Productivity, $kg \cdot g_{Cr}^{-1} \cdot h^{-1}$	Selectivity, wt %					
		polymer	C_4	C_6	C_8	C_{10+}	1-C_6 in C_6 fr.
0.0	1410	<0.1	0.1	94.8	2.8	2.3	99.5
1.6	1205	<0.1	0.2	94.0	3.3	2.5	99.4
4.3	896	0.1	0.2	93.0	3.8	2.9	99.5
6.9	530	0.1	0.3	90.9	4.2	4.5	98.9
10.3	490	0.2	0.3	89.5	4.2	5.8	99.3
13.4	570	0.5	0.3	86.5	4.9	7.8	98.0

Conditions: the loading of the chromium complex is 9×10^{-5} mmol (the concentration in the solution is 3.6×10^{-6} mol/L), total volume of the solvent is 25.0 mL, activators are TMA (a 1.0 M solution in methylcyclohexane) and MAO (a 0.085 M solution in toluene), molar ratio [Cr] : TMA : MAO is 1 : 1100 : 300, temperature is 90°C, pressure is 40 bar, and experiment duration is 0.5 h.

ear alpha-olefins and linear alkanes according to the statistical Flory–Schulz distribution.

With the progress of the trimerization process, the qualitative composition of the reaction solution changes, in particular, the concentration of 1-hexene increases from 0 to 14 wt %. The influence of the concentration of 1-hexene on the parameters of the ethylene trimerization process was studied by partial replacing of the solvent by 1-hexene. The composition of the reaction mixture at different reaction times was modeled in this way. The results of the experiments are presented in Table 6.

The obtained data give the evidence that the productivity of the trimerization process decreases with an increase in the concentration of 1-hexene in the solvent. The reason for this fact is the drop in activity of the catalytic system for ethylene trimerization to 1-hexene because of the concurrent equilibrium processes of coordination of ethylene and 1-hexene to the metal atom. The 1-hexene molecule has a higher electron-donating power in comparison with the ethylene molecule and is capable of forming a stronger bond with the chromium atom, as a result of which increasing the concentration of the α-olefin promotes the blocking of the active sites of the catalytic. The productivity of the process of ethylene trimerization to 1-hexene is maximum in the initial period of the reaction time, when the concentration of α-olefins in the reaction mixture is minimal. With an increase in the concentration of the product olefins, mainly 1-hexene, the performance of the catalytic system decreases together with the productivity of the process and the process becomes less selective for the target product.

Thus introducing an *ortho*-substituent into the diphosphine ligand of the chromium complex of the catalytic system for ethylene oligomerization can result in not only increasing the 1-hexene selectivity of the process above 90% but can also significantly raise the productivity. Furthermore, the activation of chromium complex **13** containing the 2-methylprop-1-enyl group leads to the formation of a highly selective catalytic system for ethylene trimerization, which

demonstrates the productivity above 2800 kg · g_{Cr}^{-1} · h^{-1} (145600 kg · (of olefins) · mol_{Cr}^{-1} · h^{-1}), which exceeding several times the productivity of the so far most active Chevron Phillips ethylene trimerization catalytic system based on a chromium complex with a *N*-phosphinoamidine ligand (54670 kg · (of olefins) · mol_{Cr}^{-1} · h^{-1}) [12].

Summarizing the obtained results, the following conclusions can be drawn. A series of new chromium complexes with diphosphine ligands containing alkenyl substitutes was synthesized and characterized. A new procedure involving chromium(III) chloride hexahydrate as a reactant was used for the synthesis. The obtained complexes can be the basis for catalytic systems for selective ethylene trimerization to 1-hexene, making it possible to carry out the ethylene trimerization process with selectivity above 90%. For these systems, the optimum conditions of the ethylene trimerization process were revealed, namely, a temperature of 60–90°C and a pressure of 40 bar. The influence of the solvent nature and 1-hexene concentration in the reaction medium on the parameters of the selective ethylene oligomerization process was studied. It was shown that the activity and selectivity for 1-hexene of the tested catalytic systems for ethylene trimerization based on diphosphine chromium complexes can be targetedly adjusted by varying the substituents at the double bond of the alkenyl moiety. This approach can be utilized for the effective selection and design of new catalysts, based on metal complexes with polydentate ligands, for the selective production of alpha-olefins. In this study, the use of a chromium complex containing the 2-methylprop-1-enyl *ortho*-substituent to the phosphorus atom linked with the phenyl radical of the diphosphine ligand in the catalytic system for ethylene trimerization turned out to be the most effective. With the catalyst of this specific structure, it turned out to be possible to simultaneously solve several problems, namely, to achieve high selectivity of the process, the highest productivity, and a minimal yield of the polymer.

EXPERIMENTAL

Methods and Instruments

All the works on the synthesis of compounds and preparation of catalytic systems were carried out in an inert atmosphere using standard Schlenk technique. Ethylene (Linde Gas, 99.9 vol %) which was passed through three successively connected columns packed with activated charcoal and zeolites (3A and 13X) and high-purity argon (Moscow Gas Processing Plant, 99.998 vol %) were used in the study. Argon was additionally purified by passing through three successively connected columns packed with zeolites 3A and 13X and CuO (reduced to Cu), respectively, and a finishing Entegris gas purifier CE35KF. This operation ensured the residual concentration of oxygen, water, CO, and other impurities at the level of 1 ppb. The solvents were dehydrated by refluxing over appropriate dehydrating agents followed by distillation in an argon flow. Commercially available chemicals (with the purity above 97%) were used without additional purification except for chlorodiphenylphosphine (Aldrich 95%), which was distilled in a vacuum (bp 124–126°C/3 mm Hg). Methylaluminoxane (a 10% solution in toluene, Sigma-Aldrich) was analyzed prior to the experiments according to a procedure described in [13]. An *iso*-PrMgCl–LiCl solution was prepared according to the procedure described in [14]. *N*,*N*-Diethylaminophenylchlorophosphine $PhP(Cl)NEt_2$ was obtained according to the patent [15]. The chromium complexes and diphosphine ligands were synthesized according to procedures similar to those described in the patent [16]. 1,2-Bis(diphenylphosphino)benzene (**2**) used in the study was purchased from Sigma-Aldrich (purity of 97%). The reactants for the synthesis of diphosphine ligands **14** and **15**, 1-(1-pentenyl)-2-bromobenzene and 1-(2-phenylethenyl)-2-bromobenzene, were obtained in accordance with the modified method [17]. The reactant 1,2-didecylbenzene for the synthesis of ligand **16** was synthesized from 1,2-dichlorobenzene and decylbromide according to the published methods [18–20]. The syntheses of 1-bromo-2-diphenylphosphinobenzene and 1-bromo-2-diphenylphosphino-4,5-didecylbenzene were performed using the modified procedures [14, 21]. The syntheses of ((2-diphenylphosphino)phenyl)phenylphosphine chloride and (2-diphenylphosphino)-4,5-didecylphenyl(phenyl)phosphine chloride were performed according to the modified procedure [21]. The purity of the obtained compounds was determined using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry.

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AM-300 and Bruker Avance-400 instruments using tetramethylsilane as the internal standard and 85% H_3PO_4 as the external standard, respectively. The mass spectra were recorded on an Agilent Technologies 6890, Network Mass Selective Detector 5973 instrument. The elemental analysis was performed at the Analytical Laboratory of the LLC "RN-RD Centre."

General Procedure for Testing catalytic Systems in Ethylene Oligomerization Process

The general testing procedure as well as analysis procedure of the liquid phase of the reaction mixture containing the products of ethylene trimerization are presented in [5].

The overall scheme of the synthesis of the diphosphine ligands and chromium complexes:

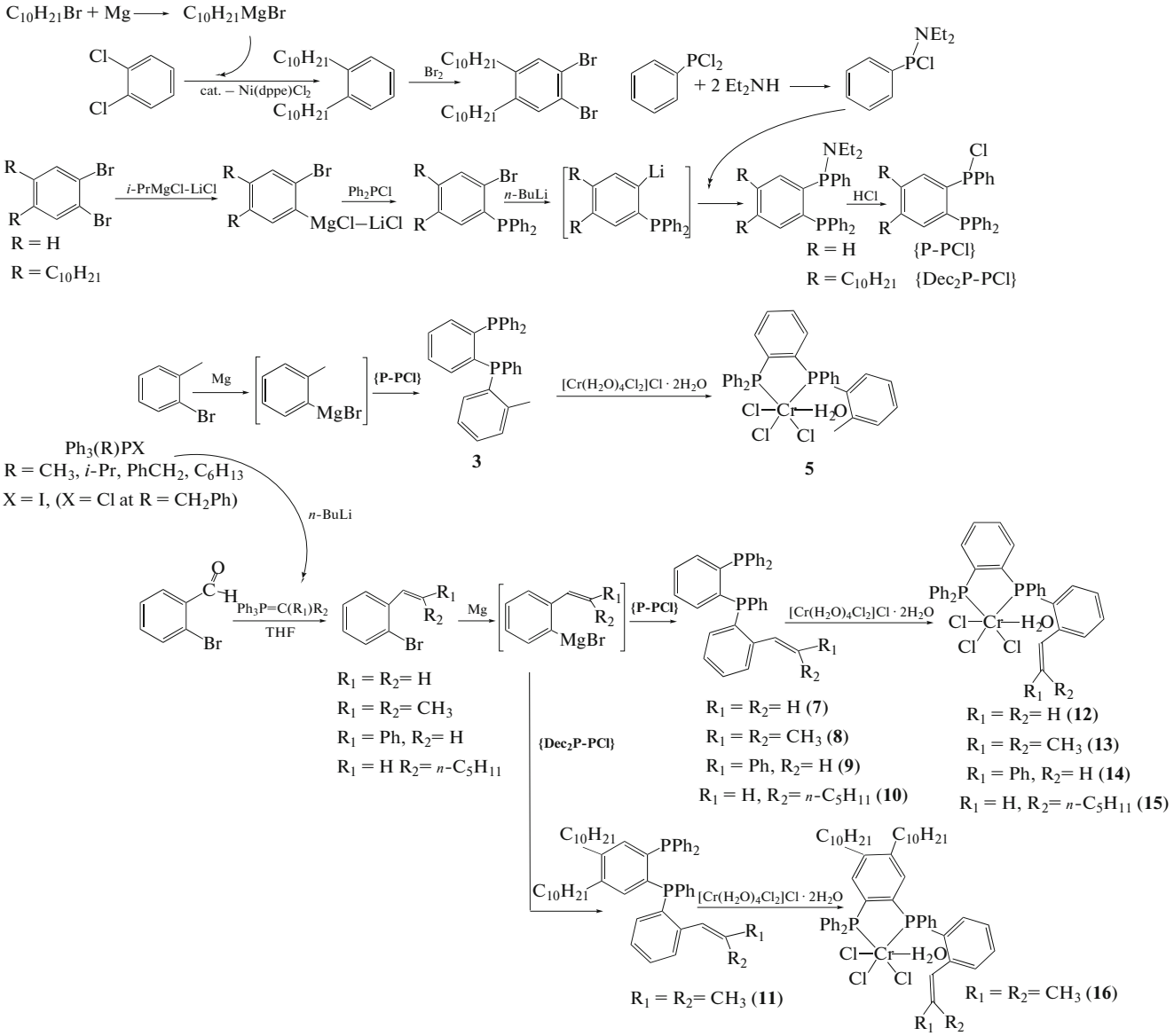

Fig. 6. General scheme of synthesis of ligands and chromium complexes.

Syntheses of Compounds

Synthesis of 1,2-didecylbenzene. 80 mL of a freshly prepared 2.4 M solution of decylmagnesium bromide (2.3-fold molar excess) was added dropwise to a suspension of 0.3 g (0.49 mmol) of $Ni(dppe)Cl_2$ in a solution of 9.4 mL (83 mmol) of 1,2-dichlorobenzene in 50 mL of diethyl ether cooled to −5°C in an argon stream. Then the reaction mixture was heated to reflux upon stirring, and an ample white precipitate was formed. The mixture was refluxed for 3 h, then cooled down to 0°C followed by addition of 50 mL of a 1 M hydrochloric acid solution, and fractionated. The organic phase was separated, dried over anhydrous sodium sulfate, and evaporated. The distillation residue was purified on a column with silica gel (Acros, 60−200 μm, the eluent was diethyl ether). After evaporation, 28 g of a colorless oily liquid was obtained. Yield 94%. ^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.17 (m, 2H, Ar–H), 7.13 (m, 2H, Ar–H), 2.82 (t, 4H, CH_2), 1.71 (m, 4H, CH_2), 1.37 (m, 28H, CH_2), 0.99 (m, 6H, CH_3).

Synthesis of 1,2-dibromo-4,5-didecylbenzene. 1,2-Didecylbenzene (20.3 g, 56.8 mmol) was placed into a Schlenk flask and 150 mL of distilled dichloromethane and 0.754 g (2.8 mmol) of crystalline iodine were added. The obtained solution was cooled down to −2°C, and 20.1 g (125.9 mmol) of bromine was added to it dropwise with stirring and maintaining the preset temperature. After the addition of the whole amount of bromine, the mixture was allowed to warm up to

room temperature, and stirring was continued for 20 h. A solution of sodium hydrosulfite was added to the obtained solution, stirred, and the mixture was allowed to settle until gas evolution ceased. The yellow-brown organic phase was separated and washed with water and a sodium chloride solution. The organic phase was dried over anhydrous sodium sulfate and evaporated. The liquid residue was chromatographed on a column with silica gel (Acros, 60–200 μm, hexane as the eluent). The yield of 1,2-dibromo-4,5-didecylbenzene was 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.25 (s, 2H), 2.63 (t, J = 7 Hz, 4H), 1.58 (br. t, 4H), 1.40–1.10 (a set of m, 28H), 0.92 (t, J = 6 Hz, 6H).

Synthesis of 1-bromo-2-diphenylphosphinobenzene and 1-bromo-2-diphenylphosphino-4,5-didecylbenzene. A solution of 5.38 g (22.8 mmol) of 1,2-dibromobenzene in 12 mL of tetrahydrofuran was added to 30 mL of a preliminarily prepared 1 M *iso*-PrMgLiCl solution in tetrahydrofuran and stirred at −17 to −13°C. After 3 h, 5.12 g (23.25 mmol) of chlorodiphenylphosphine was added dropwise to the solution at −20 to −10°C. The resulting solution was stirred for 30 min at −10°C, allowed to warm up to room temperature, stirred for additional 16 h, and evaporated. To the residue, 30 mL of dichloromethane and 20 mL of a saturated aqueous solution of ammonium chloride were added. The organic phase was separated and dried over anhydrous sodium sulfate. The residue after the evaporation was recrystallized from an ethanol–acetone mixture.

The yield of 1-bromo-2-diphenylphosphinobenzene was 65.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.60 (m, J = 4 Hz, 1H), 7.41–7.26 (m, J = 3 Hz, 10H), 7.20 (m, J = 4 Hz, 2H), 6.75 (q, J = 4 Hz, 1H). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ (ppm) −5.12 (s).

1,2-Dibromo-4,5-didecylbenzene was used for the synthesis of 1-bromo-2-diphenylphosphino-4,5-didecylbenzene instead of 1,2-dibromobenzene. The yield of 1-bromo-2-diphenylphosphino-4,5-didecylbenzene was 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45–7.25 (a set of m, 11H), 6.50 (s, 1H), 2.57 (t, J = 7 Hz, 2H), 2.40 (t, J = 7 Hz, 2H), 1.58 (br. t, 2H), 1.40–1.10 (a set of m, 30H), 0.92 (t, J = 6 Hz, 6H). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): δ (ppm) −6.02 (s).

Synthesis of ((2-diphenylphosphino)phenyl)phenylphosphine chloride {P–PCl} and (2-diphenylphosphino)-4,5-didecylphenyl(phenyl)phosphine chloride {Dec_2P–PCl}. 1.15 mL of a 1.6 M *n*-BuLi solution in hexane was slowly added to a solution of 0.6 g (1.76 mmol) of 1-bromo-2-diphenylphosphinobenzene in 8 mL of absolute tetrahydrofuran at −78°C. The solution turned bright orange. The reaction mixture was stirred for 2.5 h at −65°C, and then a solution of 0.38 g of diethylaminophenylchlorophosphine in 1.5 mL of absolute tetrahydrofuran was slowly added at this temperature. The mixture was allowed to warm up to room temperature with stirring. The mixture was stirred at this temperature for additional 18 h, the solvent was evaporated, and the residue was dissolved in 4 mL of toluene and filtered. Then dry HCl (HCl was obtained by the slow dropwise addition of concentrated sulfuric acid to ammonium chloride upon stirring; hydrogen chloride was dried by passing the formed gas through a column with P_2O_5) was bubbled through the obtained red filtrate for 3 h. Immediate formation of a white precipitate of diethylammonium hydrochloride and a change in the color of the solution to pale yellow were observed. The mixture was stirred for 18 h in an argon atmosphere. The pale yellow solution was filtered from the white precipitate under argon, and the solvent was evaporated. The residue (yellow oil) was dried in a vacuum.

The yield of ((2-diphenylphosphino)phenyl)phenylphosphine chloride {P–PCl} was 87%. ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): δ (ppm) 73.40 (d, $^3J_{PP}$ = 282 Hz, P(Ph)Cl), −19.60 (d, $^3J_{PP}$ = 282 Hz, PPh_2).

1-Bromo-2-diphenylphosphino-4,5-didecylbenzene was used for the synthesis of (2-diphenylphosphino)-4,5-didecylphenyl(phenyl)phosphine chloride **{Dec_2P-PCl}** instead of 1-bromo-2-diphenylphosphinobenzene. The yield of (2-diphenylphosphino)-4,5-didecylphenyl(phenyl)phosphine chloride **{Dec_2P-PCl}** was 74%. ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ (ppm) 74.8 (d, $^3J_{PP}$ = 275 Hz, P(Ph)Cl), −20.1 (d, $^3J_{PP}$ = 275 Hz, PPh_2).

Synthesis of [(2-diphenylphosphino)phenyl][2-(methyl)phenyl]phenylphosphine (3). 0.05 g (2 mmol) of magnesium was placed into a 50-mL Schlenk flask, calcined in a vacuum, and purged with argon. To the flask, 7 mL of absolute tetrahydrofuran and a catalytic amount of iodine were added. A solution of 0.30 g (1.75 mmol) of 2-bromotoluene in 10 mL of tetrahydrofuran was separately prepared, and several drops of the prepared solution were added to the reaction flask. The mixture was heated to reflux without stirring, the solution gradually became colorless, and the remaining solution of 2-bromotoluene was slowly added to the refluxing mixture. Additional 10 mL of tetrahydrofuran was added. The solution was refluxed with stirring for 3 h. The prepared solution of the Grignard reagent was decanted in an argon flow and cooled down to −30°C, and a solution of 0.59 g (1.47 mmol) of [(2-diphenylphosphino)phenyl]phenylphosphine chloride {P–PCl} in 4 mL of tetrahydrofuran was added to it dropwise. The temperature rose to −15°C. The cooling was removed, and the reaction mixture was allowed to warm up to room temperature and then stirred at this temperature for 24 h. The solvent was evaporated, the reaction mixture was quenched with a saturated aqueous solution of ammonium chloride (10 mL), 10 mL of dichloromethane was added, the

organic phase was separated (the aqueous phase was extracted with CH_2Cl_2), the combined organic phase was dried over sodium sulfate, and the solvent was evaporated. The residue was washed with anhydrous methyl alcohol several times, and a colorless crystalline substance was obtained, which was dried under high vacuum. Yield 0.59 g (87%). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) −14.0 (d, $^3J_{PP}$ = 160 Hz, 1P), −21.0 (d, $^3J_{PP}$ = 160 Hz, 1P). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82–7.52 (m, 20H, Ar–H), 7.50–7.40 (m, 2H, Ar–H), 7.15–7.20 (m, 1H, Ar–H), 2.72 (s, 3H, CH_3–Ar).

Synthesis of 2-bromostyrene. Methyltriphenylphosphonium bromide (19.1 g, 53.5 mmol) was placed into a Schlenk flask, and 150 mL of absolute tetrahydrofuran was added. The obtained suspension was cooled to 0°C, and 33.4 mL (53.5 mmol) of a 1.6 M *n*-BuLi solution in hexane was slowly added. The yellow-orange mixture was stirred at 0°C for 40 min, and then a solution of 9 g (48.61 mmol) of 2-bromobenzaldehyde was slowly added to the mixture at this temperature. A white-yellow viscous, difficult-to-stir precipitate was formed. The mixture was stirred at room temperature for 16 h, then 100 mL of an aqueous solution of NaCl was added, and it was twice extracted with ethyl acetate; the combined organic phases were repeatedly washed with a solution of NaCl, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over magnesium sulfate, and the solvent was evaporated. The solid yellow residue was applied onto a column with silica gel (Acros, 60–200 μm), the colorless first fraction was eluted with a 9 : 1 hexane–ethyl acetate solvent blend, and the solvent was evaporated. 2-Bromostyrene was obtained as a yellowish liquid (it is light-sensitive and should be stored upon cooling). Yield 7.64 g (86%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (m, 2H, Ar–H), 7.33–7.29 (m, 1H, Ar–H), 7.17–7.07 (m, 2H, Ar–H, C<u>H</u>=CH_2), 5.74 (dd, 1H, J_{HH} = 17 Hz, J_{HH} = 1 Hz, CH=C<u>H</u>$_A$H$_B$), 5.41 (dd, 1H, J_{HH} = 11 Hz, J_{HH} = 1 Hz, CH=CH$_A$<u>H</u>$_B$).

Synthesis of isopropyltriphenylphosphonium iodide. A solution of 26.20 g (100 mmol) of triphenylphosphine and 42.70 g (250 mmol) of isopropyl iodide in 50 mL of toluene was refluxed for 18 h. The white precipitate formed was filtered off, washed with toluene, and dried in a vacuum. Yield 18.14 g (42%); mp 195–196°C.

Synthesis of hexyltriphenylphosphonium iodide. A mixture of 5.12 g (19.55 mmol) of triphenylphosphine (PPh_3), 2.81 mL (19.55 mmol) of *n*-hexyl iodide, and 60 mL of toluene was heated to reflux with stirring under argon for 2.5 h. Then the reaction mixture was cooled to room temperature, and stirring was continued for 16 h. The precipitate formed was washed with toluene (2 × 30 mL) and dried in a vacuum. Yield 3.04 g (33%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (m, 6H, Ar–H), 7.73 (m, 6H, Ar–H), 7.18 (m, 3H, CH_2), 3.67 (m, 2H, CH_2), 1.68 (m, 4H, CH_2), 1.26 (m, 4H, CH_2), 0.84 (t, 3H, J = 7 Hz, CH_3). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) 24.3 (s).

Synthesis of 1-bromo-2-(2-methyl-1-propenyl)benzene. Isopropyltriphenylphosphonium iodide (18.1 g, 41.87 mmol) was placed into a Schlenk flask and 150 mL of absolute tetrahydrofuran was added. The obtained suspension was cooled to 0°C, and 26.2 mL (41.87 mmol) of a 1.6 M *n*-BuLi solution in hexane was slowly added to it. The obtained mixture was stirred at 0°C for 1 h, and then a solution of 7.04 g (38.06 mmol) of 2-bromobenzaldehyde was slowly added to the resulting red-brown solution at this temperature. The reaction mixture turned orange. The mixture was stirred at room temperature for 16 h, 100 mL of an aqueous solution of NaCl was added, and it was twice extracted with ethyl acetate; the combined organic phases were repeatedly washed with a solution of NaCl, and the aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over magnesium sulfate, and the solvent was evaporated. The solid yellow residue was applied onto a column with silica gel (Acros, 60–200 μm), the colorless first fraction was eluted with hexane, and the solvent was evaporated. 1-Bromo-2-(2-methyl-1-propenyl)benzene was obtained as a clear colorless liquid. Yield 7.1 g (88.5%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53–6.45 (m, 5H, Ar–H, C<u>H</u>=$C(CH_3)_2$), 1.77 (s, 3H, CH=C(C<u>H</u>$_3$)$_2$), 1.60 (s, 3H, CH=C(C<u>H</u>$_3$)$_2$).

Synthesis of 2-bromostilbene. Benzyltriphenylphosphonium chloride (1.67 g, 4.29 mmol) was placed into a Schlenk flask, and 50 mL of absolute tetrahydrofuran was added. The obtained suspension was cooled to 0°C, and 4.29 mmol of a 1.6 M *n*-BuLi solution in hexane was slowly added to it. The red-brown mixture was stirred at 0°C for 1 h, and then a solution of 0.72 g (3.90 mmol) of 2-bromobenzaldehyde was slowly added to the mixture at this temperature. The mixture was stirred at room temperature for 24 h, 50 mL of an aqueous solution of NaCl was added, and it was twice extracted with ethyl acetate; the combined organic phases were repeatedly washed with a solution of NaCl, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over magnesium sulfate, and the solvent was evaporated. The yellow solid residue was applied onto a column with silica gel (Acros, 60–200 μm), the colorless first fraction was eluted with hexane, and the solvent was evaporated. 2-Bromostilbene was obtained as a viscous colorless liquid (a mixture of *cis*- and *trans*-isomers). Yield 0.85 g (84%). Mass spectrum: m/z = 258 [M^+] (74%), 258 [M^+] (26%).

Synthesis of 1-bromo-2-(hept-1-enyl)benzene (a mixture of isomers). Hexyltriphenylphosphonium

iodide (3.04 g, 6.41 mmol) was dissolved in 50 mL of tetrahydrofuran in an argon flow, and 4 mL of a 1.6M solution of *n*-BuLi in hexane was added dropwise to the obtained solution cooled down to −5°C. After the addition of all the solution of *n*-BuLi, the resulting mixture was stirred for 1 h, and then a solution of 0.68 mL (5.83 mmol) of 2-bromobenzaldehyde in 10 mL of tetrahydrofuran was added dropwise. The temperature of the reaction mixture was maintained at −2 to +2°C. The solution turned orange, and a white precipitate was formed. The mixture was warmed up to room temperature, and stirred for 3 h; then, 30 mL of a saturated solution of NaCl 30 mL of ethyl acetate were successively added. The phases were separated, and the bottom aqueous layer was twice extracted with 30 mL of ethyl acetate. The combined organic phases were dried over anhydrous sodium sulfate and evaporated. The residue after evaporation was purified by column chromatography (silica gel (Acros), 60–200 μm, hexane as the eluent). Yield 1.4 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of E- and Z-isomers at a molar ratio of 1 : 2.5): δ (ppm) 7.61 (d, J = 7 Hz, 2.5H, Ar–H), 7.56 (d, J = 7 Hz, 1H, Ar–H), 7.36–7.23 (a set of m, 7H, Ar–H), 7.18–7.04 (a set of m, 3.5H, Ar–H), 6.75 (br. dt, J = 16 Hz, 1H, CH=CH), 6.49 (br. dt, J = 12 Hz, 2.5H, CH=CH), 6.21 (dt, J = 7 Hz, 1H, CH=CH), 5.81 (dt, J = 7 Hz, 2.5H, CH=CH), 2.29 (dq, J = 7 Hz, J = 1.5 Hz, 2H, =CH–CH_2), 2.21 (dq, J = 7 Hz, J = 1.5 Hz, 5H, =CH–CH_2), 1.59–1.24 (a set of m, 21H, CH_2), 0.95 (t, J = 7 Hz, 3H, CH_3), 0.91 (t, J = 7 Hz, 7.5H, CH_3).

General procedure for the synthesis of diphosphine ligands 7–11 exemplified by the synthesis of [(2-diphenylphosphino)phenyl][2-(vinyl)phenyl]phenylphosphine (7). Magnesium in amount of 0.28 g (11.54 mmol) was placed into a 100-mL Schlenk flask, calcined in a vacuum, and purged with argon, and 50 mL of absolute tetrahydrofuran and a catalytic amount of iodine were added. A solution of 1.92 g (10.49 mmol) of 2-bromostyrene in 20 mL of tetrahydrofuran was separately prepared, and several drops of the prepared solution were added to the reaction flask. The mixture was heated to reflux without stirring, the solution gradually became colorless, and the remaining solution of 2-bromostyrene was slowly added to the refluxing mixture. The solution turned brown-yellow. The solution was refluxed with stirring for 4 h. The mixture was cooled to room temperature. An additional amount of tetrahydrofuran was added to dilute the resulting thick brown solution. The prepared solution of the Grignard reagent was filtered in an argon flow. The solution was cooled to −30°C, and a solution of 2.97 g (7.34 mmol) of [(2-diphenylphosphino)phenyl]phenylphosphine chloride **{P–PCl}** in 20 mL of tetrahydrofuran was added to it dropwise. The temperature rose to −15°C. The cooling was removed, and the reaction mixture was allowed to warm up to room temperature, after which the mixture was stirred at this temperature for one day. The solvent was evaporated, the reaction mixture was quenched with a saturated aqueous solution of ammonium chloride (30 mL), 50 mL of dichloromethane was added, the organic layer was separated (the aqueous phase was extracted with CH_2Cl_2), the combined organic phase was dried over sodium sulfate, and the solvent was evaporated. The pale yellow solid was dissolved in CH_2Cl_2, 5 mL of hexane was added, and a white finely dispersed precipitate was formed. The solution was filtered from the precipitate through a Schlenk filter tube in an argon flow, the solvent was evaporated, and a pale yellow crystalline substance was obtained after drying under high vacuum.

The yield of [(2-diphenylphosphino)phenyl][2-(vinyl)phenyl]phenylphosphine (**7**) was 92%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) −13.7 (d, $^3J_{PP}$ = 160 Hz, P($C_6H_4CH=CH_2$)Ph), −21.2 (d, $^3J_{PP}$ = 160 Hz, PPh_2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 6.76–7.62 (m, 24H, CH=CH_2, Ar–H), 5.54 (dt, 1H, J_{HH} = 17 Hz, J_{HH} = 1 Hz, CH=CH_AH_B), 5.08 (dd, 1H, J_{HH} = 12 Hz, J_{HH} = 1 Hz, CH=CH_AH_B).

1-Bromo-2-(2-methyl-1-propenyl)benzene was used for the synthesis of [(2-diphenylphosphino)phenyl][2-(2-methyl-1-propenyl)phenyl]phenylphosphine instead of 2-bromostyrene. The yield of [(2-diphenylphosphino)phenyl][2-(2-methyl-1-propenyl)phenyl]phenylphosphine (**8**) was 91%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) −14.4 (d, $^3J_{PP}$ = 159 Hz, P($C_6H_4CH=C(CH_3)_2$)Ph), −19.7 (d, $^3J_{PP}$ = 159 Hz, PPh_2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ (ppm) 7.14–7.03 (m, 23H, Ar–H), 6.68 (m, 1H, CH=$C(CH_3)_2$), 1.55 (s, 3H, CH=C(CH_3)$_2$), 1.38 (s, 3H, CH=C(CH_3)$_2$).

2-Bromostilbene was used for the synthesis of [(2-diphenylphosphino)phenyl][2-(2-phenyl-1-ethenyl)phenyl]phenylphosphine instead of 2-bromostyrene. The yield of [(2-diphenylphosphino)phenyl][2-(2-phenyl-1-ethenyl)phenyl]phenylphosphine (**9**) was 96%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) (a mixture of isomers of 1 : 0.7) −13.8 (d, $^3J_{PP}$ = 160 Hz, 1P, P($C_6H_4CH=CH_2$)Ph), −14.9 (d, $^3J_{PP}$ = 157 Hz, 0.7P, P($C_6H_4CH=CH_2$)Ph); −20.4 (d, $^3J_{PP}$ = 160 Hz, 1P, PPh_2), −21.3 (d, $^3J_{PP}$ = 157 Hz, 0.7P, PPh_2).

1-Bromo-2-(hept-1-enyl)benzene was used for the synthesis of [(2-diphenylphosphino)phenyl][2-(2-*n*-pentyl-1-ethenyl)phenyl]phenylphosphine instead of 2-bromostyrene. The yield of [(2-diphenylphosphino)phenyl][2-(2-*n*-pentyl-1-ethenyl)phenyl]phenylphosphine (**10**) was 82%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) (a mixture of isomers of 1 : 2.5 (*cis*- and *trans*-isomers)) −13.8 (d, $^3J_{PP}$ = 160 Hz, 2.5P, P($C_5H_{11}CH=CH_2$)Ph), −14.2 (d, $^3J_{PP}$ = 158.5 Hz, 1P, P($C_5H_{11}CH=CH_2$)Ph), −20.4 (d, $^3J_{PP}$ = 158.5 Hz, 1P, PPh_2), −20.5 (d, $^3J_{PP}$ = 160 Hz, 2.5P, PPh_2).

Table 7. Crystallographic data and structure refinement parameters for compounds **4**, **12**, and **13**

	4	**12**	**13**
Formula	$C_{32}H_{28}Cl_9CrOP_2$	$C_{32}H_{28}Cl_3CrOP_2 \cdot 0.25H_2O \cdot 0.75C_6H_{14} \cdot 0.875CH_2Cl_2$	$(C_{34}H_{32}Cl_3CrOP_2) \cdot (CH_2Cl_2)$
Molecular weight	861.53	792.28	761.81
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1
a, Å	13.6686(15)	13.7866(5)	10.0845(6)
b, Å	18.223(2)	15.9078(5)	14.1067(9)
c, Å	15.3665(17)	17.5486(6)	14.9376(13)
α, deg	90	86.7050(10)	61.9000(10)
β, deg	108.397(2)	80.5430(10)	75.668(2)
γ, deg	90	70.0670(10)	78.9410(10)
V, Å^3	3631.8(7)	3568.9(2)	1482.0(4)
Z	4	4	2
ρ_{calc}, g cm^{-3}	1.576	1.475	1.398
F(000)	1740	1639	782
μ, mm^{-1}	1.093	0.798	0.801
Range of θ scanning, deg	1.57–26.00	1.36–26.00	1.50–30.03
Number of measured reflections	33828	13878	23040
Number of independent reflections	7125	13878	10521
θ completeness, %	100.0	99.0	99.5
Number of refined parameters	414	703	402
GOF (F^2)	0.877	1.071	1.023
Number of reflections with $I > 2\sigma(I)$	4221	10976	7170
$R_1(F)$ ($I > 2\sigma(I)$)[a]	0.0633	0.0427	0.0498
$wR_2(F^2)$ (for all the reflections)[b]	0.1640	0.1272	0.1362
Residual electron density, e Å^{-3}	1.019/–0.705	0.872/–0.383	0.963/–1.027

[a] $R_1 = \sum||F_o| - |F_c||/\sum(F_o)$;

[b] $wR_2 = \left(\sum\left[w\left(F_o^2 - F_c^2\right)^2\right]\Big/\sum\left[w\left(F_o^2\right)^2\right]\right)^{1/2}$.

1-Bromo-2-(2-methyl-1-propenyl)benzene and (2-diphenylphosphino)-4,5-didecylphenyl(phenyl)phosphine chloride **{Dec$_2$P–PCl}** were used for the synthesis of [(2-diphenylphosphino)-4,5-didecylphenyl][2-(2-methyl-1-propenyl)-phenyl]phenylphosphine instead of 2-bromostyrene and [(2-diphenylphosphino)phenyl]phenylphosphine chloride **{P–PCl}**, respectively. The yield of [(2-diphenylphosphino)-4,5-didecylphenyl][2-(2-methyl-1-propenyl)-phenyl]phenylphosphine (**11**) was 94%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) –13.8 (d, $^3J_{PP}$ = 156 Hz, 1P), –19.4 (d, $^3J_{PP}$ = 156 Hz, 1P).

General procedure for the synthesis of chromium(III) diphosphine complexes 4, 5, and 12–16. Chromium(III) chloride hexahydrate ($[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$) was added to a suspension of a diphosphine (**2**, **3**, and **7**–**11**) in acetone (the suspension was prepared using 18 mL of acetone per 1 g of the diphosphine) in a 20% molar excess relative to the diphosphine. The reaction mixture immediately took a green color to become pale blue after 1.5 h of stirring. The mixture was stirred at room temperature for 24 h. Upon the completion of stirring, the blue crystalline precipitate formed in the solution was filtered off through a Schlenk filter tube in an argon flow, thoroughly washed with acetone and hexane, and dried under high vacuum.

The yield of ([2-(diphenylphosphino)phenyl]diphenylphosphine-P,P)-(aqua)-trichlorochromium(III) (**4**) was 95%. Found, %: C 59.06; H 4.60. Calculated for $C_{30}H_{26}Cl_3CrOP_2$, %: C 57.85; H 4.21.

The yield of ([(2-diphenylphosphino)phenyl][2-(methyl)phenyl]phenylphosphine-P,P)-(aqua)-trichlorochromium(III) (**5**) was 96%. Found, %: C 59.45; H 4.65. Calculated for $C_{31}H_{28}Cl_3CrOP_2$, %: C 58.46; H 4.43.

The yield of ([(2-diphenylphosphino)phenyl][2-(vinyl)phenyl]phenylphosphine-P,P)-(aqua)-trichlorochromium(III) (**12**) was 90%. Found, %: C 56.42; H 5.06. Calculated for $C_{32}H_{28}Cl_3CrOP_2 \cdot H_2O$, %: C 56.12; H 4.71.

The yield of ([(2-diphenylphosphino)phenyl][2-(2-methyl-1-propenyl)phenyl]phenylphosphine-P,P)-(aqua)-trichlorochromium(III) (**13**) was 87%. Found, %: C 59.03; H 5.08. Calculated for $C_{34}H_{32}Cl_3CrOP_2$, %: C 58.76; H 4.89.

The yield of ([(2-diphenylphosphino)phenyl][2-(2-phenyl-1-ethenyl)phenyl]phenylphosphine-P,P)-(aqua)-trichlorochromium(III) (mixture of isomers) (**14**) was 75%. Found, %: C 64.12; H 4.75. Calculated for $C_{38}H_{32}Cl_3CrOP_2$, %: C 62.96; H 4.44.

The yield of ([(2-diphenylphosphino)phenyl][2-(2-*n*-pentyl-1-ethenyl)phenyl]phenylphosphine-P,P)-(aqua)-trichlorochromium(III) (mixture of isomers) (**15**) was 73%. Found, %: C 62.25; H 5.75. Calculated for $C_{37}H_{38}Cl_3CrOP_2$, %: C 62.33; H 5.37.

The yield of ([(2-diphenylphosphino)-4,5-didecylphenyl][2-(2-methyl-1-propenyl)phenyl]phenylphosphine-P,P)-(aqua)-trichlorochromium(III) (**16**) was 83%. Found, %: C 69.95; H 5.55. Calculated for $C_{54}H_{50}Cl_3CrOP_2$, %: C 69.20; H 5.38.

X-Ray Structure Study of Compounds 4, 12, and 13

Single crystals of compounds **4**, **12**, and **13** for the X-ray structure study were obtained from the solutions of the respective compounds in a dichloromethane–hexane mixture. The crystallographic data and main refinement parameters for the compounds are presented in Table 7. The experimental procedure of the X-ray structure study is presented in [5].

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CONFLICT OF INTEREST

The authors declare no conflict of interest to be disclosed in this paper.

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