

5 **LIGAND BASED CHROMIUM CATALYST AND**
 APPLICATION IN CATALYZING ETHYLENE OLIGOMERIZATION

Cross Reference to Related Application

10 The present application claims priority of Chinese patent application CN 201510674794.4, filed on October 19, 2015, the entirety of which is incorporated herein by reference.

Field of the Invention

15 The present disclosure relates to a ligand based chromium catalyst and its application in catalyzing ethylene oligomerization.

Background of the Invention

20 The selective oligomerization of ethylene provides a vital route to the production of specific linear alpha-olefins (LAO), and is an important technological research task in olefin polymerization and catalysis field. Among the linear alpha-olefins, 1-hexene and 1-octene have become important comonomer for production of linear low density
25 polyolefin (LLDPE). Compared with polyethylene, multiple performances of the polyolefin products, which are produced with 1-hexene and 1-octene as the comonomer, can be significantly improved, such as mechanical performance, optical performance, tearing resistance strength, and impact resistance strength. The polyolefin products can be used as film materials, and have a wide use and a large
30 demand in industrial production.

 In traditional ethylene oligomerization reaction, aluminum-based catalyst,

titanium-based catalyst, nickel-based catalyst, zirconium-based catalyst, iron-based catalyst, or cobalt-based catalyst are used. The reaction mainly follows the Cossee-Arlman mechanism. That is, ethylene proceeds with linear chain-growth in the presence of the metal catalyst, and then proceeds with chain-elimination by β -hydrogen migration, thereby generating linear alpha-olefins. During the reaction procedure, the chain-growth rate is slightly larger than or roughly equal to the chain-elimination rate. Therefore, the carbon chain grows within a certain limit, and the number of carbon atoms mainly ranges from 4 to 30, and the alpha-olefin products generated therein are in consistent with Schulz-Flory or Poisson distribution. The content of 1-hexene and 1-octene in the products is relatively low (J. Organomet. Chem. 2004, 689, 3641). US patent (3676523) discloses a Shell Higher Olefin Process (SHOP) for producing alpha-olefins using nickel-based catalyst, and the content of C₆ to C₁₀ olefins in the alpha-olefin products ranges from 21.0% to 52.0%. A oligomerization product under a catalytic effect of an iron-based catalyst is reported by Brookhart et al, wherein the content of C₆ and C₈ olefins ranges from 47% to 52% (J. Am. Chem. Soc., 1998, 120, 7143; US 6103946).

The selective oligomerization reaction of ethylene is a subsequently developed method, which has a very important application prospect and an important role in industrial synthesis of specific linear alpha-olefins. The production of 1-hexene through selective trimerization of ethylene is firstly discovered by Union Carbide Corporation (US 3300458). In 1999, the catalytic reaction for ethylene trimerization using a system of 2-ethylhexanoate chromium, 2,5-dimethylpyrrole, triethylaluminum, and diethylaluminum chloride in cyclohexane solvent under a temperature being 115 °C and a pressure being 100 bar is reported by Phillips. The reaction has a high selectivity, 1-hexene accounts for 93% of the products, and an activity of the catalyst reaches 1.56×10^5 g/(g Cr·h) (US 5856612). In 2002, the catalytic reaction for trimerization of ethylene using a system of chromium trichloride, PNP-ligand, and methylaluminoxane in toluene solvent under a temperature being 80 °C and a pressure being 20 bar is reported by British Petroleum (BP). The reaction also has a high selectivity, 1-hexene accounts almost for 90% of the products, and an activity of the catalyst reaches 1.03×10^6 g/(g Cr·h). Besides, the reaction condition is relatively mild

(Chem. Commun. 2002, 858; US 5856612). In 2004, based on the research of British Petroleum, the aryl substituent on the phosphorus atom of the PNP-ligand, i.e., the methoxyl is replaced to be H or alkyl group by researchers of Sasol limited, and the new ligand forms a system with chromium trichloride and methylaluminoxane. The catalytic reaction for ethylene tetramerization is then performed using the aforesaid system in toluene solvent under a temperature being 65 °C and a pressure being 30 bar or under a temperature being 45 °C and a pressure being 45 bar. 1-octene accounts for 70% of the products, and an activity of the catalyst ranges from 8.05×10^3 g/(g Cr·h) to 4.36×10^4 g/(g Cr·h). Then, various replacements of substituents on phosphorus atom and nitrogen atom are performed, and the catalytic results of selective tetramerization of ethylene obtained therein are similar to the above result (J. Am. Chem. Soc., 2004, 126, 14712; WO 056478).

The catalytic reaction mechanism of selective trimerization of ethylene is different from the Cossee-Arlman mechanism of linear chain growth. The catalytic reaction for selective trimerization of ethylene mainly follows a metal cyclization reaction mechanism. That is, ethylene molecules are trimerized in the presence of the metal catalyst to form a CrC_6 seven-membered ring intermediate compound, and then form hexane after intra-ring β -H migration and reduction elimination reaction. During selective tetramerization of ethylene, an ethylene molecule is inserted into the CrC_6 seven-membered ring intermediate so as to form a CrC_8 nine-membered ring intermediate compound, and then form octane after intra-ring β -H migration and reduction elimination reaction. The selective tetramerization of ethylene is relatively difficult, because the CrC_8 nine-membered ring intermediate has a poor structural stability compared with the CrC_6 seven-membered ring intermediate. However, the selective tetramerization of ethylene can be realized through electronic and steric structural regulation on the ligand around Cr of the catalyst, which is fully recognized by the researchers in the art. Nevertheless, related work is done very little.

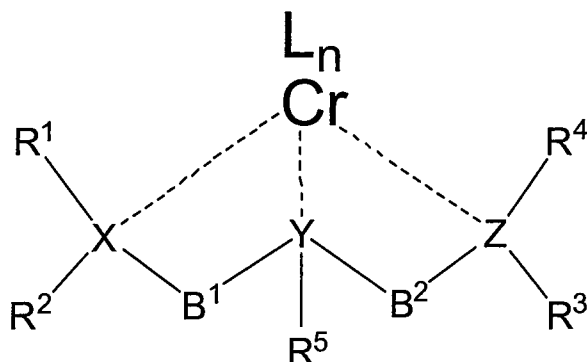
At present, the industrial directional production of 1-hexene is realized by selective trimerization of ethylene. For example, Phillips successfully built a 1-hexene production equipment in Qatar during 2003. The product of this equipment is single,

and the selectivity of 1-hexene reaches 90% or above. Besides, the production equipment has less by-products, a high catalytic activity, and a simple work flow. The 1-hexene production equipment through selective trimerization of ethylene in Daqing Petrochemical Company in China is already put into production, and the similar equipment in Yanshan Petrochemical Company in China is about to be put into production. The industrial production of 1-octene is about to be realized by selective tetramerization of ethylene, but there are still theoretical and technological difficulties in this respect.

10 Summary of the Invention

The first purpose of the present disclosure is to provide a ligand based chromium catalyst.

15 A general formula of the ligand based chromium catalyst is as follows:



wherein in above structure, X, Y, and Z represent one element of N and P respectively, R¹, R², R³, R⁴, and R⁵ represent one of H, linear or branched alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, substituted aryl and derivatives thereof respectively, B¹ and B² represent a structural system which can transmit an electronic induction or conjugative effect of a group respectively, and L_n represents a group which has a chemical bond with chromium; and

wherein when X and Y both are N element, and Z is P element, B¹ represents one methylene group or a plurality of methylene groups. It is discovered that, when B¹ is selected to be one methylene group or a plurality of methylene groups, the catalytic ability of the ligand of regulating chromium to form CrC₆ and/or CrC₈ cyclic transition

states and further form 1-hexene and/or 1-octene products can be significantly improved.

According to one preferred embodiment of the present disclosure, the chromium catalyst is formed by a chromium compound and an organic ligand containing P and/or N.

The chromium comes from a chromium inorganic compound or a chromium organic compound. The chromium inorganic compound is chromium dichloride or chromium trichloride. The chromium organic compound is one selected from a group consisting of chromium dichloride-tetrahydrofuran complex, chromium dichloride-toluene tetrahydrofuran complex, chromium trichloride-tetrahydrofuran (THF) complex, chromium dichloride-carbene complex, chromium trichloride-carbene complex, chromium acetylacetonate, chromium tris (2-ethylhexanoate), methyl chromium dichloride-tetrahydrofuran complex, triphenyl chromium-tetrahydrofuran complex, dimethyl chromium-carbene complex, diethyl chromium-carbene complex, diphenyl chromium-carbene complex, and carbonyl chromium.

The R^1 , R^2 , R^3 , R^4 , and R^5 groups, when being connected with nitrogen atom, are respectively one selected from a group consisting of H, C_1 - C_{10} linear or branched alkyl, heteroalkyl, or cycloalkyl, alkenyl, allyl, and substituted phenyl, preferably selected from a group consisting of H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, cyclobutyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, 2,6-dimethylcyclohexyl, adamantyl, vinyl, allyl, phenyl, naphthyl, 2-methylphenyl, 2,4,6-trimethylphenyl, 3,5-dimethylphenyl, 3,5-dimethoxyphenyl, 3,5-di-tert-butylphenyl, 2-thienyl, 2-furanyl, 2-pyridyl, and 3-pyridyl. The R^1 , R^2 , R^3 , R^4 , and R^5 groups, when being connected with phosphorus atom, are respectively one selected from a group consisting of C_1 - C_{10} linear or branched alkyl, substituted aryl, and derivatives thereof, preferably selected from a group consisting of methyl, ethyl, butyl, phenyl (which can be connected to be condensed nucleus compound), 2-methylphenyl, 4-methylphenyl, 3,5-dimethylphenyl, 2-methoxyphenyl, 4-methoxyphenyl, 3,5-dimethoxyphenyl, 4-tert-butylphenyl, 3,5-di-tert-butylphenyl,

2-nitrophenyl, 4-nitrophenyl, 4-cyanophenyl, 3,4-(methylenedioxy) phenyl, 4-benzoylphenyl, 4-ethoxycarbonylphenyl, 4-trifluoromethylphenyl, 1-naphthyl, 4,4'-biphenyl, 3,5-di(phenyl) phenyl, 2-thienyl, 2-furanyl, 2-pyridyl, and 3-pyridyl.

5 B^1 and B^2 represent a structural system which can transmit an electronic induction or conjugative effect of a group respectively. B^1 and B^2 can be the same as each other or different from each other. B^1 and B^2 are structural systems having two group bonds. B^1 and B^2 are respectively a double bond group containing 18 or less carbon atoms. In this manner, mutual electron transmission among atoms which has a ligand action with
10 the catalyst metal element can be realized more effectively, so that the catalyst system can be stabilized and the catalytic activity thereof can be improved. Preferably, B^1 represents one methylene group or a plurality of methylene groups.

When the catalyst is used in an oligomerization action, the organic ligand
15 containing P and/or N and the chromium compound can be mixed with each other in situ and used in the catalytic reaction, or a compound can be produced by the organic ligand containing P and/or N and the chromium compound through a chemical method and then used in the catalytic reaction.

20 The second purpose of the present disclosure is to provide an ethylene oligomerization method using the aforesaid catalyst.

The ethylene oligomerization method comprises performing ethylene oligomerization reaction in the presence of the catalyst according to the present
25 disclosure in an organic solvent.

The oligomerization comprises selective trimerization and tetramerization of ethylene so as to obtain 1-hexene and 1-octene.

30 Specifically, the method further comprises the step of mixing the ligand based chromium catalyst with a co-catalyst in an organic solvent medium, so that the mixture contacts with olefin and oligomerization reaction is performed.

According to one embodiment of the present disclosure, in the method, a reaction temperature ranges from 0 °C to 200 °C, an ethylene pressure ranges from 0.1 MPa to 20 MPa, a reaction time ranges from 0.01 h to 200 h, and a concentration of the catalyst ranges from 0.001 mmol/L to 1000 mmol/L.

According to one embodiment of the present disclosure, a ratio of the NP-ligand based chromium catalyst to the co-catalyst ranges from 1:10 to 1:4000, preferably ranges from 1:10 to 1:700.

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The co-catalyst is at least one selected from a group consisting of alkyl aluminum compound, aluminosilane compound, and organic boron compound, preferably is at least one selected from a group consisting of triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, methylaluminosilane, ethylaluminosilane, isobutylaluminosilane and modified aluminosilane, methylaluminosilane loaded on silica gel, alkylaluminum halide, tris (pentafluorophenyl) aluminum, tris (trifluoromethyl butanol) aluminum, triphenylmethyl-tetra (trifluoromethyl butanol) aluminum salts, tetrafluoroborate, ether tetrafluoroborate, epoxy borane, triethylborane, tris (pentafluorophenyl) borane, tetra (pentafluorophenyl) borate, tri-perfluoroaryl boranes, tetra-perfluoroaryl borate, tributyl borate, tetra (3,5-ditrifluoromethyl) phenyl borohydride salt, and tetra (3,5-ditrifluoromethyl) phenyl boron-sodium salts.

The organic solvent is at least one selected from a group consisting of toluene, xylene, n-butane, n-pentane, cyclopentane, methyl cyclopentane, n-hexane, n-heptane, cyclohexane, methylcyclohexane, tetrahydrofuran, dichloromethane, dichloroethane, ethyl ether, and isopropyl ether.

The third purpose of the present disclosure is to provide a usage of the ligand based chromium catalyst, and specifically, it serves as a catalyst in ethylene oligomerization reaction.

The ethylene oligomerization reaction comprises selective trimerization and tetramerization of ethylene.

With respect to the ligand based chromium catalyst according to the present disclosure, selective trimerization and tetramerization of ethylene can be realized by replacing the substituents on N, P, and the ligand so as to produce 1-hexene and 1-octene at the same time. The productivity of 1-hexene and 1-octene ranges from 81% to 87%. 1-hexene and 1-octene can be separated from each other through a rectification method.

Brief Description of the Drawings

Fig. 1 shows the gas chromatogram of the oligomerization product of Example 5; and

Fig. 2 shows the gas chromatogram of the oligomerization product of Example 7.

Detailed Description of the Embodiments

The present disclosure will be illustrated in detail hereinafter with reference to the Examples. However, the present disclosure is not limited by the contents of the Examples disclosed herein.

Example 1

1. A ligand is prepared.

O-diphenylphosphino-N-methylaniline (2.91 g, 10 mmol) and toluene (40 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The solution is cooled to -78 °C, and an n-hexane solution containing 10 mmol of n-butyl lithium is added into the solution under stirring. The reaction proceeds until a temperature thereof reaches room temperature, and the solution is stirred for another 3 hours. The reaction solution

is then cooled to $-78\text{ }^{\circ}\text{C}$, and a toluene solution containing 10 mmol of bis (2,4,6-trimethylphenyl)-bromopropyl phosphonium is added into the solution under stirring. The reaction proceeds until the temperature thereof reaches room temperature, and the solution is stirred for another 12 hours.

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After completion of the reaction, insoluble substance, i.e., lithium bromide is removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All of the solution is collected, and all solvent is removed by a rotary evaporator so as to obtain a yellow solid product. A productivity of the product is 45%.

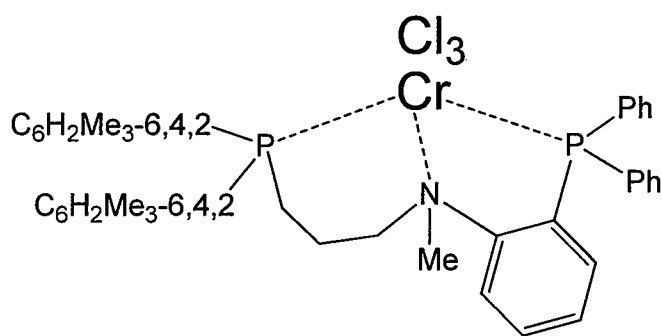
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The elemental analysis results are shown as follows. Calculation values: N, 2.33; C, 79.84; H, 7.54. Measured values: N, 2.15; C, 79.89; H, 7.46.

15 2. A ligand chromium compound is prepared.

The ligand (0.60 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 91%, and a structure thereof is shown in formula (1) as follows:

20



(1)

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The elemental analysis results are shown as follows. Calculation values: N, 1.84; C, 63.21; H, 5.97. Measured values: N, 1.75; C, 63.30; H, 5.86.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (1) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

5

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a
10 temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as
15 shown in formula (1) is added into the reactor. A temperature of the reactor is raised to 30 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 3.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured
20 to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage
25 content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 1.

30

Example 2

A reaction temperature is changed to be 40 °C from 30 °C in Example 1, and other operating conditions are not changed. The reaction results are shown in Table 1.

Example 3

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A reaction temperature is changed to be 50 °C from 30 °C in Example 1, and other operating conditions are not changed. The reaction results are shown in Table 1.

Example 4

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A reaction temperature is changed to be 60 °C from 30 °C in Example 1, and other operating conditions are not changed. The reaction results are shown in Table 1.

Example 5

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A reaction temperature is changed to be 70 °C from 30 °C in Example 1, and other operating conditions are not changed. The reaction results are shown in Table 1, and a gas chromatogram of an oligomerization product thereof is shown in Fig. 1.

Example 6

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A reaction pressure is changed to be 3.5 MPa from 3.0 MPa in Example 1, a reaction temperature is changed to be 50 °C from 30 °C in Example 1, and other operating conditions are not changed. The reaction results are shown in Table 1.

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Example 7

A reaction pressure is changed to be 4.0 MPa from 3.0 MPa in Example 1, a reaction temperature is changed to be 50 °C from 30 °C in Example 1, and other operating conditions are not changed. The reaction results are shown in Table 1, and a gas chromatogram of an oligomerization product thereof is shown in Fig. 2.

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Example 8

A reaction pressure is changed to be 4.5 MPa from 3.0 MPa in Example 1, a reaction temperature is changed to be 50 °C from 30 °C in Example 1, and other
5 operating conditions are not changed. The reaction results are shown in Table 1.

Example 9

A catalyst formed by the NP-ligand prepared in step 1 of Example 1, chromium
10 compound chromium trichloride(THF)₃, and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours with a temperature
15 being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

A toluene solution (20 mL) containing 20 μmol of NP-ligand prepared in step 1 of
20 Example 1, a toluene suspension (20 mL) containing 20 μmol of chromium trichloride(THF)₃, and toluene solvent (20 mL) are added into the reactor in sequence in an ethylene atmosphere. A temperature of the reactor is raised to 50 °C, and the mixed solution is stirred for 5 minutes. Methylaluminoxane (MAO) (10 mL) as co-catalyst is then added into the reactor. Reaction proceeds for 30 minutes under
25 stirring with ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by
30 adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof

reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in
5 Table 2.

Example 10

According to the present Example, chromium trichloride(THF)₃ in Example 9 is
10 replaced to be chromium dichloride(THF)₂, and other operating conditions are not changed. The reaction results are shown in Table 2.

Example 11

15 According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be chromium acetylacetonate, i.e., Cr(acac)₃, and other operating conditions are not changed. The reaction results are shown in Table 2.

Example 12

20

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be chromium tris (2-ethylhexanoate), i.e., Cr(EH)₃, and other operating conditions are not changed. The reaction results are shown in Table 2.

Example 13

25 According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be chromium dichloride(tolyl)(THF)₃, and other operating conditions are not changed. The reaction results are shown in Table 2.

30

Example 14

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be chromium dichloride, and other operating conditions are not changed. The reaction results are shown in Table 2.

5 **Example 15**

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be chromium trichloride, and other operating conditions are not changed. The reaction results are shown in Table 2.

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Example 16

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be CrMe₂(:C)₂ (:C is a nitrogen heterocyclic carbene, and a molecular formula thereof is C[N(iPr)C(Me)]₂), and other operating conditions are not changed. The reaction results are shown in Table 2.

15

Example 17

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be CrEt₂(:C)₂ (:C is a nitrogen heterocyclic carbene, and a molecular formula thereof is C[N(iPr)C(Me)]₂), and other operating conditions are not changed. The reaction results are shown in Table 2.

20

25 **Example 18**

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be CrPh₂(:C)₂ (:C is a nitrogen heterocyclic carbene, and a molecular formula thereof is C[N(iPr)C(Me)]₂), and other operating conditions are not changed. The reaction results are shown in Table 2.

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Example 19

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be CrPh₃(THF)₃, and other operating conditions are not changed. The reaction results are shown in Table 2.

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Example 20

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be Cr(CO)₆, and other operating conditions are not changed. The reaction results are shown in Table 2.

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Example 21

According to the present Example, chromium trichloride(THF)₃ in Example 9 is replaced to be CrMeCl₂(THF)₃, and other operating conditions are not changed. The reaction results are shown in Table 2.

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Example 22

20 1. A ligand is prepared.

O-(diphenylphosphino)aniline (2.77 g, 10 mmol) and toluene (40 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The solution is cooled to -78 °C, and an n-hexane solution containing 10 mmol of n-butyl lithium is added into the solution under stirring. The reaction proceeds until a temperature thereof reaches room temperature, and the solution is stirred for another 3 hours. The reaction solution is then cooled to -78 °C, and a toluene solution containing 10 mmol of bis (2,4,6-trimethylphenyl)-bromopropyl phosphonium is added into the solution under stirring. The reaction proceeds until the temperature thereof reaches room temperature, and the solution is stirred for another 12 hours.

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After completion of the reaction, insoluble substance, i.e., lithium bromide is

removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All of the solution is collected, and all solvent is removed by a rotary evaporator so as to obtain a light yellow solid product. A productivity of the product is 33%.

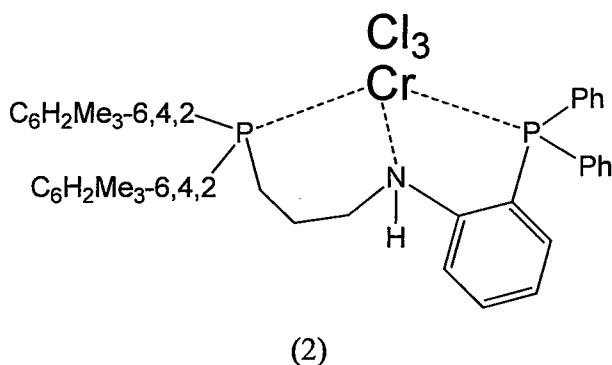
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The elemental analysis results are shown as follows. Calculation values: N, 2.38; C, 79.70; H, 7.37. Measured values: N, 2.35; C, 79.78; H, 7.36.

2. A ligand chromium compound is prepared.

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The ligand (0.59 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 93%, and a structure thereof is shown in formula (2) as follows:



20 The elemental analysis results are shown as follows. Calculation values: N, 1.88; C, 62.78; H, 5.81. Measured values: N, 1.92; C, 62.89; H, 5.76.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (2) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

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A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature

being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

5 Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (2) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure
10 being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried
15 by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

20 An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 23

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1. A ligand is prepared.

O-diphenylphosphino-N-methylaniline (2.91 g, 10 mmol) and toluene (40 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The solution is cooled to
30 -78 °C, and an n-hexane solution containing 10 mmol of n-butyl lithium is added into the solution under stirring. The reaction proceeds until a temperature thereof reaches room temperature, and the solution is stirred for another 3 hours. The reaction solution

is then cooled to $-78\text{ }^{\circ}\text{C}$, and a toluene solution containing 10 mmol of diphenyl-bromopropyl phosphonium is added into the solution under stirring. The reaction proceeds until the temperature thereof reaches room temperature, and the solution is stirred for another 12 hours.

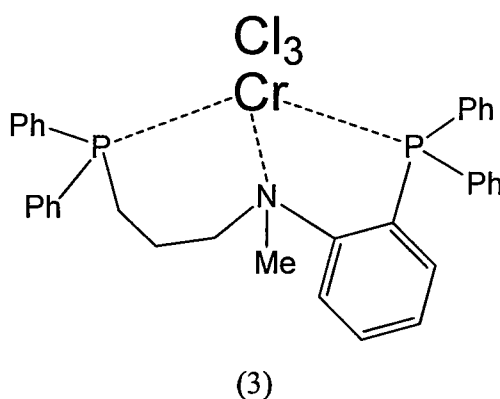
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After completion of the reaction, insoluble substance, i.e., lithium bromide is removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All of the solution is collected, and all solvent is removed by a rotary evaporator so as to obtain a light yellow solid product. A productivity of the product is 62%.

The elemental analysis results are shown as follows. Calculation values: N, 2.71; C, 78.90; H, 6.43. Measured values: N, 2.63; C, 78.89; H, 6.34.

15 2. A ligand chromium compound is prepared.

The ligand (0.52 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 90%, and a structure thereof is shown in formula (3) as follows:



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The elemental analysis results are shown as follows. Calculation values: N, 2.07; C, 60.41; H, 4.92. Measured values: N, 2.05; C, 60.59; H, 5.01.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (3) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

5

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a
10 temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as
15 shown in formula (3) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes with ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an
20 ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage
25 content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

30

Example 24

1. A ligand is prepared.

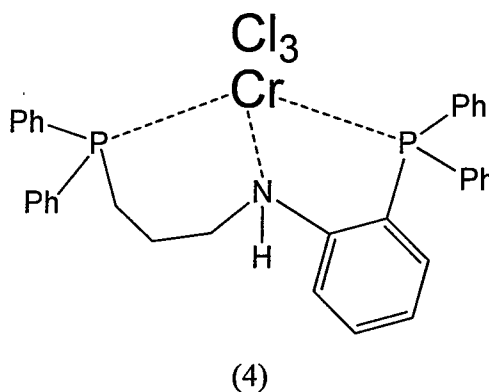
O-(diphenylphosphino) aniline (2.77 g, 10 mmol) and toluene (40 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The solution is cooled to -78 °C, and
5 an n-hexane solution containing 10 mmol of n-butyl lithium is added into the solution under stirring. The reaction proceeds until a temperature thereof reaches room temperature, and the solution is stirred for another 3 hours. The reaction solution is then cooled to -78 °C, and a toluene solution containing 10 mmol of diphenyl-bromopropyl phosphonium is added into the solution under stirring. The
10 reaction proceeds until the temperature thereof reaches room temperature, and the solution is stirred for another 12 hours.

After completion of the reaction, insoluble substance, i.e., lithium bromide is removed through filtration. The residual solution is separated by a chromatographic
15 column, and is eluted by n-hexane. All of the solution is collected, and all solvent is removed by a rotary evaporator so as to obtain a light yellow solid product. A productivity of the product is 43%.

The elemental analysis results are shown as follows. Calculation values: N, 2.78;
20 C, 78.71; H, 6.21. Measured values: N, 2.73; C, 78.68; H, 6.16.

2. A ligand chromium compound is prepared.

The ligand (0.51 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37
25 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 88%, and a structure thereof is shown in formula (4) as follows:



The elemental analysis results are shown as follows. Calculation values: N, 2.12;
 5 C, 59.88; H, 4.72. Measured values: N, 2.15; C, 60.02; H, 4.66.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula
 (4) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction,
 and a method is described as follows.

10

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an
 electric drier and is installed. The reactor is evacuated for 2 hours under a temperature
 being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain
 pressure is pumped into the reactor after N₂ replacement for three times, and then a
 15 temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst
 are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a
 toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as
 20 shown in formula (4) is added into the reactor. A temperature of the reactor is raised to
 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure
 being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a
 supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5
 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured
 25 to an ethanol solution acidified with hydrochloric acid with a concentration being 10%.
 Organic products are separated by adding 100 mL of water. Liquid products are dried
 by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through

GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

- 5 An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 25

10

1. A ligand is prepared.

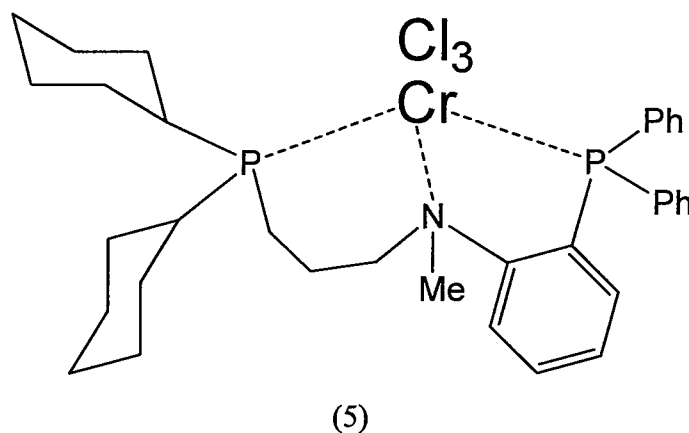
O-diphenylphosphino-N-methylaniline (2.91 g, 10 mmol) and toluene (40 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The solution is cooled to
15 -78 °C, and an n-hexane solution containing 10 mmol of n-butyl lithium is added into the solution under stirring. The reaction proceeds until a temperature thereof reaches room temperature, and the solution is stirred for another 3 hours. The reaction solution is then cooled to -78 °C, and a toluene solution containing 10 mmol of dicyclohexyl-bromopropyl phosphonium is added into the solution under stirring. The
20 reaction proceeds until the temperature thereof reaches room temperature, and the solution is stirred for another 12 hours.

After completion of the reaction, insoluble substance, i.e., lithium bromide is removed through filtration. The residual solution is separated by a chromatographic
25 column, and is eluted by n-hexane. All of the solution is collected, and all solvent is removed by a rotary evaporator so as to obtain a light yellow solid product. A productivity of the product is 51%.

The elemental analysis results are shown as follows. Calculation values: N, 2.64;
30 C, 77.10; H, 8.56. Measured values: N, 2.55; C, 77.15; H, 8.49.

2. A ligand chromium compound is prepared.

The ligand (0.53 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with
5 reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 90%, and a structure thereof is shown in formula (5) as follows:



10

The elemental analysis results are shown as follows. Calculation values: N, 2.04; C, 59.35; H, 6.59. Measured values: N, 2.01; C, 58.89; H, 6.47.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula
15 (5) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature
20 being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst
25 are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as

shown in formula (5) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 26

1. A ligand is prepared.

20

O-(diphenylphosphino) aniline (2.77 g, 10 mmol) and toluene (40 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The solution is cooled to -78 °C, and an n-hexane solution containing 10 mmol of n-butyl lithium is added into the solution under stirring. The reaction proceeds until a temperature thereof reaches room temperature, and the solution is stirred for another 3 hours. The reaction solution is then cooled to -78 °C, and a toluene solution containing 10 mmol of dicyclohexyl-bromopropyl phosphonium is added into the solution under stirring. The reaction proceeds until the temperature thereof reaches room temperature, and the solution is stirred for another 12 hours.

30

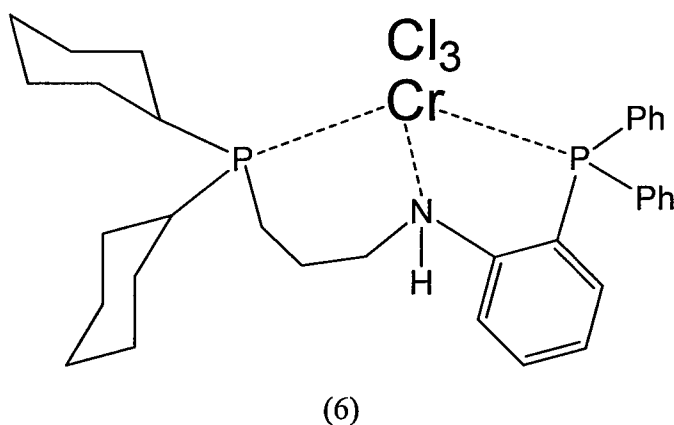
After completion of the reaction, insoluble substance, i.e., lithium bromide is removed through filtration. The residual solution is separated by a chromatographic

column, and is eluted by n-hexane. All of the solution is collected, and all solvent is removed by a rotary evaporator so as to obtain a light yellow solid product. A productivity of the product is 22%.

5 The elemental analysis results are shown as follows. Calculation values: N, 2.71; C, 76.71; H, 8.50. Measured values: N, 2.65; C, 76.70; H, 8.46.

2. A ligand chromium compound is prepared.

10 The ligand (0.51 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 85%, and a structure thereof is shown in formula (6) as follows:



20 The elemental analysis results are shown as follows. Calculation values: N, 2.08; C, 58.72; H, 6.57. Measured values: N, 2.15; C, 68.84; H, 6.43.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (6) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

25

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an

electric drier and is installed. The reactor is evacuated for 2 hours with a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

5

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (6) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

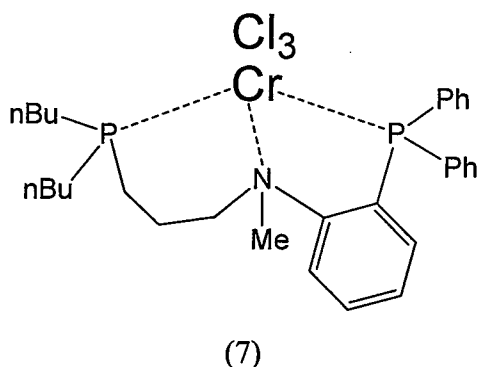
20

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

25 **Example 27**

In the present Example, a ligand and a ligand chromium compound can be prepared according to the method of Example 1.

30 A catalyst formed by an NP-ligand chromium compound as shown in formula (7) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.



5 A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

10

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (7) is added into the reactor. A temperature of the reactor is raised to

15 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%.

20 Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

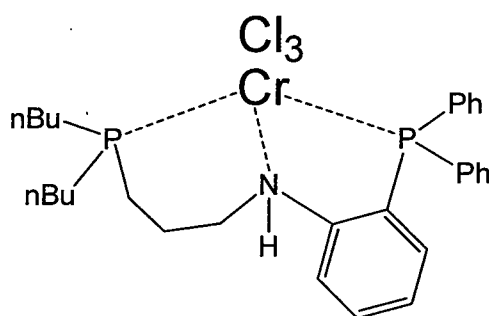
25

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 28

In the present Example, a ligand and a ligand chromium compound can be prepared according to the method of Example 1.

A catalyst formed by an NP-ligand chromium compound as shown in formula (8) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.



(8)

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (8) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured

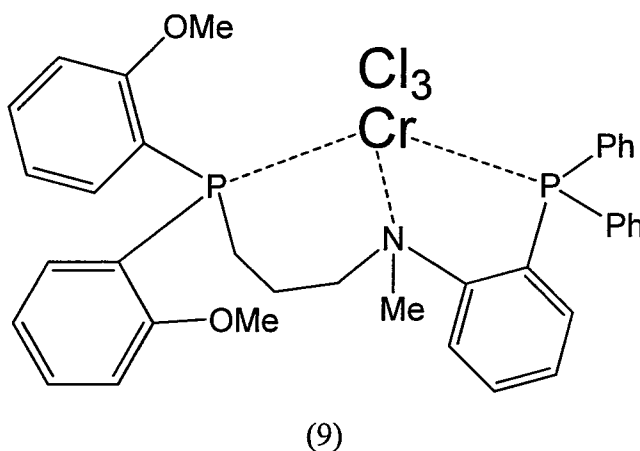
to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum
5 at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in
10 Table 3.

Example 29

In the present Example, a ligand and a ligand chromium compound can be
15 prepared according to the method of Example 1.

A catalyst formed by an NP-ligand chromium compound as shown in formula (9) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.
20



A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an
25 electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain

pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

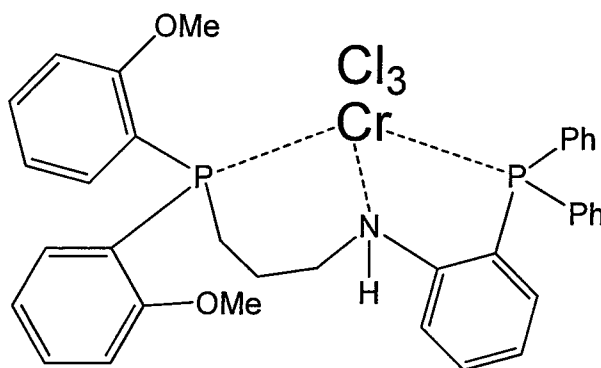
Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst
5 are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a
toluene solution (20 mL) containing 5 μ mol of the NP-ligand chromium compound as
shown in formula (9) is added into the reactor. A temperature of the reactor is raised to
50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure
being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a
10 supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5
°C. A pressure of the reactor is reduced slowly, and a product after reaction is poured
to an ethanol solution acidified with hydrochloric acid with a concentration being 10%.
Organic products are separated by adding 100 mL of water. Liquid products are dried
by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through
15 GC-FID methods. Solid products are collected after filtration, and are dried in vacuum
at 50 °C until a weight thereof reaches a constant weight, and the mass percentage
content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis
20 and calculation, and the activity of the catalyst and product compositions are shown in
Table 3.

Example 30

25 In the present Example, a ligand and a ligand chromium compound can be
prepared according to the method of Example 1.

A catalyst formed by an NP-ligand chromium compound as shown in formula (10)
and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a
30 method is described as follows.



(10)

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (10) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in

Table 3.

Example 31

- 5 1. A ligand is prepared.

O-(diphenylphosphino)bromobenzene (20 mmol), N,N-dimethyl methylamine (50 mmol), N,N-dimethyl methanamide solvent (40 mL), and CuI catalyst (0.5 g) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The mixed liquid is heated to
10 80 °C and kept for 12 hours at such a temperature.

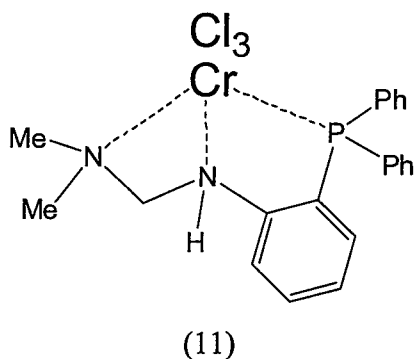
After completion of the reaction, the liquid is cooled to room temperature. Insoluble substances are removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All solution is collected, and
15 all solvent and volatile compositions are removed through a vacuum decompression method so as to obtain a white solid product. A productivity of the product is 31%.

The elemental analysis results are shown as follows. Calculation values: N, 8.38; C, 75.43; H, 6.93. Measured values: N, 8.35; C, 75.50; H, 6.95.

20

2. A ligand chromium compound is prepared.

The ligand (0.33 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂
25 atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane so as to obtain a dark green solid product. A productivity of the product is 80%, and a structure thereof is shown in formula (11) as follows:



The elemental analysis results are shown as follows. Calculation values: N, 5.69;
 5 C, 51.19; H, 4.70. Measured values: N, 5.62; C, 51.41; H, 4.66.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula
 (11) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction,
 and a method is described as follows.

10

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an
 electric drier and is installed. The reactor is evacuated for 2 hours under a temperature
 being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain
 pressure is pumped into the reactor after N₂ replacement for three times, and then a
 15 temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst
 are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a
 toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as
 20 shown in formula (11) is added into the reactor. A temperature of the reactor is raised
 to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure
 being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a
 supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5
 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured
 25 to an ethanol solution acidified with hydrochloric acid with a concentration being 10%.
 Organic products are separated by adding 100 mL of water. Liquid products are dried
 by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through
 GC-FID methods. Solid products are collected after filtration, and are dried in vacuum

at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

5 An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 32

10 1. A ligand is prepared.

O-(diphenylphosphino)bromobenzene (20 mmol), N,N-dimethyl ethylamine (50 mmol), N,N-dimethyl methanamide solvent (40 mL), and CuI catalyst (0.5 g) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The mixed liquid is heated to
15 80 °C and kept for 12 hours at such a temperature.

After completion of the reaction, the liquid is cooled to room temperature. Insoluble substances are removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All solution is collected, and
20 all solvent and volatile compositions are removed through a vacuum decomposition method so as to obtain a white solid product. A productivity of the product is 37%.

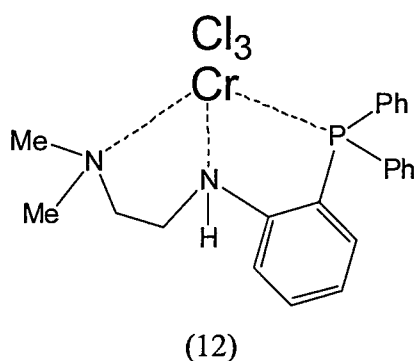
The elemental analysis results are shown as follows. Calculation values: N, 8.04; C, 75.84; H, 7.23. Measured values: N, 8.05; C, 75.69; H, 7.27.

25

2. A ligand chromium compound is prepared.

The ligand (0.35 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂
30 atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane so as to obtain a dark green solid product. A productivity of the product is 91%, and a structure thereof is shown in

formula (12) as follows:



5 The elemental analysis results are shown as follows. Calculation values: N, 5.53; C, 52.14; H, 4.97. Measured values: N, 5.65; C, 52.12; H, 4.76.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (12) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction,
10 and a method is described as follows.

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours with a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain
15 pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a
20 toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (12) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5
25 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through

GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

- 5 An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 33

10

1. A ligand is prepared.

O-(diphenylphosphino)bromobenzene (20 mmol), diphenylphosphino methylamine (20 mmol), triethylamine (50 mmol), N,N-dimethyl methanamide solvent
15 (40 mL), and CuI catalyst (0.5 g) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The mixed liquid is heated to 80 °C and kept for 12 hours at such a temperature.

After completion of the reaction, the liquid is cooled to room temperature.
20 Insoluble substances are removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All solution is collected, and all solvent and volatile compositions are removed through a vacuum decompression method. Solid product obtained therein is recrystallized so as to obtain a light yellow crystalline product. A productivity of the product is 28%.

25

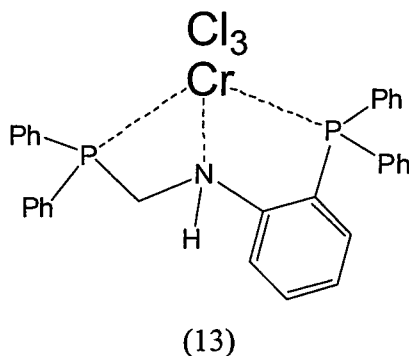
The elemental analysis results are shown as follows. Calculation values: N, 2.95; C, 78.30; H, 5.72. Measured values: N, 2.87; C, 78.41; H, 5.76.

2. A ligand chromium compound is prepared.

30

The ligand (0.48 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂

atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane so as to obtain a dark green solid product. A productivity of the product is 90%, and a structure thereof is shown in formula (13) as follows:



The elemental analysis results are shown as follows. Calculation values: N, 2.21; C, 58.74; H, 4.29. Measured values: N, 2.15; C, 58.89; H, 4.26.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (13) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (1) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured

to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Example 34

1. A ligand is prepared.

O-(diphenylphosphino)bromobenzene (20 mmol), diphenylphosphino ethylamine (20 mmol), triethylamine (50 mmol), N,N-dimethyl methanamide solvent (40 mL), and CuI catalyst (0.5 g) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The mixed liquid is heated to 80 °C and kept for 12 hours at such a temperature.

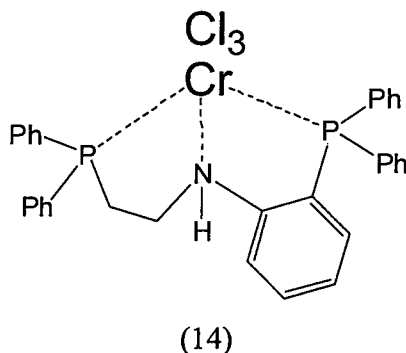
After completion of the reaction, the liquid is cooled to room temperature. Insoluble substances are removed through filtration. The residual solution is separated by a chromatographic column, and is eluted by n-hexane. All solution is collected, and all solvent and volatile compositions are removed through a vacuum decompression method so as to obtain a white solid product. A productivity of the product is 46%.

The elemental analysis results are shown as follows. Calculation values: N, 2.86; C, 78.51; H, 5.97. Measured values: N, 2.89; C, 78.49; H, 5.96.

2. A ligand chromium compound is prepared.

The ligand (0.49 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37

g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid is stirred for 25 hours. The solvent is removed with reduced temperature. Crude product is washed by n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 91%, and a structure thereof is shown in formula (14) as follows:



The elemental analysis results are shown as follows. Calculation values: N, 2.16; C, 59.32; H, 4.51. Measured values: N, 2.13; C, 59.29; H, 4.47.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (14) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction, and a method is described as follows.

15

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

20

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (14) is added into the reactor. A temperature of the reactor is raised to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5

25

°C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Reference Example 1

1. A ligand is prepared.

N-2,6-diisopropyl phenyl-2-phenyl-2-chloro-imine (29.98 g, 100 mmol), o-(diphenyl phosphino) aniline (27.73 g, 100 mmol), and toluene (400 ml) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The mixed liquid is heated to 120 °C and refluxed for 20 hours so as to obtain a hydrochloride of the ligand.

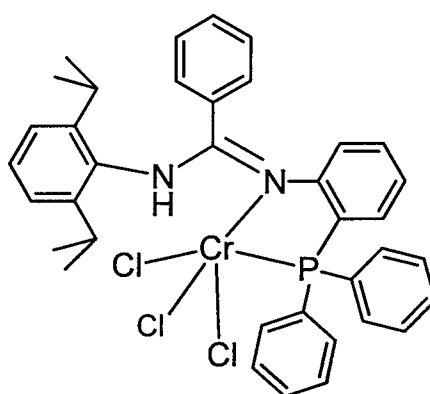
The hydrochloride is dissolved in ethanol (300 ml, 95%), and is dropwise added to aqueous ammonia (300 ml, 25%) for neutralization. Solid product obtained therein is collected after filtration, is dried in vacuum for 4 hours, and is recrystallized in toluene so as to obtain a white crystalline product. A productivity of the product is 85%.

The elemental analysis results are shown as follows. Calculation values: N, 5.18; C, 82.19; H, 6.71. Measured values: N, 5.06; C, 81.88; H, 6.67.

30

2. A ligand chromium compound is prepared.

The ligand (0.54 g, 1 mmol) prepared in step 1, chromium trichloride(THF)₃ (0.37 g, 1 mmol) and THF solvent (50 mL) are added into a Schlenk bottle (100 mL) in N₂ atmosphere. The reaction liquid turns to dark green. The reaction liquid is stirred for 25 hours, and then solvent is removed in vacuum. Crude product is washed by
5 n-hexane for several times so as to obtain a dark green solid product. A productivity of the product is 92.9%, and a structure thereof is shown in formula (15) as follows:



(15)

10 The elemental analysis results are shown as follows. Calculation values: N, 4.01; C, 63.57; H, 5.19. Measured values: N, 3.91; C, 62.79; H, 5.38.

3. A catalyst formed by the NP-ligand chromium compound as shown in formula (15) and methylaluminoxane (MAO) is used in an ethylene oligomerization reaction,
15 and a method is described as follows.

A high pressure reactor (300 mL) is pre-treated. That is, the reactor is dried by an electric drier and is installed. The reactor is evacuated for 2 hours under a temperature being 50 °C to form a vacuum therein. A fully dried ethylene gas with a certain
20 pressure is pumped into the reactor after N₂ replacement for three times, and then a temperature of the reactor drops to room temperature.

Toluene solvent (60 mL) and methylaluminoxane (MAO) (2.5 mL) as co-catalyst are added into the reactor in an ethylene atmosphere. After stirring for 5 minutes, a
25 toluene solution (20 mL) containing 5 μmol of the NP-ligand chromium compound as shown in formula (15) is added into the reactor. A temperature of the reactor is raised

to 50 °C under stirring, and reaction proceeds for 30 minutes under ethylene pressure being 4.0 MPa. The reaction goes on until a predetermined time, the stirring stops, a supply of ethylene gas stops, and the temperature of the reactor is reduced to about 5 °C. A pressure of the reactor is reduced slowly, and a product after reaction is poured to an ethanol solution acidified with hydrochloric acid with a concentration being 10%. Organic products are separated by adding 100 mL of water. Liquid products are dried by anhydrous sodium sulfate, and are qualitatively and quantitatively analyzed through GC-FID methods. Solid products are collected after filtration, and are dried in vacuum at 50 °C until a weight thereof reaches a constant weight, and the mass percentage content is calculated separately.

An activity of the catalyst can be obtained through gas chromatographic analysis and calculation, and the activity of the catalyst and product compositions are shown in Table 3.

Table 1 Activities of the catalysts and product compositions of Examples 1-8

Examp les	Activity (10 ⁶ g/(mol Cr·h))	C ₆ [#] (wt%)	1-C ₆ in C ₆ (%)	C ₈ [#] (wt%)	1-C ₈ in C ₈ (%)	C ₁₀₊ [#] (wt%)	PE* (wt%)
1	1.32	26.0	87.0	57.5	96.4	16.5	3.4
2	7.92	38.5	85.5	51.6	96.9	9.9	1.9
3	8.42	36.2	75.4	54.2	97.3	9.6	2.5
4	7.32	37.3	92.5	57.5	97.6	7.2	2.1
5	7.48	21.5	84.7	69.0	98.3	9.5	2.5
6	8.42	24.3	95.1	68.2	98.6	7.5	3.0
7	9.52	23.2	84.5	70.1	97.3	6.7	4.1
8	6.43	20.8	73.5	68.9	98.1	10.3	2.1

According to Table 1, data in columns with sign “#” represent mass percentage content of each composition in the oligomerization products, and *PE represents mass

percentage content thereof in total mass.

Table 2 Activities of the catalysts and product compositions of Examples 9-21

Exempl es	Activity ($10^6\text{g}/(\text{mol Cr}\cdot\text{h})$)	$\text{C}_6^\#$ (wt%)	1- C_6 in C_6 (%)	$\text{C}_8^\#$ (wt%)	1- C_8 in C_8 (%)	$\text{C}_{10+}^\#$ (wt%)	PE* (wt%)
9	6.24	25.1	75.9	71.1	98.5	3.8	1.4
10	0.42	27.1	64.2	57.6	97.1	15.3	1.0
11	1.32	24.7	69.5	61.5	97.9	13.8	2.6
12	3.03	34.3	82.5	58.5	98.1	7.2	1.8
13	0.52	20.6	74.5	67.6	99.2	11.8	1.0
14	0.06	23.8	75.2	68.5	98.4	7.7	1.3
15	4.61	29.2	94.6	63.3	98.6	7.5	2.6
16	5.31	27.3	86.2	67.4	97.3	5.3	1.0
17	4.67	32.1	87.4	65.5	97.8	2.4	1.1
18	0.87	26.0	77.1	55.2	98.5	18.8	1.0
19	3.21	23.8	92.3	69.3	97.1	6.9	2.1
20	1.17	24.3	82.2	66.9	96.5	8.8	1.2
21	1.78	21.4	73.9	68.6	97.9	10.0	3.2

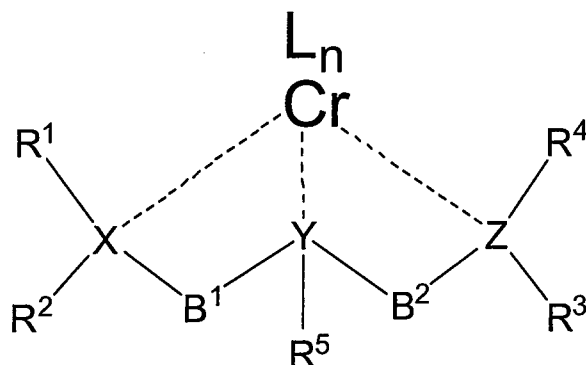
5 Table 3 Activities of the catalysts and product compositions of Examples 22-34 and Reference Example 1

Examples	Activity ($10^6\text{g}/(\text{mol Cr}\cdot\text{h})$)	C_6 (wt%)	1- C_6 in C_6 (%)	C_8 (wt%)	1- C_8 in C_8 (%)	C_{10+} (wt%)	PE (wt%)
22	5.75	29.7	67.3	62.3	99.2	8.0	3.2
23	6.25	26.5	96.3	69.2	97.2	4.3	2.5
24	3.46	29.2	62.7	55.5	98.3	15.3	3.8

25	2.43	31.6	79.5	57.3	98.2	11.1	2.4
26	2.67	30.5	94.6	60.3	97.7	9.2	1.6
27	2.53	21.8	93.2	67.5	98.2	10.7	2.0
28	3.92	22.5	91.5	67.6	97.6	9.9	2.4
29	3.18	22.3	96.8	65.4	98.3	12.3	2.4
30	2.71	24.8	75.6	59.7	98.2	15.5	3.0
31	3.12	86.2	76.3	3.4	98.4	10.4	2.2
32	2.18	90.2	90.6	3.1	99.0	6.7	1.0
33	1.43	92.1	96.5	3.4	99.0	4.5	1.0
34	1.32	89.3	92.5	4.6	99.0	6.1	1.2
Reference Example 1	0.38	59.8	68.0	30.2	100.0	10.5	50.9

Claims

1. A ligand based chromium catalyst, which has a general formula as follows:



5 wherein in above structure, X, Y, and Z represent one element of N and P respectively, R^1 , R^2 , R^3 , R^4 , and R^5 represent one of H, linear or branched alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, substituted aryl and derivatives thereof respectively, B^1 and B^2 represent a structural system which can transmit an electronic induction or conjugative effect of a group respectively, and L_n represents a group
10 which has a chemical bond with metal chromium; and

 wherein when X and Y both are N element, and Z is P element, B^1 represents one methylene group or a plurality of methylene groups.

2. The chromium catalyst according to claim 1, wherein the chromium catalyst is
15 formed by a chromium compound and an organic ligand containing P and/or N.

3. The chromium catalyst according to claim 1,
 wherein the R^1 , R^2 , R^3 , R^4 , and R^5 groups, when being connected with nitrogen atom, are respectively one selected from a group consisting of H, C_1 - C_{10} linear or
20 branched alkyl, heteroalkyl, cycloalkyl, alkenyl, allyl, and substituted phenyl; and

 wherein the R^1 , R^2 , R^3 , R^4 , and R^5 groups, when being connected with phosphorus atom, are respectively one selected from a group consisting of C_1 - C_{10} linear or branched alkyl, substituted aryl, and derivatives thereof.

25 4. The chromium catalyst according to claim 3, wherein the R^1 , R^2 , R^3 , R^4 , and R^5 groups, when being connected with nitrogen atom, are respectively one selected from a

group consisting of H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, cyclobutyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, 2,6-dimethylcyclohexyl, adamantyl, vinyl, allyl, phenyl, naphthyl, 2-methylphenyl, 2,4,6-trimethylphenyl, 3,5-dimethylphenyl, 3,5-dimethoxyphenyl, 3,5-di-tert-butylphenyl, 2-thienyl, 2-furanyl, 2-pyridyl, and 3-pyridyl; and
5 wherein the R¹, R², R³, R⁴, and R⁵ groups, when being connected with phosphorus atom, are respectively one selected from a group consisting of methyl, ethyl, butyl, phenyl (which can be connected to be condensed nucleus compound), 2-methylphenyl, 4-methylphenyl, 3,5-dimethylphenyl, 2-methoxyphenyl, 4-methoxyphenyl, 10 3,5-dimethoxyphenyl, 4-tert-butylphenyl, 3,5-di-tert-butylphenyl, 2-nitrophenyl, 4-nitrophenyl, 4-cyanophenyl, 3,4-(methylenedioxy) phenyl, 4-benzoylphenyl, 4-ethoxycarbonylphenyl, 4-trifluoromethylphenyl, 1-naphthyl, 4,4'-biphenyl, 3,5-di(phenyl) phenyl, 2-thienyl, 2-furanyl, 2-pyridyl, and 3-pyridyl.

15 5. The chromium catalyst according to claim 1, wherein the chromium comes from a chromium inorganic compound or a chromium organic compound;

 wherein the chromium inorganic compound is chromium dichloride or chromium trichloride; and

 wherein the chromium organic compound is one selected from a group consisting
20 of chromium dichloride-tetrahydrofuran complex, chromium dichloride-toluene tetrahydrofuran complex, chromium trichloride-tetrahydrofuran complex, chromium dichloride-carbene complex, chromium trichloride-carbene complex, chromium acetylacetonate, chromium tris (2-ethylhexanoate), methyl chromium dichloride-tetrahydrofuran complex, triphenyl chromium-tetrahydrofuran complex, 25 dimethyl chromium-carbene complex, diethyl chromium-carbene complex, diphenyl chromium-carbene complex, and carbonyl chromium.

 6. The chromium catalyst according to claim 1, wherein the structural systems B¹ and B² which can transmit an electronic induction or conjugative effect of a group are
30 respectively a double bond group containing 18 or less carbon atoms.

 7. An ethylene oligomerization method using the chromium catalyst according to

any one of claims 1 to 6, comprising performing ethylene oligomerization reaction in the presence of the NP-ligand based chromium catalyst.

8. The ethylene oligomerization method according to claim 7, wherein a reaction
5 temperature ranges from 0 °C to 200 °C, an ethylene pressure ranges from 0.1 MPa to 20 MPa, a reaction time ranges from 0.01 h to 200 h, and a concentration of the catalyst ranges from 0.001 mmol/L to 1000 mmol/L.

9. The ethylene oligomerization method according to claim 8, further comprising
10 mixing the NP-ligand based chromium catalyst with a co-catalyst in an organic solvent medium, so that a mixture obtained therein contacts with olefin and oligomerization reaction is performed.

10. The ethylene oligomerization method according to claim 9, wherein a ratio of
15 the NP-ligand based chromium catalyst to the co-catalyst ranges from 1:10 to 1:4000.

11. The ethylene oligomerization method according to claim 9, wherein the
co-catalyst is at least one selected from a group consisting of alkyl aluminum
compound, aluminoxane compound, and organic boron compound, preferably is at
20 least one selected from a group consisting of triethylaluminum, triisobutylaluminum,
tri-n-butylaluminium, tri-n-hexylaluminium, tri-n-octylaluminium, methylaluminoxane,
ethylaluminoxane, isobutylaluminoxane and modified aluminoxane,
methylaluminoxane loaded on silica gel, alkylaluminum halide, tris (pentafluorophenol)
aluminum, tris (trifluoromethyl butanol) aluminum, triphenylmethyl-tetra
25 (trifluoromethyl butanol) aluminum salts, tetrafluoroborate, ether tetrafluoroborate,
epoxy borane, triethylborane, tris (pentafluorophenyl) borane, tetra (pentafluorophenyl)
borate, tri-perfluoroaryl boranes, tetra-perfluoroaryl borate, tributyl borate, tetra
(3,5-ditrifluoromethyl) phenyl borohydride salt, and tetra (3,5-ditrifluoromethyl)
phenyl boron-sodium salts.

30

12. The ethylene oligomerization method according to claim 9, wherein the
organic solvent is at least one selected from a group consisting of toluene, xylene,

n-butane, n-pentane, cyclopentane, methyl cyclopentane, n-hexane, n-heptane, cyclohexane, methylcyclohexane, tetrahydrofuran, dichloromethane, dichloroethane, ethyl ether, and isopropyl ether.

- 5 13. The ethylene oligomerization method according to claim 7, wherein the oligomerization comprises selective trimerization and tetramerization of ethylene so as to obtain 1-hexene and 1-octene.