



(11) **EP 2 918 591 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
13.09.2017 Bulletin 2017/37

(51) Int Cl.:
C07F 7/08 ^(2006.01) **C07B 61/00** ^(2006.01)
C07F 17/00 ^(2006.01) **C07F 7/00** ^(2006.01)
C08F 4/659 ^(2006.01)

(21) Application number: **13861676.8**

(86) International application number:
PCT/KR2013/010512

(22) Date of filing: **19.11.2013**

(87) International publication number:
WO 2014/092352 (19.06.2014 Gazette 2014/25)

(54) **NOVEL LIGAND COMPOUND, PREPARATION METHOD THEREFOR, TRANSITION METAL COMPOUND, AND PREPARATION METHOD THEREFOR**

NEUARTIGE LIGANDENVERBINDUNG, HERSTELLUNGSVERFAHREN DAFÜR, ÜBERGANGSMETALLVERBINDUNG UND HERSTELLUNGSVERFAHREN DAFÜR

NOUVEAU COMPOSÉ DE LIGAND, SON PROCÉDÉ DE PRÉPARATION, COMPOSÉ DE MÉTAL DE TRANSITION ET SON PROCÉDÉ DE PRÉPARATION

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

- **KIM, Seul Ki**
Daejeon 305-738 (KR)
- **LEE, Eun Jung**
Daejeon 305-738 (KR)
- **LEE, Choong Hoon**
Daejeon 305-738 (KR)
- **PARK, In Sung**
Daejeon 305-738 (KR)

(30) Priority: **11.12.2012 KR 20120143809**
11.12.2012 KR 20120143806
18.11.2013 KR 20130140006

(43) Date of publication of application:
16.09.2015 Bulletin 2015/38

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(73) Proprietor: **LG Chem, Ltd.**
Seoul 150-721 (KR)

(72) Inventors:

- **JANG, Jae Kwon**
Daejeon 305-738 (KR)
- **HAN, Hyo Jung**
Daejeon 305-738 (KR)
- **HAN, Ki Won**
Daejeon 305-738 (KR)

(56) References cited:
EP-A1- 0 728 773 WO-A1-2012/084961
US-B2- 7 834 205 US-B2- 7 858 717

- **CAMILLE DESCOUR ET AL.: 'Catalyst behaviour for 1-pentene and 4-methyl-1-pentene polymerisation for C2-, Cs- and Cl-symmetric zirconocenes' POLYM. CHEM. February 2011, pages 2261 - 2272, XP055256511**

EP 2 918 591 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**BACKGROUND OF THE INVENTION**5 **(a) Field of the Invention**

[0001] The present invention relates to a novel ligand compound, a preparation method thereof, a transition metal compound including the ligand compound, and a preparation method thereof.

10 **(b) Description of the Related Art**

[0002] For a long time, there have been many advances in metallocene catalyst for olefin polymerization. Metallocene compounds are generally activated by an aluminoxane, a borane, a borate, or other activators to be used. For example, a metallocene compound having a ligand including cyclopentadienyl group and two sigma chloride ligands uses an aluminoxane as an activator. It was reported that the activity of the catalyst may increase when the chloride group of such metallocene compound is substituted with other ligands (for example, benzyl group or trimethylsilylmethyl group (-CH₂SiMe₃)).

[0003] European Patent No. 1462464 discloses a polymerization example using a hafnium metallocene compound including chloride, benzyl, and trimethylsilylmethyl groups. In addition, it was reported that the generation energy of activated species may vary according to the alkyl ligand combined to the center metal (J. Am. Chem. Soc. 2000, 122, 10358). Korean Patent No. 820542 discloses a catalyst for olefin polymerization having a quinoline-based ligand, and this patent relates to a catalyst having a leaving group including silicone or germanium atom in addition to methyl group.

[0004] Dow Co. had presented [Me₂Si(Me₄C₅)NtBu]TiCl₂ (Constrained-Geometry Catalyst, hereinafter 'CGC') in the early 1990's (US Patent No. 5,064,802), the superior aspects of the CGC to prior known metallocene catalysts in copolymerization reaction of ethylene and α -olefin can be largely summarized into two ways as follows: (1) it shows high activity even in high polymerization temperature and forms a polymer of high molecular weight, (2) the copolymerizing ability of α -olefin such as 1-hexene and 1-octene which have large steric hindrance is also very excellent. As various characteristics in the polymerization reaction of the CGC became gradually known, there have been many efforts to synthesize derivatives of the same for using it as a polymerization catalyst in the academic world and the industrial world.

[0005] As an approaching method, a synthesis of a metal compound to which various bridges and nitrogen substituents are introduced instead of silicone bridges and a polymerization using the same have been attempted. Representative metal compounds known up to recently include phosphorus, ethylene or propylene, methylidene, and methylene bridges respectively introduced thereto instead of silicone bridge of CGC structure, but they didn't show excellent results in the aspects of polymerization activity or copolymerization performance in comparison to CGC when they were applied to polymerization of ethylene or copolymerization of ethylene and alpha olefins.

[0006] As other approaching method, compounds including oxido ligands instead of amido ligands of the CGC have been largely synthesized and polymerizations using the same have been partially attempted.

[0007] EP728773 A1 discloses dimethylsilylenebis[4-(1-indolyl)-2-methylindenyl]-zirconium dichloride for use in the polymerisation of olefins. However, very few catalysts have been being applied in practice in commercial factories among above attempts.

SUMMARY OF THE INVENTION

[0008] It is an aspect of the present invention to provide a novel ligand compound and a preparation method thereof for resolving the problems.

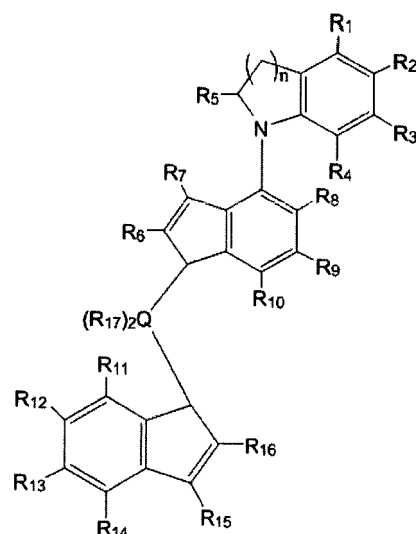
[0009] It is another aspect of the present invention to provide a transition metal compound including the ligand compound and a preparation method thereof.

[0010] In order to achieve the goals, the present invention provides the ligand compound represented by the following Chemical Formula 1:

50

55

[Chemical Formula 1]



here, n is an integer of 1 to 2;

R₁ to R₁₆ are equal to or different from each other, and are independently hydrogen, a C₁-C₂₀ alkyl, a C₁-C₂₀ alkoxy, a C₂-C₂₀ alkenyl, a C₆-C₂₀ aryl, a C₇-C₂₀ alkylaryl, a C₇-C₂₀ arylalkyl, a C₃-C₂₀ cycloalkyl, a C₅-C₂₀ heteroring, or silyl, and 2 or more adjacent groups among R₁ to R₁₆ may be connected together via an alkylidene group including a C₁-C₂₀ alkyl group or a C₆-C₂₀ aryl group to form a ring;

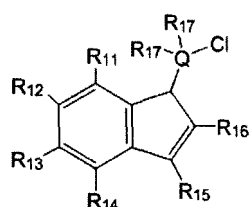
R₁₇ is hydrogen, a halogen, a C₁-C₂₀ alkyl, a C₆-C₂₀ aryl, or a C₁-C₂₀ alkoxy; and Q is carbon or silicon.

25

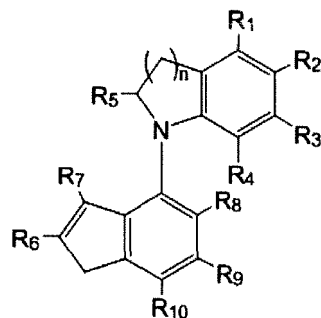
30

[0011] Furthermore, the present invention provides a preparation method of the ligand compound represented by the following Chemical Formula 1 including the step of carrying out the reaction of the compound represented by the following Chemical Formula 3 and the compound represented by the following Chemical Formula 4 or the lithium salt thereof:

[Chemical Formula 3]



[Chemical Formula 4]



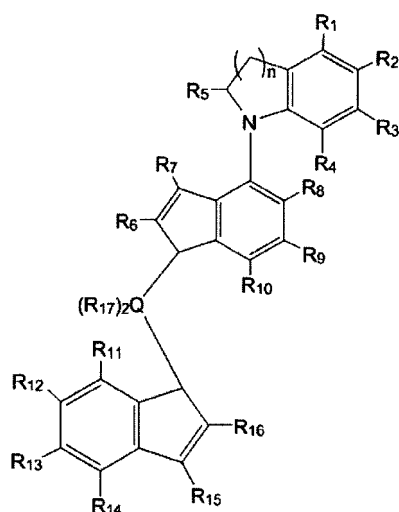
[Chemical Formula 1]

5

10

15

20



[0012] In Chemical Formulae 1, 3, and 4,

R_1 to R_{17} , Q , and n are the same as defined in Chemical Formula 1.

25

[0013] Furthermore, the present invention provides the transition metal compound represented by the following Chemical Formula 2:

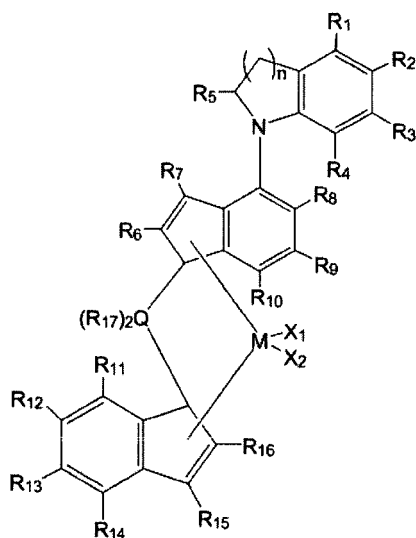
[Chemical Formula 2]

30

35

40

45



[0014] In Chemical Formula 2,

R_1 to R_{17} , Q , and n are the same as defined in Chemical Formula 1;

50

M is a Group 4 transition metal; and

X_1 and X_2 are equal to or different from each other, and are independently a halogen, a C_1 - C_{20} alkyl, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_1 - C_{20} alkylamino, a C_6 - C_{20} arylamino, or a C_1 - C_{20} alkylidene group.

55

[0015] Furthermore, the present invention provides a preparation method of the transition metal compound represented by the following Chemical Formula 2 including the step of carrying out the reaction of the ligand compound represented by the following Chemical Formula 1 and the compound represented by the following Chemical Formula 9.

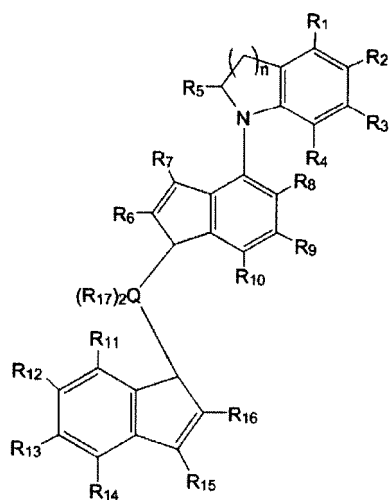
[Chemical Formula 1]

5

10

15

20



[Chemical Formula 9]

 $M(X_1X_2)_2$

25

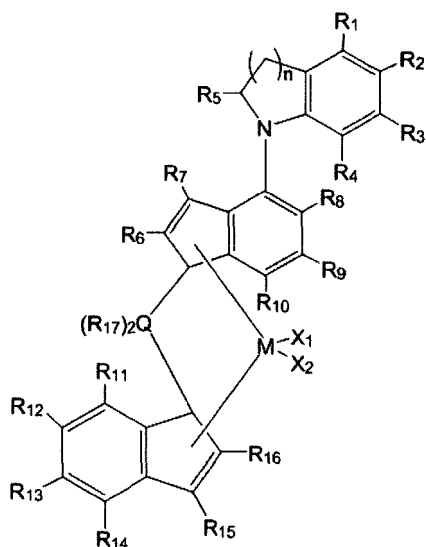
[Chemical Formula 2]

30

35

40

45



[0016] In Chemical Formulae 1, 2, and 9,
 R_1 to R_{17} , Q, and n are the same as defined in Chemical Formula 1;
 M is a Group 4 transition metal; and

[0017] X_1 and X_2 are equal to or different from each other, and are independently a halogen, a C_1 - C_{20} alkyl, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_1 - C_{20} alkylamino, a C_6 - C_{20} arylamino, or a C_1 - C_{20} alkylidene group.

[0018] The novel ligand compound of the present invention and the transition metal compound including the same may be usefully used as a catalyst for a polymerization reaction in the preparation of an olefin-based polymer.

55

DETAILED DESCRIPTION OF THE EMBODIMENTS

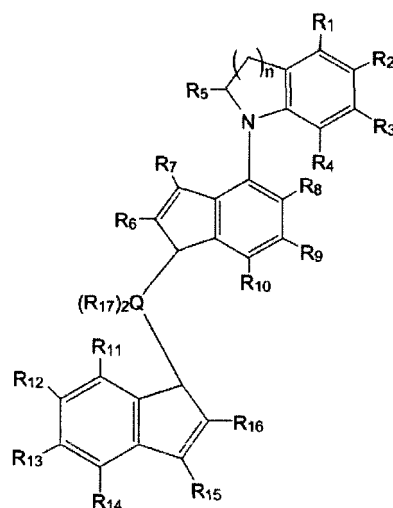
[0019] The terms used in this description are just for explaining exemplary examples and it is not intended to restrict

the present invention. The singular expression may include the plural expression unless it is differently expressed contextually. It must be understood that the terms such as "include", "equip", and "have" in the present description are only used for designating the existence of characteristics taken effect, numbers, steps, components, or combinations thereof, and do not exclude the existence or the possibility of addition of one or more different characteristics, numbers, steps, components of combinations thereof beforehand.

[0020] The present invention can be variously modified and have various examples, and specific examples of the present invention are explained in this description. However, it is not intended to limit the present invention to the specific examples. Hereinafter, the present invention is explained in more detail.

[0021] According to one aspect of the present invention, the ligand compound represented by the following Chemical Formula 1 is provided.

[Chemical Formula 1]



[0022] In Chemical Formula 1, n is an integer of 1 to 2;

R_1 to R_{16} are equal to or different from each other, and are independently hydrogen, a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_3 - C_{20} cycloalkyl, a C_5 - C_{20} heteroring, or silyl, and 2 or more adjacent groups among R_1 to R_{16} may be connected together via an alkylidene group including a C_1 - C_{20} alkyl group or a C_6 - C_{20} aryl group to form a ring;

R_{17} is hydrogen, a halogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, or a C_1 - C_{20} alkoxy; and Q is carbon or silicon.

[0023] Details of each substituent defined in Chemical Formulae 1 to 9 of the present invention are as follows.

[0024] The alkyl includes a linear or branched alkyl group.

[0025] The alkenyl includes a linear or branched alkenyl group.

[0026] According to one embodiment of the present invention, the aryl is preferably a C_6 - C_{20} aryl group and, specifically, it may be phenyl, naphthyl, anthracenyl, pyridyl, dimethylaniliny, anisoyl, and so on, but it is not limited to or by them.

[0027] The alkylaryl means an aryl group substituted with the alkyl group.

[0028] The arylalkyl means an alkyl group substituted with the aryl group.

[0029] The halogen means fluorine, chlorine, bromine, or iodine.

[0030] The silyl may be trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, trihexylsilyl, triisopropylsilyl, triisobutylsilyl, triethoxysilyl, triphenylsilyl, tris(trimethylsilyl)silyl, and so on, but it is not limited to or by them.

[0031] The aryl is preferably a C_6 - C_{20} aryl group and, specifically, may be phenyl, naphthyl, anthracenyl, pyridyl, dimethylaniliny, anisoyl, and so on, but it is not limited to or by them.

[0032] The heteroring means a primary aliphatic or aromatic hydrocarbon group including C_5 - C_{20} ring atoms and one or more hetero atoms, and it may be a single ring or a condensed ring of 2 or more rings. And, the heteroring may be substituted with an alkyl group or not. For example, it may be indoline, tetrahydroquinoline, and so on, but it is not limited to or by them.

[0033] According to one embodiment of the present invention, R_1 to R_{16} may be independently hydrogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, or a C_5 - C_{20} heteroring, and R_{17} may be a C_1 - C_{20} alkyl or a C_6 - C_{20} aryl.

[0034] The ligand compound represented by Chemical Formula 1 has a structure in which bisindenyl groups are crosslinked by Q (carbon or silicon), and any one indenyl group is connected to indoline group or tetrahydroquinoline group so as to show C1-asymmetric crosslinking structure.

[0035] According to one embodiment of the present invention, the ligand compound represented by Chemical Formula 1 may be represented by any one of the following structural formulae but it is not limited to or by them.

5

10

15

20

25

30

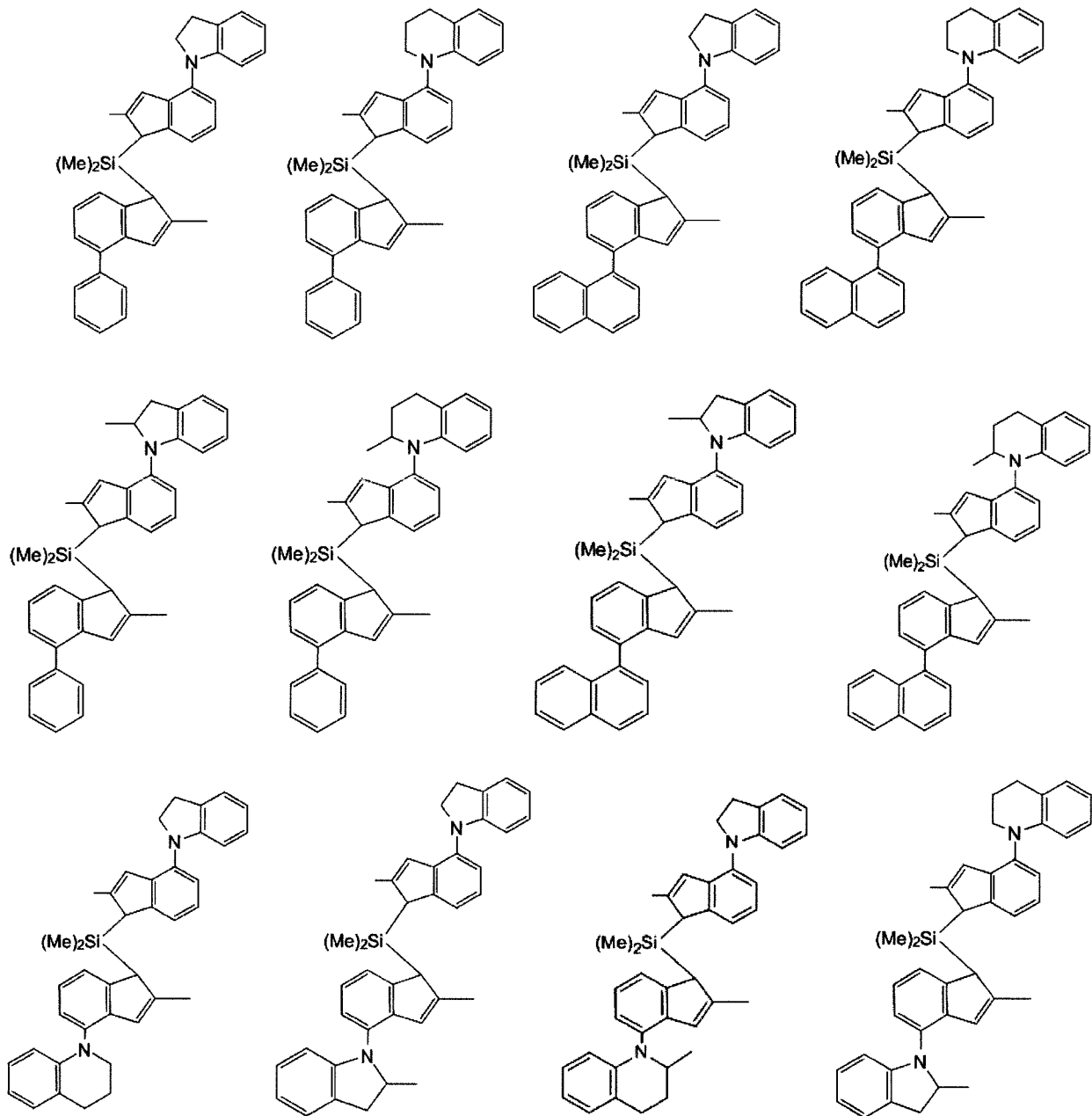
35

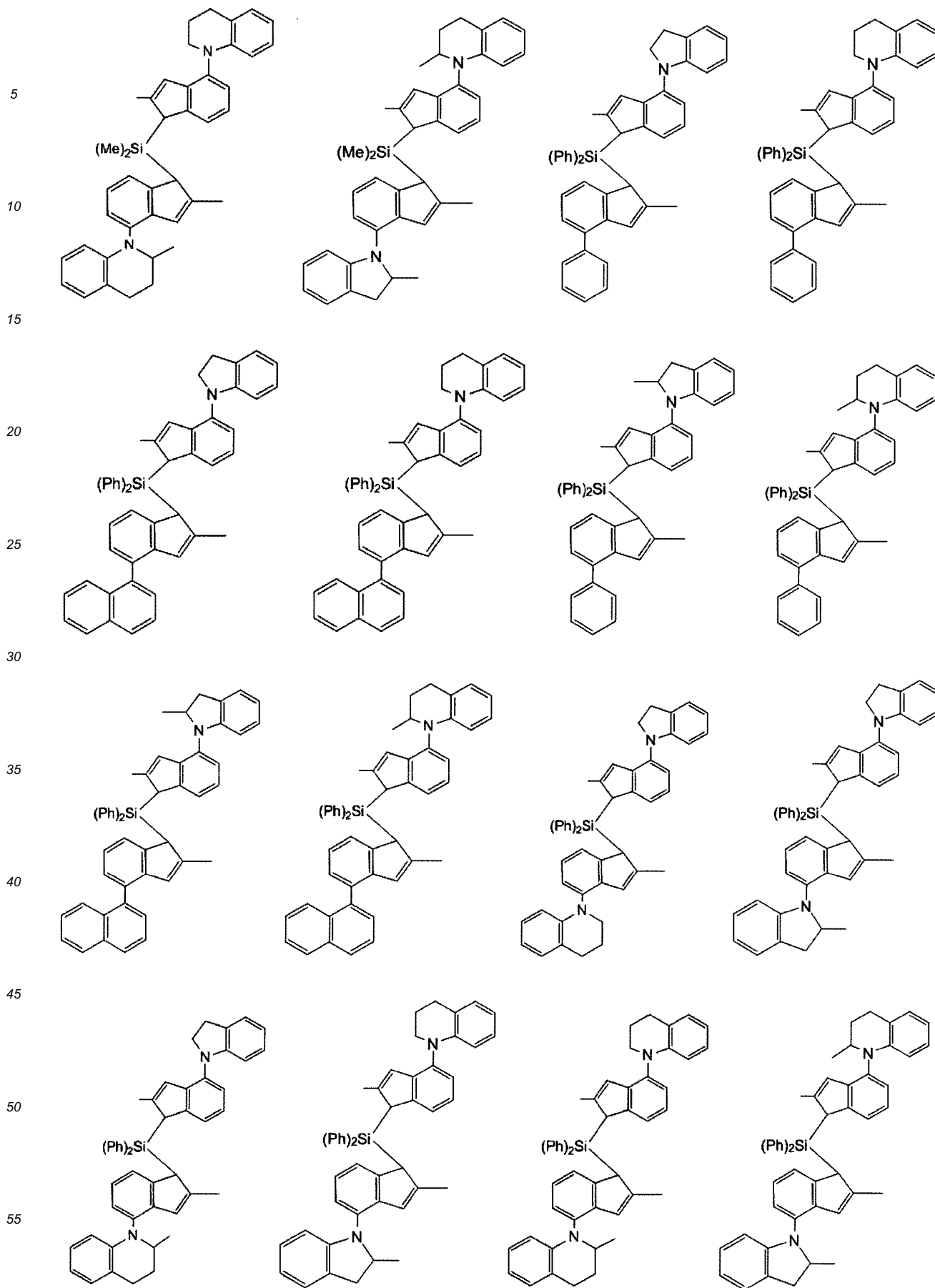
40

45

50

55





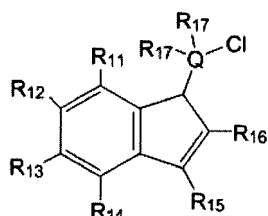
EP 2 918 591 B1

[0036] In structural formulae, Me means methyl group and Ph means phenyl group.

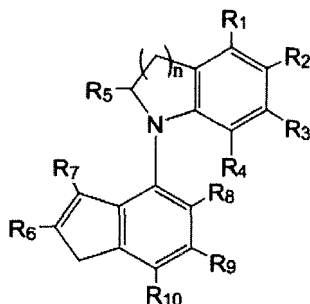
[0037] The compound represented by Chemical Formula 1 may be a ligand compound which can form a chelate with a metal

[0038] Furthermore, according to another aspect of the present invention, a preparation method of the ligand compound represented by the following Chemical Formula 1 including the step of carrying out the reaction of the compound represented by the following Chemical Formula 3 and the compound represented by the following Chemical Formula 4 or the lithium salt thereof is provided.

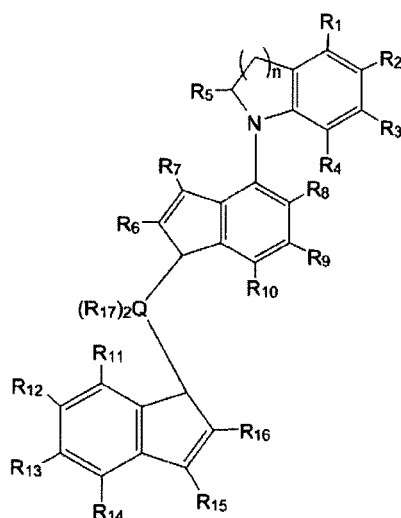
[Chemical Formula 3]



[Chemical Formula 4]



[Chemical Formula 1]



[0039] In Chemical Formulae 1, 3, and 4,
n is an integer of 1 to 2;

R₁ to R₁₆ are equal to or different from each other, and are independently hydrogen, a C₁-C₂₀ alkyl, a C₁-C₂₀ alkoxy, a

C₂-C₂₀ alkenyl, a C₆-C₂₀ aryl, a C₇-C₂₀ alkylaryl, a C₇-C₂₀ arylalkyl, a C₃-C₂₀ cycloalkyl, a C₅-C₂₀ heteroring, or silyl, and 2 or more adjacent groups among R₁ to R₁₆ may be connected together via an alkylidene group including a C₁-C₂₀ alkyl group or a C₆-C₂₀ aryl group to form a ring;

R₁₇ is hydrogen, a halogen, a C₁-C₂₀ alkyl, a C₆-C₂₀ aryl, or a C₁-C₂₀ alkoxy; and

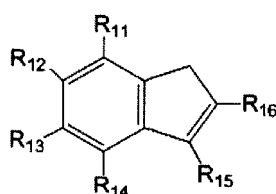
Q is carbon or silicon.

[0040] In the preparation method of the ligand compound, the compound represented by Chemical Formula 1 is prepared by the reaction of the compound represented by Chemical Formula 3 and the compound represented by Chemical Formula 4 or the lithium salt thereof.

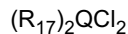
[0041] More specifically, according to one embodiment of the present invention, the lithium salt of the compound represented by Chemical Formula 4 is prepared by the reaction of the compound represented by Chemical Formula 4 and an organic lithium compound such as n-BuLi. After mixing the lithium salt with the compound represented by Chemical Formula 3, the ligand compound represented by Chemical Formula 1 may be obtained by carrying out the reaction of the mixture in the presence of ether and CuCN.

[0042] At this time, the compound represented by Chemical Formula 3 may be obtained by the reaction of the compound represented by Chemical Formula 5 or the lithium salt thereof and the compound represented by Chemical Formula 6. More specifically, the lithium salt of the compound represented by Chemical Formula 5 is prepared by the reaction of the compound represented by Chemical Formula 5 and an organic lithium compound such as n-BuLi. After mixing the lithium salt with the compound represented by Chemical Formula 6, the compound represented by Chemical Formula 3 may be obtained by carrying out the reaction of the mixture with stirring.

[Chemical Formula 5]

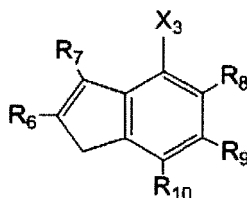


[Chemical Formula 6]

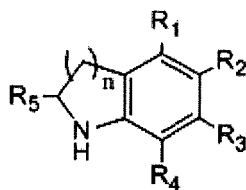


[0043] Furthermore, the compound represented by Chemical Formula 4 may be prepared by carrying out the coupling reaction of the indenyl halide compound represented by Chemical Formula 7 and the derivative compound of indoline or tetrahydroquinoline represented by Chemical Formula 8 in the presence of a base or a palladium catalyst to form C-N bond. At this time, the palladium catalyst is not limited particularly and, for example, it may be bis(tri(tert-butyl)phosphine)palladium (((tert-Bu)₃P)₂Pd), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄), palladium chloride (PdCl₂), palladium acetate (Pd(OAc)₂), bis(dibenzylideneacetone)palladium (Pd(dba)₂), and the like.

[Chemical Formula 7]



[Chemical Formula 8]

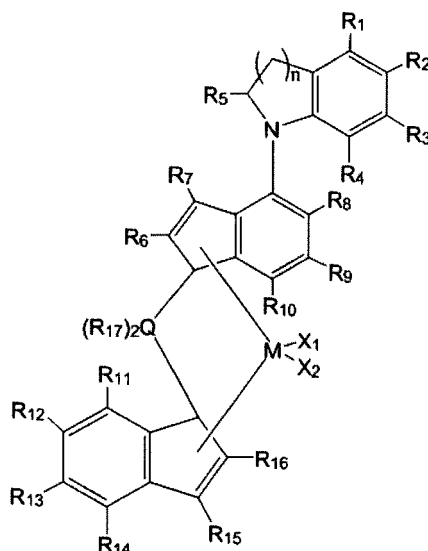


[0044] In Chemical Formulae 3 to 8, R_1 to R_{17} , Q, and n are the same as defined in Chemical Formula 1, and X_3 is a halogen.

[0045] According to the preparation method of the present invention, the ligand compound represented by Chemical Formula 1 may be obtained as any one form of racemic body or meso compound, or a mixture of the racemic body and the meso compound.

[0046] Furthermore, according to another aspect of the present invention, the transition metal compound represented by Chemical Formula 2 is provided. The transition metal compound of the present invention has the structure in which a Group 4 transition metal is combined with the ligand compound represented by Chemical Formula 1 by coordinate bond, and it may be represented by the following Chemical Formula 2.

[Chemical Formula 2]



[0047] In Chemical Formula 2,
n is an integer of 1 to 2;

R_1 to R_{16} are equal to or different from each other, and are independently hydrogen, a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_3 - C_{20} cycloalkyl, a C_5 - C_{20} heteroring, or silyl, and 2 or more adjacent groups among R_1 to R_{16} may be connected together via an alkyldiene group including a C_1 - C_{20} alkyl group or a C_6 - C_{20} aryl group to form a ring;

R_{17} is hydrogen, a halogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, or a C_1 - C_{20} alkoxy;

Q is carbon or silicon;

M is a Group 4 transition metal; and

X_1 and X_2 are equal to or different from each other, and are independently a halogen, a C_1 - C_{20} alkyl, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_1 - C_{20} alkylamino, a C_6 - C_{20} arylamino, or a C_1 - C_{20} alkyldiene group.

[0048] According to one embodiment of the present invention, R_1 to R_{16} may be independently hydrogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, or a C_5 - C_{20} heteroring, and R_{17} may be a C_1 - C_{20} alkyl or a C_6 - C_{20} aryl.

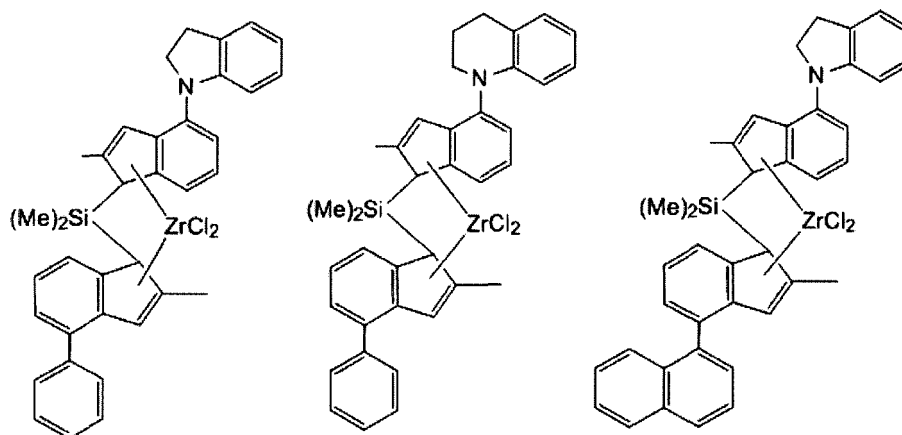
[0049] According to one embodiment of the present invention, the Group 4 transition metal corresponding to M may be Ti, Zr, Hf, and so on but it is not limited to or by them.

[0050] Furthermore, according to one embodiment of the present invention, the transition metal compound represented by Chemical Formula 2 may be represented by any one of the following structural formulae but it is not limited to or by them.

5

10

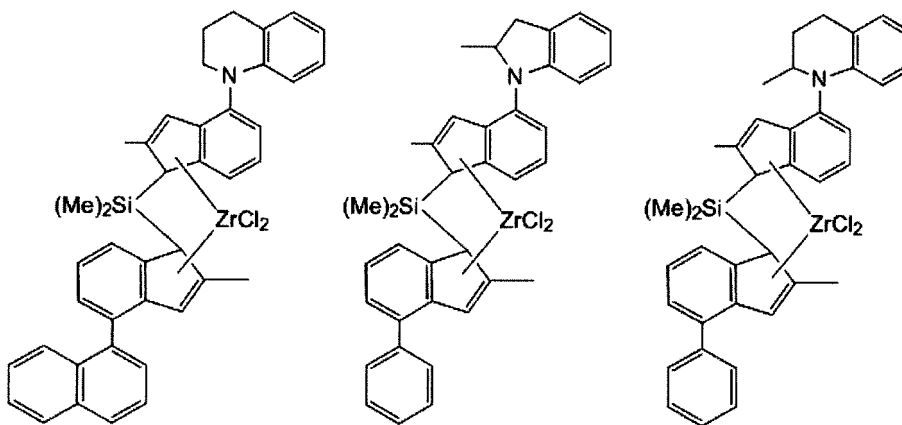
15



20

25

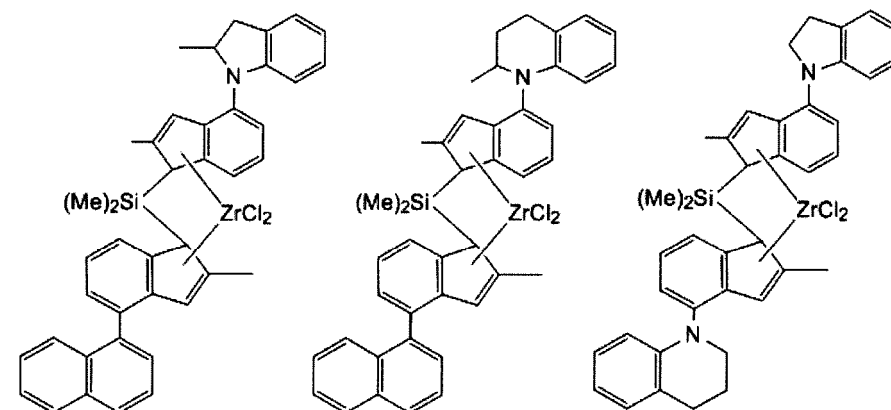
30



35

40

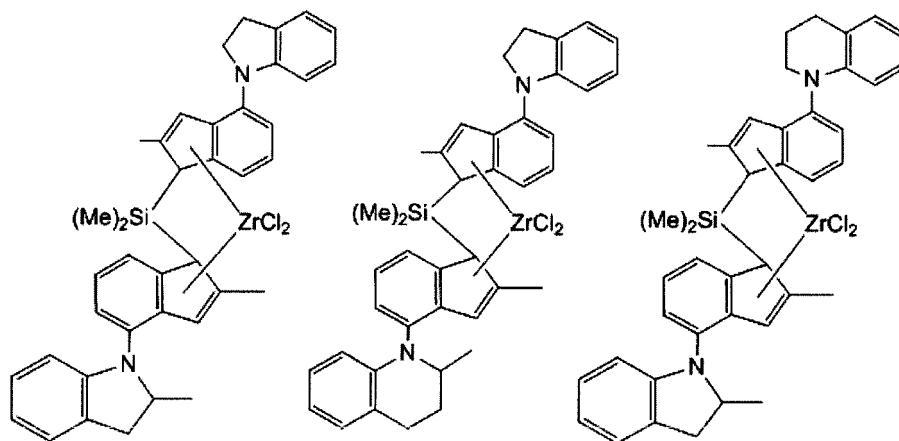
45



50

55

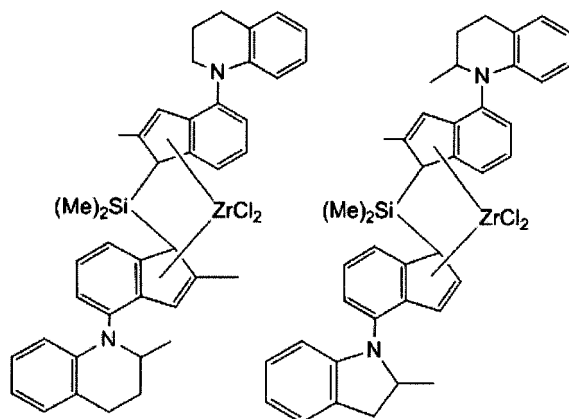
5



10

15

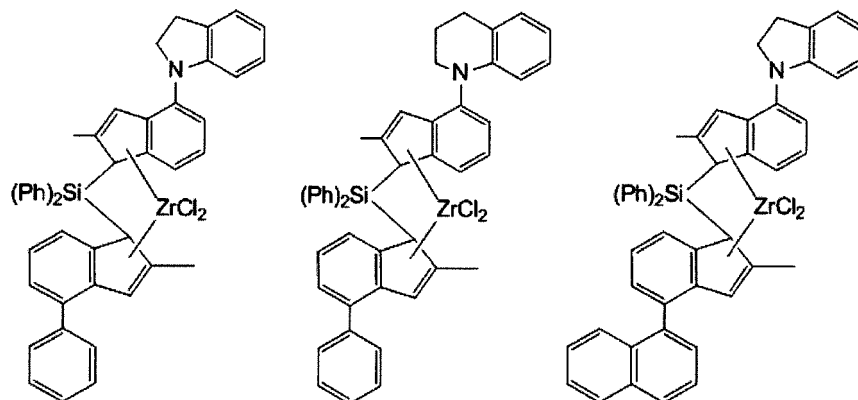
20



25

30

35



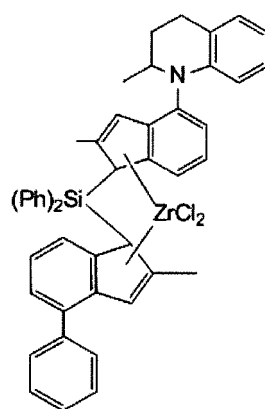
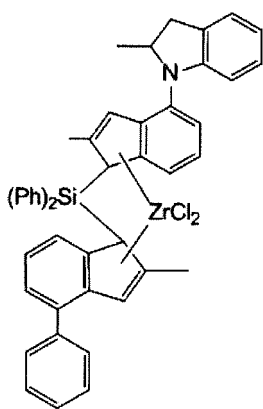
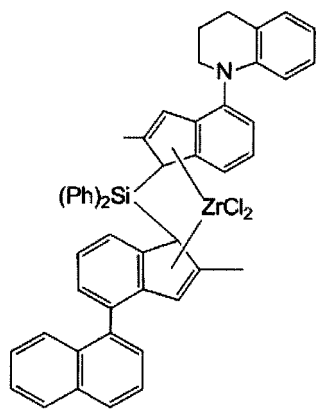
40

45

50

55

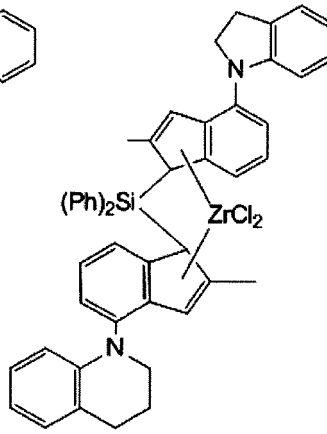
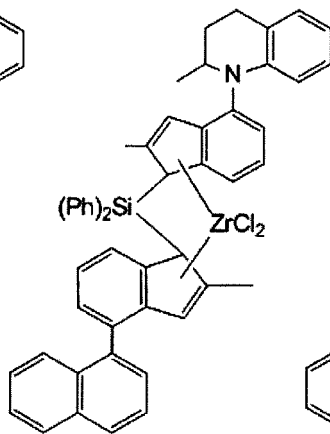
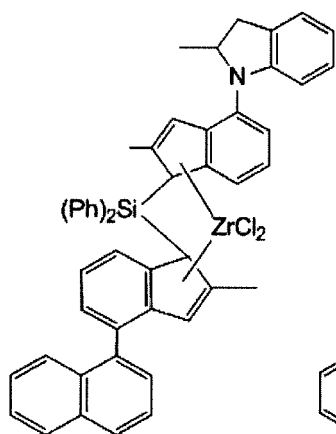
5



10

15

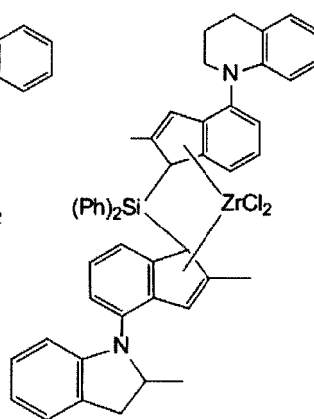
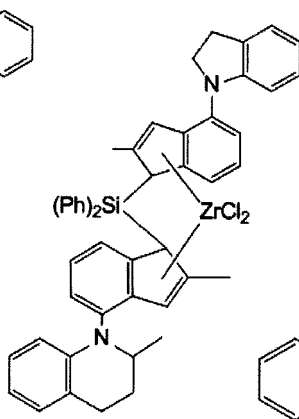
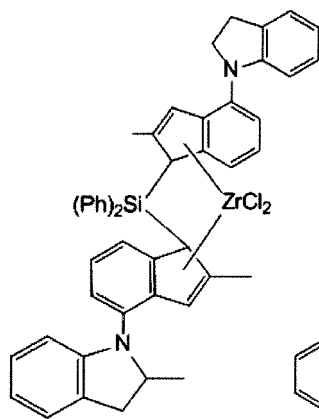
20



25

30

35



40

45

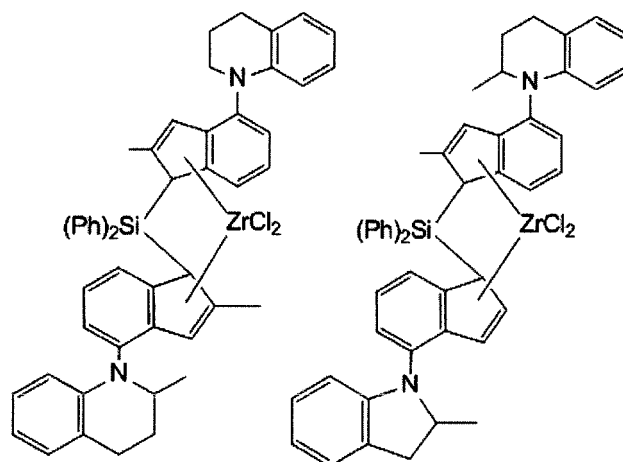
50

55

5

10

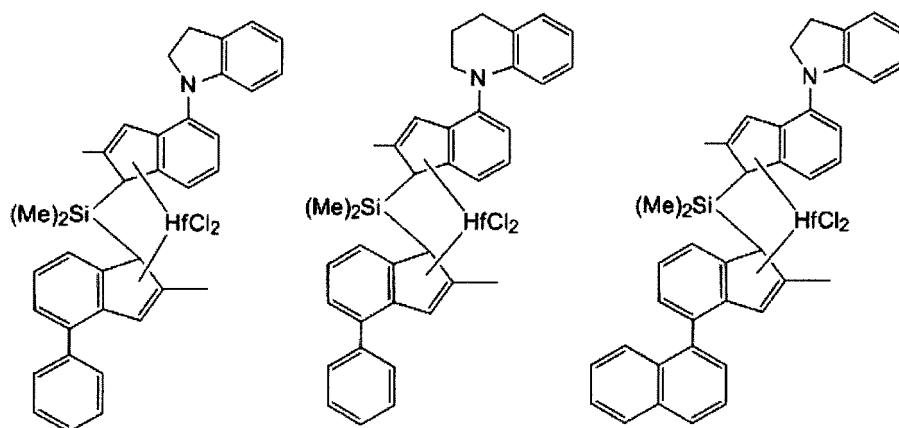
15



20

25

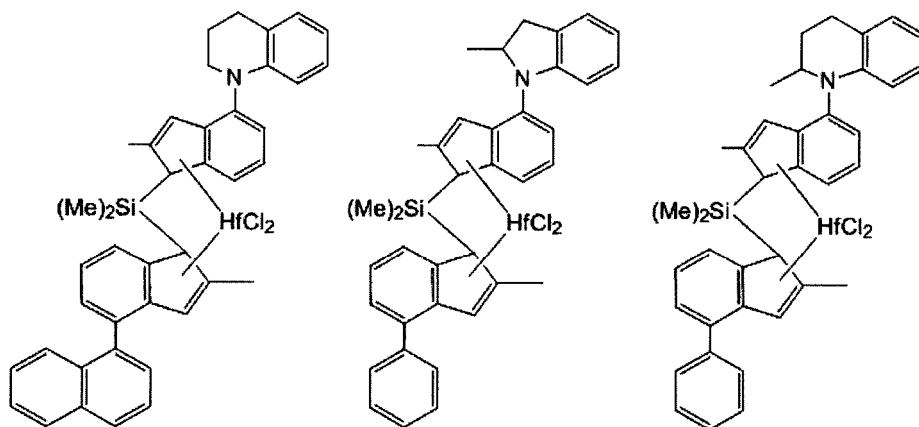
30



35

40

45



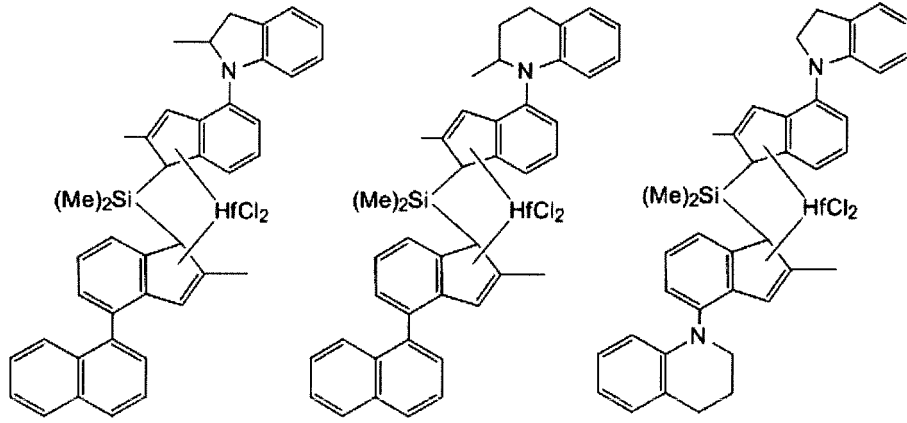
50

55

5

10

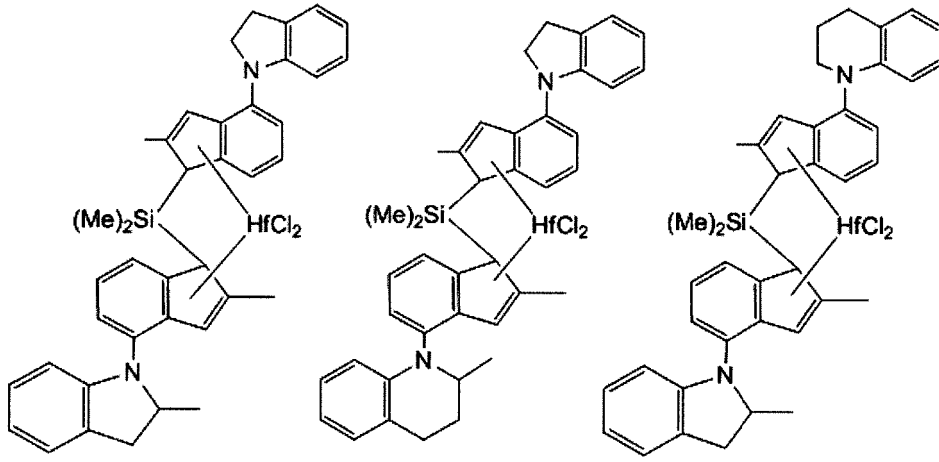
15



20

25

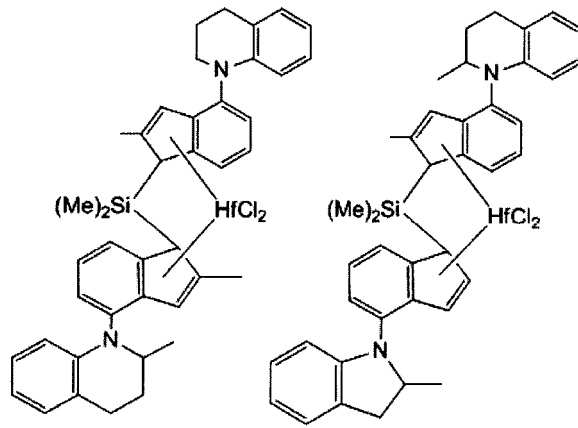
30



35

40

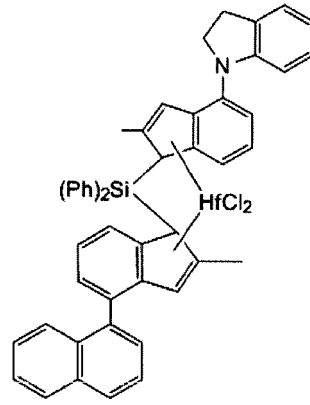
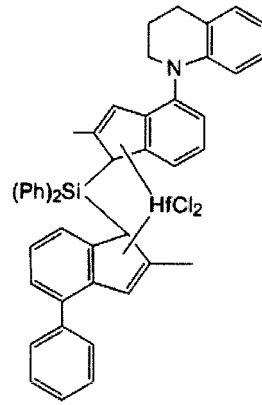
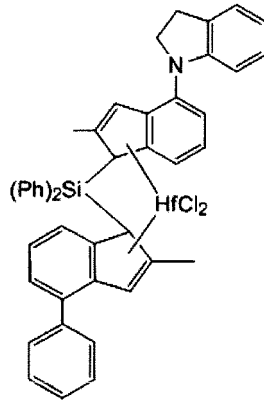
45



50

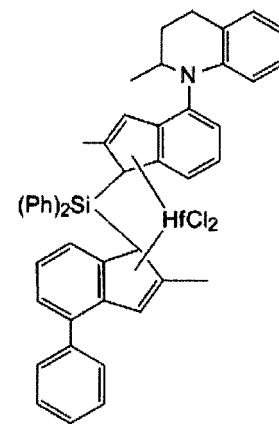
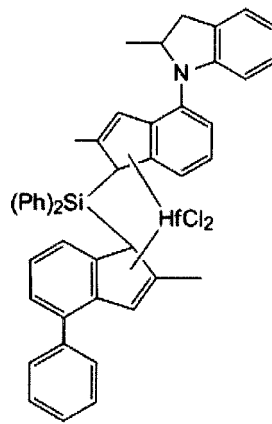
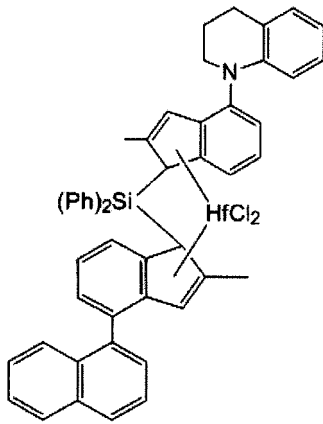
55

5



10

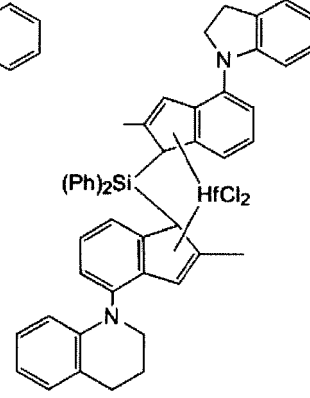
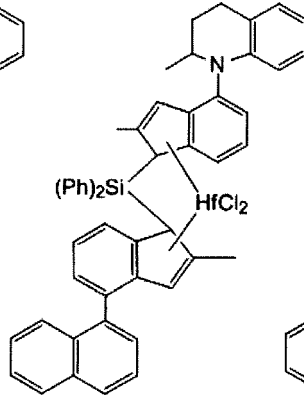
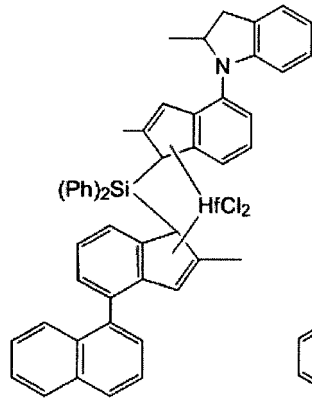
15



20

25

30



35

40

45

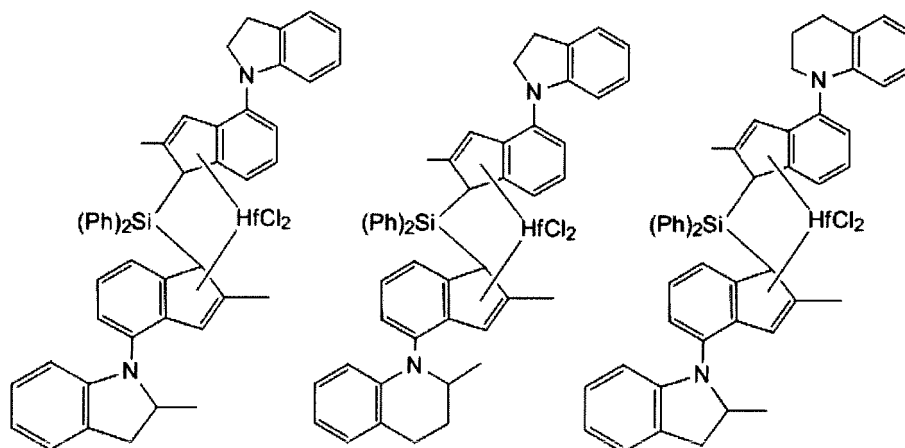
50

55

5

10

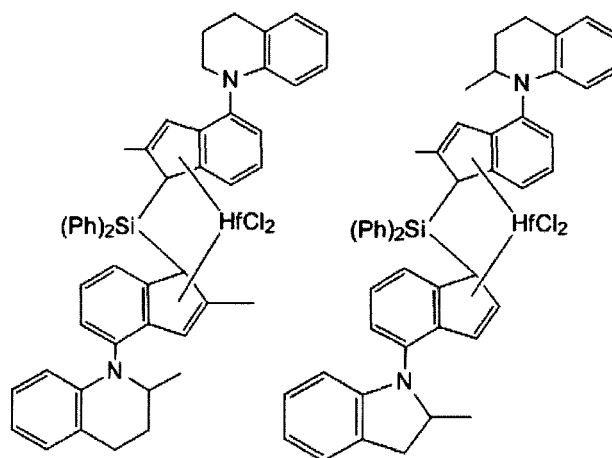
15



20

25

30



[0051] In the structural formulae, Me means methyl group and Ph means phenyl group.

35

[0052] Furthermore, according to another aspect of the present invention, a preparation method of the transition metal compound represented by Chemical Formula 2 is provided.

[0053] The preparation method of the transition metal compound according to another aspect of the present invention includes the step of carrying out the reaction of the ligand compound represented by the following Chemical Formula 1 and the compound represented by the following Chemical Formula 9.

40

45

50

55

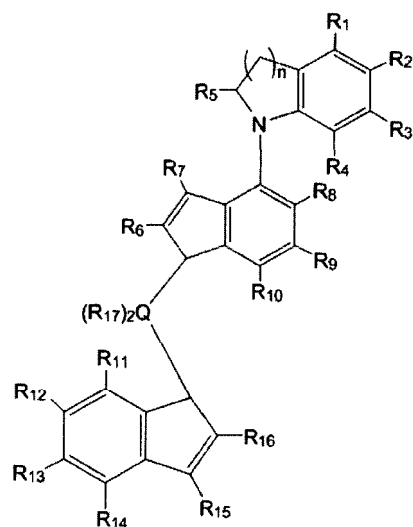
[Chemical Formula 1]

5

10

15

20



[Chemical Formula 9]

 $M(X_1X_2)_2$

25

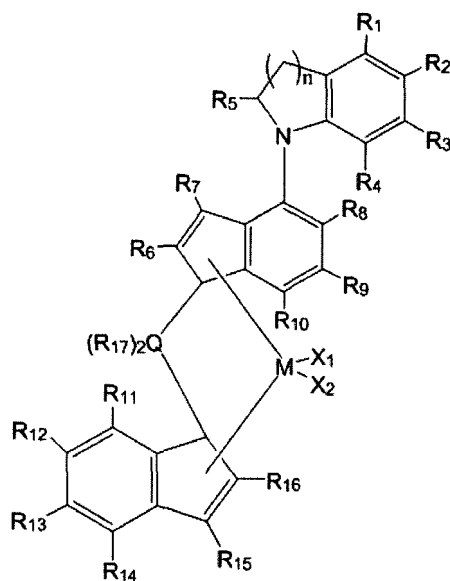
[Chemical Formula 2]

30

35

40

45



[0054] In the Chemical Formulae 1, 2, and 9,
n is an integer of 1 to 2;

50 R_1 to R_{16} are equal to or different from each other, and are independently hydrogen, a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_3 - C_{20} cycloalkyl, a C_5 - C_{20} heteroring, or silyl, and 2 or more adjacent groups among R_1 to R_{16} may be connected together via an alkylidene group including a C_1 - C_{20} alkyl group or a C_6 - C_{20} aryl group to form a ring;

R_{17} is hydrogen, a halogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, or a C_1 - C_{20} alkoxy;

55 Q is carbon or silicon;

M is a Group 4 transition metal; and

X_1 and X_2 are equal to or different from each other, and are independently a halogen, a C_1 - C_{20} alkyl, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_1 - C_{20} alkylamino, a C_6 - C_{20} arylamino, or a C_1 - C_{20} alkylidene group.

[0055] According to one embodiment of the present invention, the Group 4 transition metal corresponding to M may be Ti, Zr, Hf, and so on but it is not limited to or by them.

[0056] More specifically, at first, the ligand compound represented by Chemical Formula 1 is made into the lithium salt thereof by the reaction with an organic lithium compound such as n-BuLi. The lithium salt is mixed with the metal source represented by Chemical Formula 9 and the mixture is stirred to react. The reaction product is filtered and the precipitate is obtained. And then, the organic metal compound represented by Chemical Formula 2 having the complex form in which a metal atom is combined with the ligand compound is obtained by washing the precipitate and drying the same under decompression.

[0057] According to the preparation method of the present invention, the transition metal compound represented by Chemical Formula 2 may be obtained respectively as any one of racemic body or meso compound, or a mixture of the racemic body and the meso compound. When the compound is a mixture of the racemic body and the meso compound, it is possible to obtain only the racemic body of the transition metal compound finally through a recrystallization step.

[0058] The ligand compound represented by Chemical Formula 1 and the transition metal compound represented by Chemical Formula 2 have a structure in which bisindenyl groups are crosslinked by carbon or silicon, and each indenyl group is connected to indoline group or tetrahydroquinoline group so as to show C1-asymmetric crosslinking structure. Since the transition metal compound of the present invention includes indoline group or tetrahydroquinoline group which is plenty of electrons as disclosed above, electron density of the center metal of the same increases, the stability at high temperature thereof is high, and it can be usefully used to synthesize polyolefin polymers of high molecular weight, particularly, isotactic polyolefin polymers, for example, isotactic polypropylene.

[0059] The ligand compound of novel structure according to the present invention and the transition metal compound including the same may be used as a polymerization reaction catalyst for preparing olefin polymers.

[0060] Hereinafter, preferable examples and comparative examples are presented for understanding the present invention. However, the following examples are only for illustrating the present invention and the present invention is not limited to or by them.

<Examples>

[0061] In the following Examples, term "overnight" or "through the night" means about 12 to 16 hrs and term "room temperature" means the temperature of about 20 to 30 °C. Organic reagents and solvents were purchased from Aldrich Co., Ltd. and Merck Co., Ltd. and refined by a standard method before use. In every steps of the syntheses, contact with air or moisture was cut off for increasing repeatability of experimental. NMR spectrum was obtained by using a 500MHz NMR spectrometer for confirming the structure of the produced compound.

Synthesis of ligand compound and transition metal compound

Example 1

Example 1-1: synthesis of 1-(2-methyl-1H-inden-4-yl)-1,2,3,4-tetrahydroquinoline

[0062] After putting 4-bromo-2-methyl-1H-indene (10 g, 47.83 mmol) in a 500 mL 2-neck Schlenk flask, LiOtBu (11.49 g, 143.49 mmol) was weighed in a glove box and tetrahydroquinone (6.244 mL, 49.74 mmol) was put in the flask. The palladium catalyst Pd(P(tBu)₃)₂ (0.049 g, 0.096 mmol) in another 100 mL schlenk flask was weighed in a glove box. After transferring the palladium catalyst to the flask in which tetrahydroquinone was, the reaction was carried out at 110°C for 4 hrs 30 mins and worked up. The reaction product was quenched by putting water in the flask and extracted with methylene chloride (MC), and then water was eliminated therefrom with Na₂SO₄ and the rest was vacuum dried. The compound of orange color (10.5 g, 84 % yield) was obtained.

[0063] ¹H-NMR (CDCl₃): δ 7.41 ~ 7.36 (m, 3H in isomers), 7.27 ~ 7.16 (m, 8H in isomers), 6.98 (t, 3H in isomers), 6.74 (m, 3H in isomers), 6.61 (m, 2H in isomers), 6.44 (s, 1H in isomers), 6.43 (d, 1H in isomers), 6.38 (d, 1H in isomers), 3.74 ~ 3.72 (m, 6H in isomers), 3.46 (s, 3H in isomers), 3.24 (s, 3H in isomers), 3.04 ~ 3.02 (m, 6H in isomers), 2.32 ~ 2.22 (m, 15H in somers)

Example 1-2: synthesis of chloro(2-methyl-4-phenyl-1H-inden-1-yl) dimethyl silane

[0064] n-BuLi (2.5 M in n-Hx) (1.1 eq, 9.38 mL) was slowly added to 2-methyl-4-phenylindene (4.4 g, 21.3 mmol) and diethyl ether (100 mL) dropwise at -78 °C, and the reaction of the mixture was carried out at room temperature through the night. After the reaction, the lithium salt was obtained by vacuum drying the product and filtering the same with hexane. After dispersing the obtained lithium salt in hexane again and adding (CH₃)₂SiCl₂ (dichlorodimethyl silane) (10 eq, 27.5 mL in hexane) thereto dropwise at -78 °C, the reaction of the mixture was carried out at room temperature

through the night. The compound of light yellow solid form was obtained with the yield of 93 % by line-filtering and vacuum drying the reaction product.

[0065] $^1\text{H-NMR}$ (CDCl_3): δ 7.28 (d, 2H), 7.22 ~ 7.21 (m, 3H), 7.13 (t, 1H), 7.06 (d, 1H), 6.96 (t, 1H), 6.56 (s, 1H), 3.43 (s, 1H), 2.04 (s, 3H), 0.205 (s, 3H), -0.033 (s, 3H)

Example 1-3: synthesis of (4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-phenyl-2-methyl-1H-inden-1-yl)dimethyl silane

[0066] After putting 1-(2-methyl-1H-inden-4-yl)-1,2,3,4-tetrahydroquinole (2.2 g, 8.42 mmol) in a 100 mL Schlenk flask and dissolving the starting material by adding 40 mL of dry diethyl ether thereto, n-BuLi (2.5 M in n-Hx) (3.7 mL) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product (2.2 g, 98 % yield) of white solid was obtained. After putting the lithiated product (2.2 g, 8.03 mmol), chloro(2-methyl-4-phenyl-1H-inden-1-yl) dimethyl silane (2.40 g, 8.03 mmol), and copper cyanide (0.026 g, 0.29 mmol) in a 250 mL Schlenk flask in a glove box, 80 mL of dry diethyl ether was added thereto at -78 °C and the mixture was stirred at room temperature through the night. The reaction was terminated by adding 100 mL of aqueous NH_4Cl and 100 mL of deionized water after the reaction.

[0067] After separating the organic layer from water layer, the ligand compound of light yellowish solid (4.20 g, quantitative yield compared to the lithiated product, 99 % yield compared to the starting material) was obtained by drying the organic layer with MgSO_4 and filtering and vacuum drying the same. As the result of $^1\text{H-NMR}$ analysis, the ratio of rac:meso was about 1:1.

[0068] $^1\text{H-NMR}$ (CDCl_3): δ 7.55 ~ 7.12 (m, 22H in rac- and meso-isomers), 7.04 (dd, 2H in rac- and meso-isomers), 6.85 ~ 6.80 (m, 4H in rac- and meso-isomers), 6.63 (td, 2H in rac- and meso-isomers), 6.47 (s, 2H in rac- and meso-isomers), 6.29 (d, 2H in rac- and meso-isomers), 3.81 (s, 2H in rac-isomer), 3.80 (s, 2H in meso-isomer), 3.70 ~ 3.59 (m, 4H in rac- and meso-isomers), 2.94 (t, 4H in rac- and meso-isomers), 2.27 (d, 2H in rac- and meso-isomers), 2.20 (d, 6H in meso-isomer), 2.18 (d, 6H in rac-isomer), 2.13 ~ 2.08 (m, 8H in rac- and meso-isomers), -0.22 (s, 3H in meso-isomer), 0.23 (d, 6H in rac-isomer), -0.25 (s, 3H in meso-isomer).

Example 1-4: synthesis of rac-dimethylsilylene-(4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-phenyl-2-methyl-1H-inden-1-yl) zirconium dichloride

[0069] After putting 1.4 g of (4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-phenyl-2-methyl-1H-inden-1-yl) dimethyl silane (2.67 mmol, rac:meso=1:1) in a 100 mL Schlenk flask and dissolving the starting material by adding 30 mL of dry diethyl ether thereto, 2.4 mL of n-BuLi (2.5 M in n-Hx) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product of white solid was obtained. After putting the lithiated product and ZrCl_4 (0.69 g, 2.94 mmol) in a 100 mL Schlenk flask in a glove box, 15 mL of dry hexane and 15 mL of diethyl ether were added thereto in order at -78 °C and the mixture was stirred at room temperature through the night. After the reaction was terminated, the product was filtered with a glass frit (G4) on which celite spread. The remaining solid on the glass frit was dissolved out by using dichloromethane (DCM). The red solid was obtained by vacuum drying the DCM filtrate. As the result of $^1\text{H-NMR}$ analysis, both of two solids were Zr complex of rac:meso=1:1. The crude product was collected and recrystallized with dry toluene and hexane in a freezer of -30 °C for 3 days. The obtained red solid was filtered with a glass frit (G4) and washed twice with 10 mL of dry n-hexane, and then 0.2 g of the final product (11 % yield) of racemic body was obtained by vacuum drying the solid.

[0070] $^1\text{H-NMR}$ (CDCl_3): δ 7.61 ~ 7.30 (m, 8H), 7.14 (d, 1H), 7.07 ~ 6.99 (m, 3H), 6.88 (s, 1H), 6.80 ~ 6.75 (m, 1H), 6.63 (t, 1H), 6.57 (s, 1H), 6.29 (d, 1H), 3.79 ~ 3.75 (m, 2H), 2.83 ~ 2.78 (m, 2H), 2.23 (s, 3H), 2.18 (s, 3H), 2.05 ~ 1.94 (m, 2H), 1.29 (s, 6H)

Example 2

Synthesis of rac-dimethylsilylene-(4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-phenyl-2-methyl-1H-inden-1-yl) hafnium dichloride

[0071] After putting 1.6 g of (4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-phenyl-2-methyl-1H-inden-1-yl) dimethyl silane of Example 1-3 (3.05 mmol, rac:meso=1:1) in a 100 mL Schlenk flask and dissolving the starting material by adding 40 mL of dry diethyl ether thereto, 2.7 mL of n-BuLi (2.5 M in n-Hx) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product of white solid was obtained. After

EP 2 918 591 B1

putting the lithiated product and HfCl_4 (1.1 g, 3.36 mmol) in a 100 mL Schlenk flask in a glove box, 20 mL of dry hexane and 20 mL of diethyl ether were added thereto in order at -78°C and the mixture was stirred at room temperature through the night. After the reaction was terminated, the product was filtered with a glass frit (G4) on which celite spread. The remaining solid on the glass frit was dissolved out by using dichloromethane (DCM). The red solid was obtained by vacuum drying the DCM filtrate. As the result of $^1\text{H-NMR}$ analysis, both of two solids were Hf complex of rac:meso=1:1. After collecting the crude product and storing the same in the oil bath of 45°C , 30 mL of dry toluene was added thereto with stirring for dissolving the same. The solution was stored in a freezer of -30°C for 3 days for recrystallization. The obtained red solid was filtered with a glass frit (G4) and washed twice with 10 mL of dry n-hexane, and then 0.4 g of the final product (17 % yield) of racemic body was obtained by vacuum drying the solid.

[0072] $^1\text{H-NMR}$ (CDCl_3): δ 7.64 (td, 1H), 7.57 ~ 7.55 (m, 2H), 7.41 ~ 7.38 (m, 3H), 7.32 ~ 7.27 (m, 3H), 7.15 ~ 7.09 (m, 2H), 7.04 ~ 6.97 (m, 3H), 6.80 (t, 1H), 6.62 (td, 1H), 6.48 (s, 1H), 3.76 ~ 3.75 (m, 2H), 2.82 ~ 2.78 (m, 2H), 2.31 (s, 3H), 2.27 (s, 3H), 2.06 ~ 1.91 (m, 2H), 1.28 (s, 6H)

Example 3

Example 3-1: synthesis of (4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) dimethyl silane

[0073] After putting 1-(2-methyl-1H-inden-4-yl)-1,2,3,4-tetrahydroquinole of Example 1-1 (3.0 g, 11.5 mmol) in a 100 mL Schlenk flask and dissolving the starting material by adding 60 mL of dry diethyl ether thereto, n-BuLi (2.5 M in n-Hx) (5.1 mL) was added thereto at -78°C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product (3.0 g, 98 % yield) of white solid was obtained. After putting the lithiated product (3.0 g, 11.2 mmol), chloro(2-methyl-4-naphthyl-1H-inden-1-yl) dimethyl silane (3.9 g, 11.2 mmol), and copper cyanide (0.036 g, 0.40 mmol) in a 250 mL Schlenk flask in a glove box, 110 mL of dry diethyl ether was added thereto at -78°C and the mixture was stirred at room temperature through the night. The reaction was terminated by adding 150 mL of aqueous NH_4Cl and 150 mL of deionized water after the reaction.

[0074] After separating the organic layer from water layer, the ligand compound of light yellowish solid (6.3 g, quantitative yield compared to the lithiated product, 98 % yield compared to the starting material) was obtained by drying the organic layer with MgSO_4 and filtering and vacuum drying the same. As the result of $^1\text{H-NMR}$ analysis, the ratio of rac:meso was about 1:1.

[0075] $^1\text{H-NMR}$ (CDCl_3): δ 7.90 ~ 7.02 (m, 30H in rac- and meso-isomers), 6.86 ~ 6.83 (m, 2H in rac- and meso-isomers), 6.60 (t, 2H in rac- and meso-isomers), 6.50 ~ 6.48 (m, 2H in rac- and meso-isomers), 6.31 ~ 6.29 (s, 2H in rac- and meso-isomers), 3.88 ~ 3.80 (m, 4H in rac- and meso-isomers), 3.67 ~ 3.58 (m, 4H in rac- and meso-isomers), 2.92 ~ 2.89 (m, 4H in rac- and meso-isomers), 2.25 ~ 2.06 (m, 16H in rac- and meso-isomers), -0.18 ~ -0.23 (m, 12H in rac- and meso-isomers)

Example 3-2: synthesis of rac-dimethylsilylene-(4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) zirconium dichloride

[0076] After putting 2.9 g of (4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) dimethyl silane (5.05 mmol, rac:meso=1:1) in a 100 mL Schlenk flask and dissolving the starting material by adding 50 mL of dry diethyl ether thereto, 4.5 mL of n-BuLi (2.5 M in n-Hx) was added thereto at -78°C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product of white solid was obtained. After putting the lithiated product and ZrCl_4 (1.3 g, 5.56 mmol) in a 100 mL Schlenk flask in a glove box, 20 mL of dry hexane and 20 mL of diethyl ether were added thereto in order at -78°C and the mixture was stirred at room temperature through the night. After the reaction was terminated, the product was filtered with a glass frit (G4) on which celite spread. The remaining solid on the glass frit was dissolved out by using dichloromethane (DCM). The red solid was obtained by vacuum drying the DCM filtrate. As the result of $^1\text{H-NMR}$ analysis, the solid was Zr complex of rac:meso=3:1. The crude product was collected and recrystallized with dry toluene and pentane in a freezer of -30°C for 3 days. The obtained red solid was filtered with a glass frit (G4) and washed twice with 10 mL of dry n-pentane, and then 1.07 g of the final product (29 % yield) of racemic body was obtained by vacuum drying the solid.

[0077] $^1\text{H-NMR}$ (CDCl_3): δ 7.86 ~ 6.77 (m, 17H), 6.59 (s, 1H), 6.40 (s, 1H), 3.81 ~ 3.72 (m, 2H), 2.85 ~ 2.82 (m, 2H), 2.23 (s, 3H), 2.15 (s, 3H), 2.10 ~ 1.95 (m, 2H), 1.32 (s, 3H), 1.29 (s, 3H)

Example 4Synthesis of rac-dimethylsilylene-(4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) zirconium dichloride

5 **[0078]** After putting 2.7 g of (4-(3,4-dihydroquinolin-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) dimethyl silane of Example 3-1 (4.70 mmol, rac:meso=1:1) in a 100 mL Schlenk flask and dissolving the starting material by adding 25 mL of dry diethyl ether thereto, 4.14 mL of n-BuLi (2.5 M in n-Hx) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product of white solid was obtained. 10 After putting the lithiated product and HfCl₄ (1.66 g, 5.18 mmol) in a 100 mL Schlenk flask in a glove box, 20 mL of dry hexane and 350 mL of diethyl ether were added thereto in order at -78 °C and the mixture was stirred at room temperature through the night. After the reaction was terminated, the product was filtered with a glass frit (G4) on which celite spread. 15 The remaining solid on the glass frit was dissolved out by using dichloromethane (DCM). The orange solid was obtained by vacuum drying the DCM filtrate. As the result of ¹H-NMR analysis, the solid was Hf complex of rac:meso=4:1. The crude product was collected and recrystallized with dry toluene and pentane in a freezer of -30 °C for 3 days. The obtained yellow solid was filtered with a glass frit (G4) and washed twice with 10 mL of dry n-pentane, and then 1.00 g of the final product (26 % yield) of racemic body was obtained by vacuum drying the solid.

20 **[0079]** ¹H-NMR (CDCl₃): δ 7.85 ~ 6.62 (m, 17H), 6.50 (s, 1H), 6.31 (s, 1H), 3.75 ~ 3.74 (m, 2H), 2.84 ~ 2.82 (m, 2H), 2.32 (s, 3H), 2.23 (s, 3H), 2.07 ~ 1.92 (m, 2H), 1.31 (s, 3H), 1.28 (s, 3H)

Example 5Example 5-1: synthesis of (4-(indoline-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) dimethyl silane

25 **[0080]** After putting 1-(2-methyl-1H-inden-4-yl)-indoline (0.43 g, 1.73 mmol) in a 100 mL Schlenk flask and dissolving the starting material by adding 8.7 mL of dry diethyl ether thereto, n-BuLi (2.5 M in n-Hx) (0.76 mL) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product (0.42 g, 96 % yield) of white solid was obtained. After putting the lithiated product (0.42 g, 1.66 mmol), chloro(2-methyl-4-naphthyl-1H-inden-1-yl) dimethyl silane (0.58 g, 1.66 mmol), and copper cyanide (6.0 mg, 0.067 mmol) in a 1000 mL Schlenk flask in a glove box, 16 mL of dry diethyl ether was added thereto at -78 °C and the mixture was stirred at room temperature through the night. The reaction was terminated by adding 20 mL of deionized water after the reaction. 30

35 **[0081]** After separating the organic layer from water layer, the ligand compound of light yellowish solid (0.79 g, quantitative yield compared to the lithiated product, 85 % yield compared to the starting material) was obtained by drying the organic layer with MgSO₄ and filtering and vacuum drying the same. As the result of ¹H-NMR analysis, the ratio of rac:meso was about 1:1.

40 **[0082]** ¹H-NMR (CDCl₃): δ 7.93 ~ 6.21 (m, 19H in rac- and meso-isomers), 3.75 ~ 3.54 (m, 4H in rac- and meso-isomers), 2.90 ~ 2.76 (m, 2H in rac- and meso-isomers), 2.01 ~ 1.75 (m, 6H in rac- and meso-isomers), -0.17 ~ -0.26 (m, 6H in rac- and meso-isomers)

Example 5-2: synthesis of rac-dimethylsilylene-(4-(indoline-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) zirconium dichloride

45 **[0083]** After putting 0.772 g of (4-(indoline-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) dimethyl silane (1.39 mmol, rac:meso=1:1) in a 100 mL Schlenk flask and dissolving the starting material by adding 13 mL of dry diethyl ether thereto, 1.16 mL of n-BuLi (2.5 M in n-Hx) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product of white solid was obtained. After putting the lithiated product and ZrCl₄ (0.354 g, 1.53 mmol) in a 100 mL Schlenk flask in a glove box, 13 mL of dry hexane and 350 mL of diethyl ether were added thereto in order at -78 °C and the mixture was stirred at room temperature through the night. After the reaction was terminated, the product was filtered with a glass frit (G4) on which celite spread. The remaining solid on the glass frit was dissolved out by using dichloromethane (DCM). The orange solid was obtained by vacuum drying the DCM filtrate. As the result of ¹H-NMR analysis, the solid was Zr complex of rac:meso=3:1. The crude product was collected and recrystallized with dry toluene in a freezer of -30 °C for 3 days. The obtained orange solid was filtered with a glass frit (G4) and washed twice with 10 mL of dry toluene, and then 0.11 g of the final product (11 % yield) of racemic body was obtained by vacuum drying the solid. 55

[0084] $^1\text{H-NMR}$ (toluene- d_6): δ 8.20 ~ 8.18 (dd, 1H), 7.75 (d, 1H), 7.58 (d, 1H), 7.49 (d, 1H), 7.30 ~ 6.87 (m, 1H), 6.75 ~ 6.70 (m, 2H), 6.53 (s, 1H), 4.14 ~ 4.03 (m, 2H), 2.73 ~ 2.71 (m, 2H), 2.12 (s, 3H), 1.88 (s, 3H), 0.91 (s, 3H), 0.86 (s, 3H)

Example 6

Synthesis of rac-dimethylsilylene-(4-(indoline-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) hafnium dichloride

[0085] After putting 2.0 g of (4-(indoline-1(2H)-yl)-2-methyl-1H-inden-1-yl)(4-naphthyl-2-methyl-1H-inden-1-yl) dimethyl silane of Example 5-1 (3.57 mmol, rac:meso=1:1) in a 100 mL Schlenk flask and dissolving the starting material by adding 18 mL of dry diethyl ether thereto, 3.14 mL of n-BuLi (2.5 M in n-Hx) was added thereto at -78 °C and the mixture was stirred at room temperature through the night. And then, the mixture was filtered by using a glass frit (G4). The remaining solid on the glass frit was vacuum dried and the lithiated product of white solid was obtained. After putting the lithiated product and HfCl_4 (1.26 g, 3.93 mmol) in a 100 mL Schlenk flask in a glove box, 18 mL of dry toluene was added thereto at -78 °C and the mixture was stirred at room temperature through the night. After the reaction was terminated, the product was filtered with a glass frit (G4) on which celite spread. The remaining solid on the glass frit was dissolved out by using dichloromethane (DCM). The orange solid was obtained by vacuum drying the DCM filtrate. As the result of $^1\text{H-NMR}$ analysis, the solid was Zr complex of rac:meso=3:1. The crude product was collected and recrystallized with dry toluene in a freezer of -30 °C for 3 days. The obtained yellow solid was filtered with a glass frit (G4) and washed twice with 10 mL of dry toluene, and then 0.3 g of the final product (10 % yield) of racemic body was obtained by vacuum drying the solid.

[0086] $^1\text{H-NMR}$ (toluene- d_6): δ 8.12 (d, 1H), 7.76 (d, 1H), 7.62 (d, 1H), 7.55 (d, 1H), 7.51 (d, 1H), 7.27 ~ 6.85 (m, 10H), 6.70 ~ 6.67 (m, 2H), 6.42 (s, 1H), 4.07 ~ 3.98 (m, 2H), 2.70 ~ 2.67 (m, 2H), 2.19 (s, 3H), 1.95 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H)

Comparative Example 1

rac-1,1'-dimethylsilylene-bis(indenyl) hafnium dichloride

[0087] rac-1,1'-dimethylsilylene-bis(indenyl) hafnium dichloride compound was synthesized according to Example 1 disclosed in U.S. Patent No. 5,905,162.

Preparation of propylene homopolymer

Example 7

[0088] After putting toluene solvent (0.2 L) in a 250 mL miniclave reactor, the temperature of the reactor was preheated to 70 °C. After putting 0.2 mL of 5×10^{-6} M dimethylanilinium tetrakis(pentafluorophenyl) borate cocatalyst in the reactor with a syringe, the transition metal compound of Example 1 (1×10^{-6} M, 0.1 mL) treated with triisobutylaluminum compound was put in the reactor. The reaction was carried out for 10 mins while injecting 5 bar propylene therein. After carrying out the reaction for 10 mins, the remaining gas was removed therefrom and the precipitation was induced by adding the polymer solution to an excess of ethanol and cooling the same. The obtained polymer was washed with ethanol and acetone respectively twice or thrice and dried for 12 hrs or more in a vacuum oven of 80 °C. And then, the properties of the polymer were measured.

Example 8

[0089] The olefin polymer was prepared according to the same method as in Example 7, except that the transition metal compound of Example 2 was used.

Example 9

[0090] The olefin polymer was prepared according to the same method as in Example 7, except that the transition metal compound of Example 3 was used.

Example 10

[0091] The olefin polymer was prepared according to the same method as in Example 7, except that the transition metal compound of Example 4 was used.

Comparative Example 2

[0092] The olefin polymer was prepared according to the same method as in Example 7, except that the amount of 5×10^{-6} M dimethylanilinium tetrakis(pentafluorophenyl) borate cocatalyst was 1.0 mL and the transition metal compound of Comparative Example 1 (1×10^{-6} M, 0.5 mL) treated with triisobutylaluminum compound was used.

[0093] The melting points (T_m) of the polymers were measured by using Q100 of TA Co., Ltd. The values were obtained during the second heating scan of $10^\circ\text{C}/\text{min}$, for eliminating the thermal history of the polymers.

[0094] The properties of the polymers of Examples 7 to 10 and Comparative Example 2 were measured by the method, and the results are listed in the following Table 1.

[Table 1]

	Catalytic activity (unit: kg/mmol hr)	Weight of polymer (unit: g)	T_m (unit: $^\circ\text{C}$)
Example 7	474	7.9	147.8
Example 8	432	7.2	148.4
Example 9	156	7.8	149.5
Example 10	134	6.7	155
Comparative Example 2	151	12.6	122.5

[0095] Referring to Table 1, the propylene polymers prepared in Examples 7 to 10 show higher melting point (T_m) in comparison to the polymer of Comparative Example 2. Namely, it is recognized that the catalyst shows high catalytic activity and the olefin polymer having high isotacticity is obtained when the transition metal composition of the present invention is used as the catalyst.

Preparation of propylene-ethylene copolymer**Example 11**

[0096] After putting toluene solvent (0.8 L), propylene (250 g), and ethylene (70 psi) in a 2 L autoclave reactor, the pressure was adjusted to 500 psi with high pressure argon and the temperature of the reactor was preheated to 70°C . After putting 0.2 mL of 5×10^{-6} M dimethylanilinium tetrakis(pentafluorophenyl) borate cocatalyst in the reactor with high pressure argon, the transition metal compound of Example 1 (1×10^{-6} M, 0.1 mL) treated with triisobutylaluminum compound was put in a catalyst storage tank and subsequently put in the reactor by providing high pressure argon. The reaction was carried out for 10 mins. The heat of reaction was eliminated through a cooling coil inside the reactor and the polymerization temperature was maintained as uniform as possible. After carrying out the reaction for 10 mins, the remaining gas was removed therefrom, the polymer solution was drained through the bottom of the reactor, and the precipitation was induced by adding an excess of ethanol to the polymer solution and cooling the same. The obtained polymer was washed with ethanol and acetone respectively twice or thrice and dried for 12 hrs or more in a vacuum oven of 80°C . And then, the properties of the polymer were measured.

Example 12

[0097] The olefin polymer was prepared according to the same method as in Example 11, except that the transition metal compound of Example 3 was used.

Example 13

[0098] The olefin polymer was prepared according to the same method as in Example 11, except that the transition metal compound of Example 5 was used.

Comparative Example 3

[0099] The olefin polymer was prepared according to the same method as in Example 11, except that the amount of 5×10^{-6} M dimethylanilinium tetrakis(pentafluorophenyl) borate cocatalyst was 1.0 mL and the transition metal compound of Comparative Example 1 (1×10^{-6} M, 0.5 mL) treated with triisobutylaluminum compound was used.

[0100] The melt flow rates (MFR) of the polymers were measured by ASTM D-1238 (condition E, 230 °C, 2.16 kg load). The melting points (T_m) were measured by using Q100 of TA Co., Ltd. The values were obtained during the second heating scan of 10 °C/min, for eliminating the thermal history of the polymers.

[0101] The properties of the polymers of Examples 11 to 13 and Comparative Example 3 were measured by the method, and the results are listed in the following Table 2.

[Table 2]

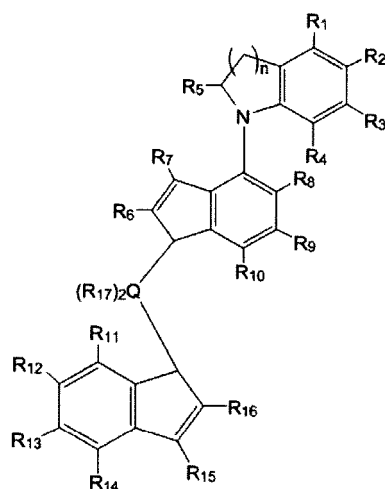
	Catalytic activity (unit: kg/mmol hr)	Weight of polymer (unit: g)	Density (unit: g/cc)	T _m (unit: °C)	MFR (unit: g/10min)
Example 11	5640	56.4	0.861	53.8	15.2
Example 12	4860	81.0	0.865	53.1	10.2
Example 13	8268	82.7	0.860	53.3	30.0
Comparative Example 3	1040	86.6	0.856	-	13

[0102] Referring to Table 2, the propylene-ethylene polymers prepared in Examples 11 to 13 showed excellent properties such as higher catalytic activity and MFR in comparison to Comparative Example 3.

Claims

1. A ligand compound, represented by the following Chemical Formula 1:

[Chemical Formula 1]



in Chemical Formula 1,

n is an integer of 1 to 2;

R₁ to R₁₆ are equal to or different from each other, and are independently hydrogen, a C₁-C₂₀ alkyl, a C₁-C₂₀ alkoxy, a C₂-C₂₀ alkenyl, a C₆-C₂₀ aryl, a C₇-C₂₀ alkylaryl, a C₇-C₂₀ arylalkyl, a C₃-C₂₀ cycloalkyl, a C₅-C₂₀ heteroring, or silyl, and 2 or more adjacent groups among R₁ to R₁₆ may be connected together via an alkylidene group including a C₁-C₂₀ alkyl group or a C₆-C₂₀ aryl group to form a ring;

R₁₇ is hydrogen, a halogen, a C₁-C₂₀ alkyl, a C₆-C₂₀ aryl, or a C₁-C₂₀ alkoxy; and Q is carbon or silicon.

2. The ligand compound according to Claim 1, wherein R₁ to R₁₆ are independently hydrogen, a C₁-C₂₀ alkyl, a C₆-C₂₀ aryl, a C₇-C₂₀ alkylaryl, a C₇-C₂₀ arylalkyl, or a C₅-C₂₀ heteroring, and R₁₇ is a C₁-C₂₀ alkyl or a C₆-C₂₀ aryl.

3. The ligand compound according to Claim 1, wherein the compound represented by Chemical Formula 1 is represented by any one of the following structural formulae:

5

10

15

20

25

30

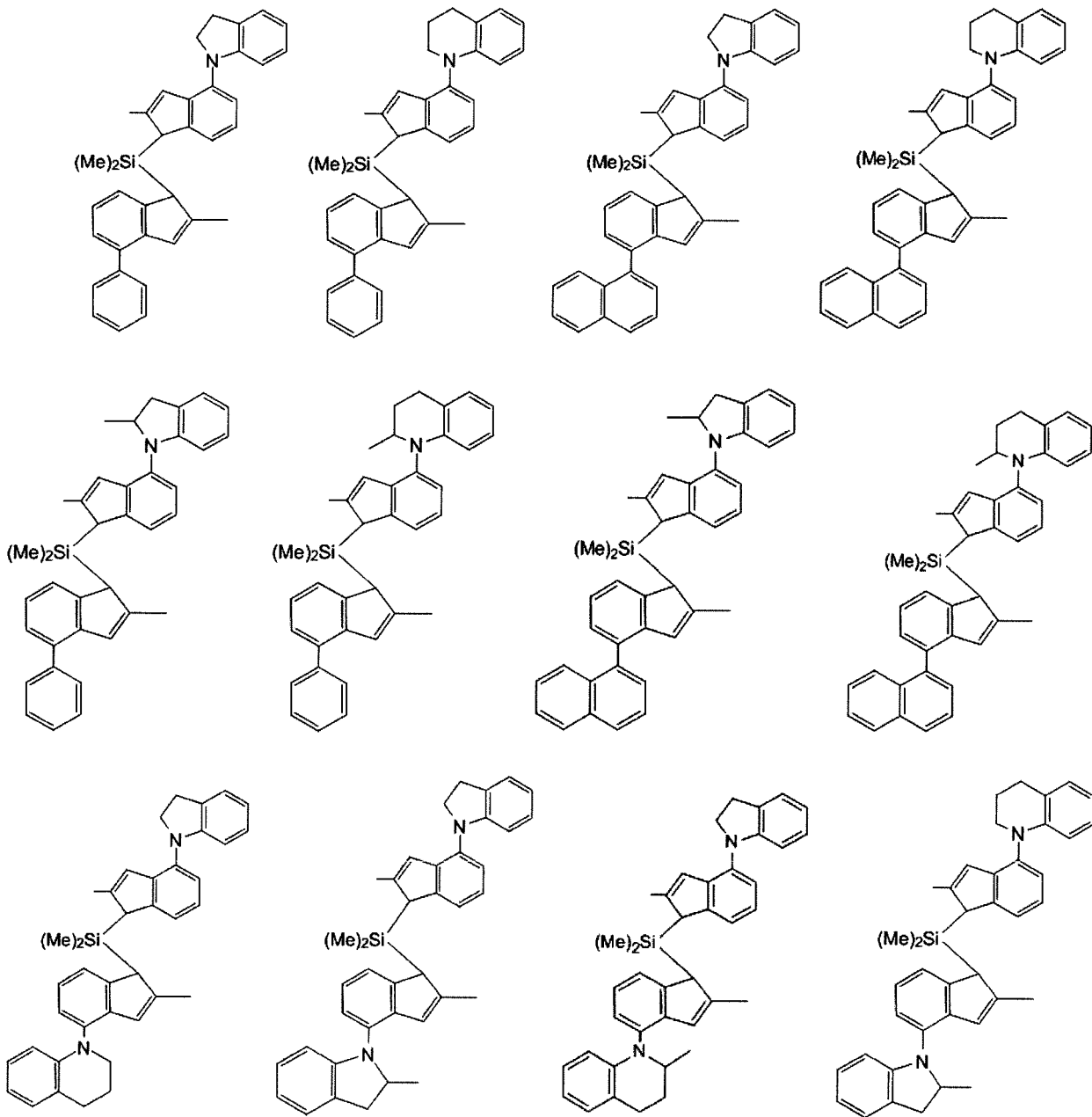
35

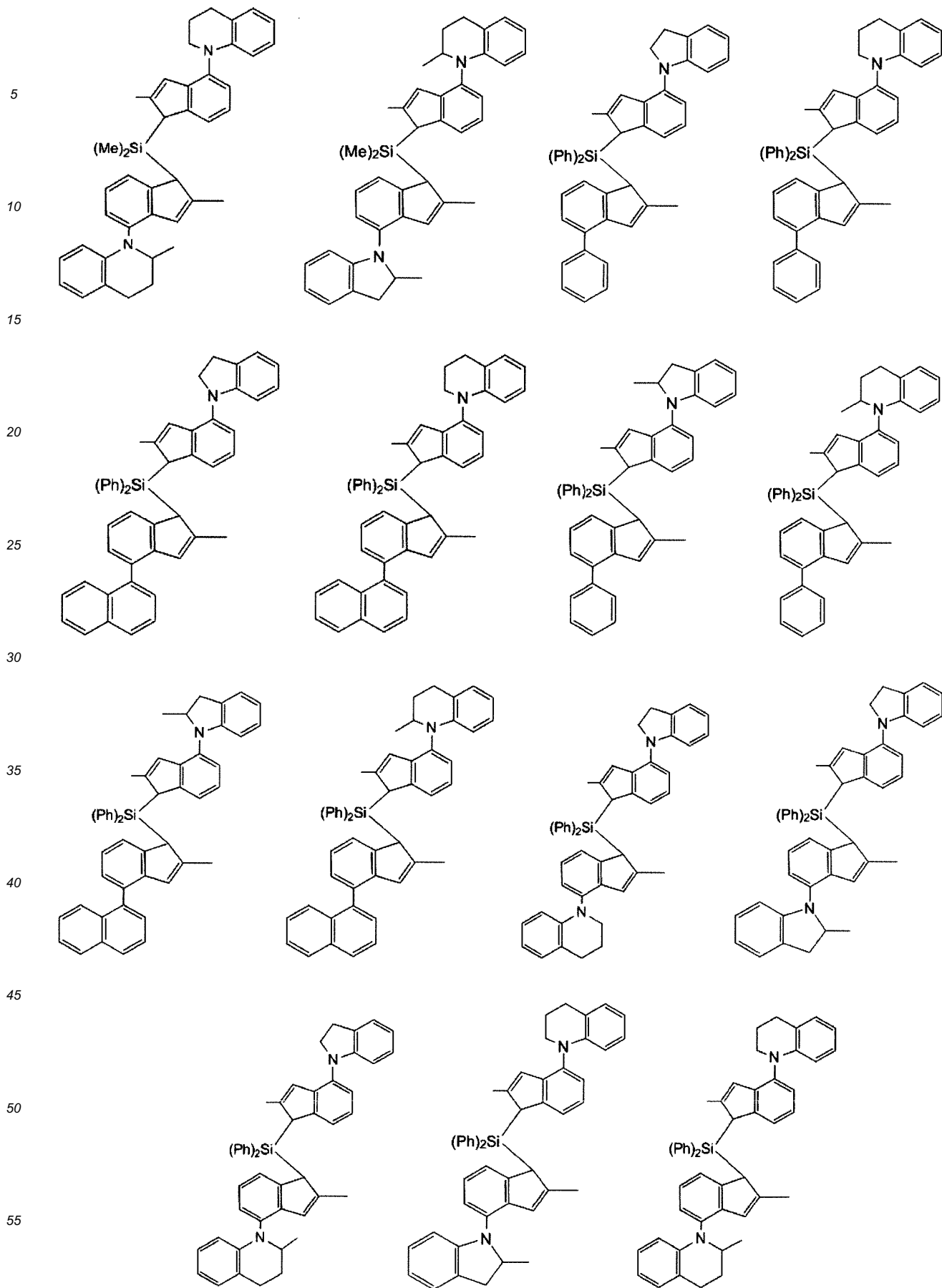
40

45

50

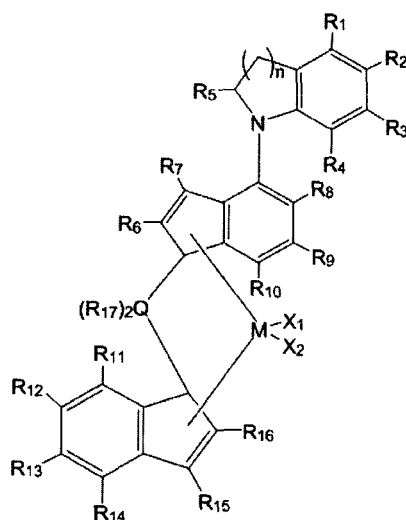
55





4. A transition metal compound, represented by the following Chemical Formula 2:

[Chemical Formula 2]



in Chemical Formula 2,

n is an integer of 1 to 2;

R_1 to R_{16} are equal to or different from each other, and are independently hydrogen, a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_3 - C_{20} cycloalkyl, a C_5 - C_{20} heteroring, or silyl, and 2 or more adjacent groups among R_1 to R_{16} may be connected together via an alkyldiene group including a C_1 - C_{20} alkyl group or a C_6 - C_{20} aryl group to form a ring;

R_{17} is hydrogen, a halogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, or a C_1 - C_{20} alkoxy;

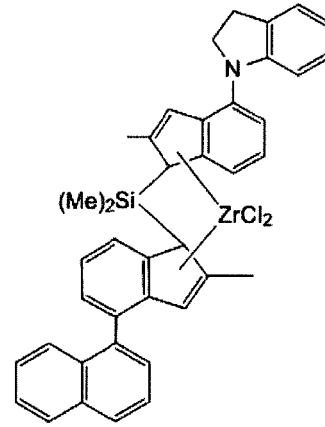
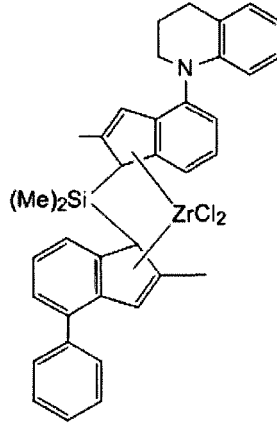
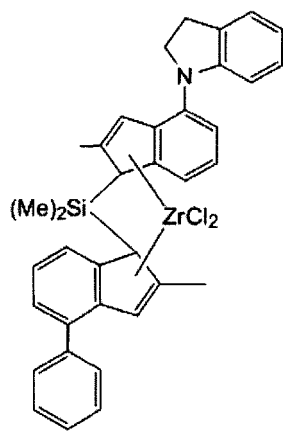
Q is carbon or silicon;

M is a Group 4 transition metal; and

X_1 and X_2 are equal to or different from each other, and are independently a halogen, a C_1 - C_{20} alkyl, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_1 - C_{20} alkylamino, a C_6 - C_{20} arylamino, or a C_1 - C_{20} alkyldiene group.

5. The transition metal compound according to Claim 4, wherein R_1 to R_{16} are independently hydrogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, or a C_5 - C_{20} heteroring, and R_{17} is a C_1 - C_{20} alkyl or a C_6 - C_{20} aryl.
6. The transition metal compound according to Claim 4, wherein the M is a metal selected from the group consisting Ti, Zr, and Hf.
7. The transition metal compound according to Claim 4, wherein the transition metal compound represented by Chemical Formula 2 is represented by any one of the following structural formulae:

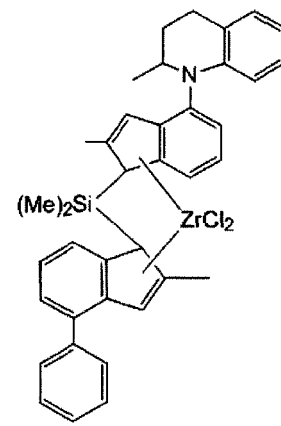
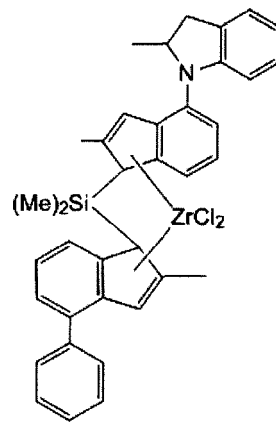
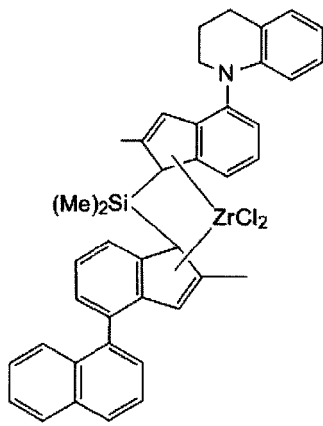
5



10

15

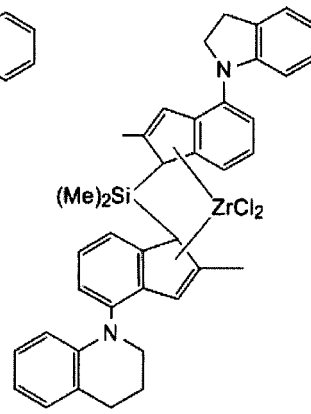
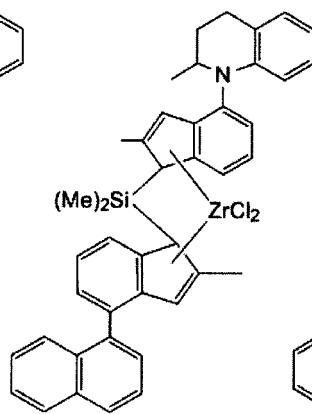
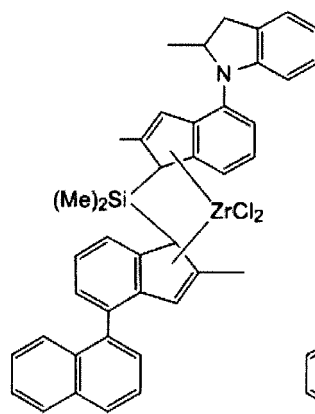
20



25

30

35



40

45

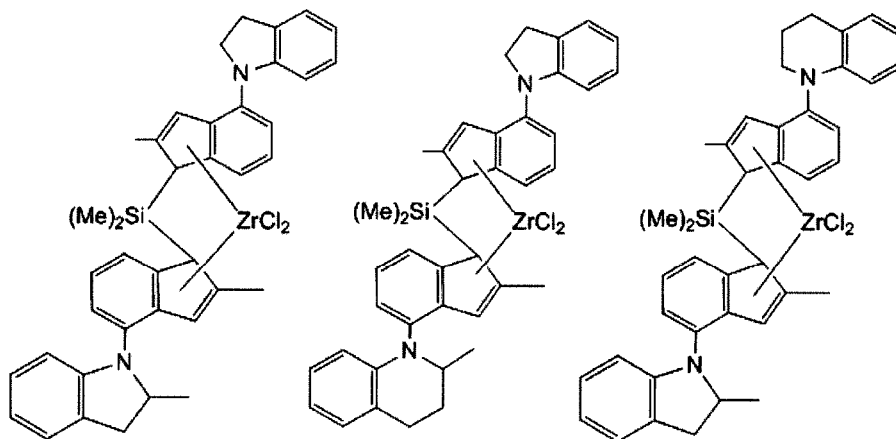
50

55

5

10

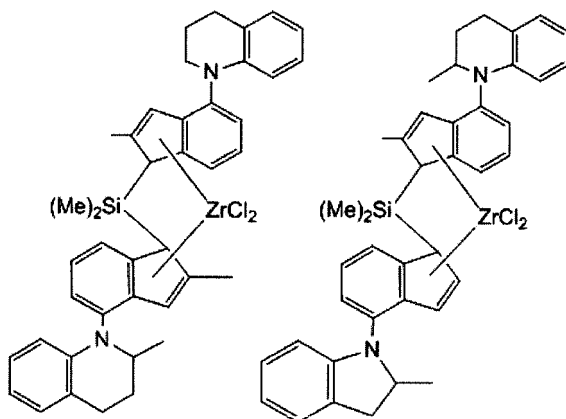
15



20

25

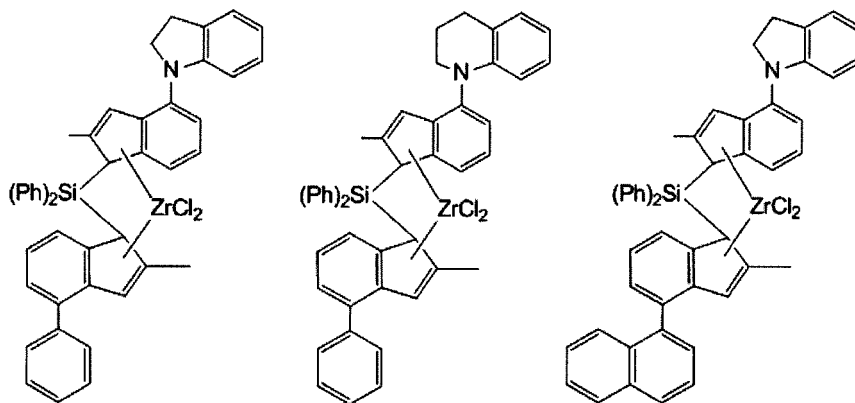
30



35

40

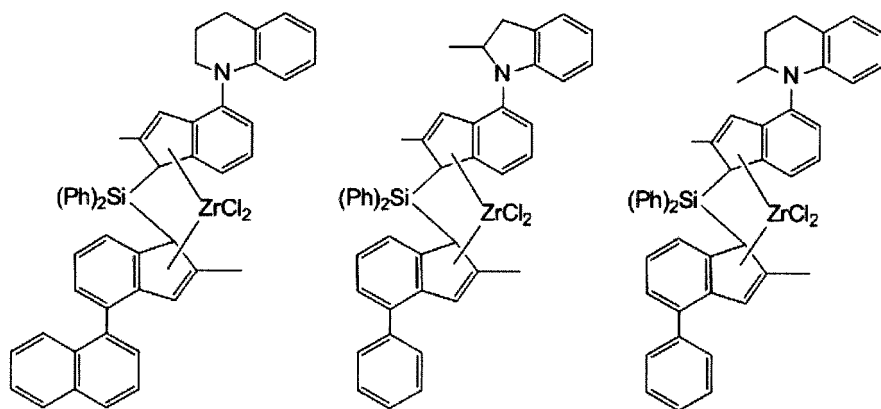
45



50

55

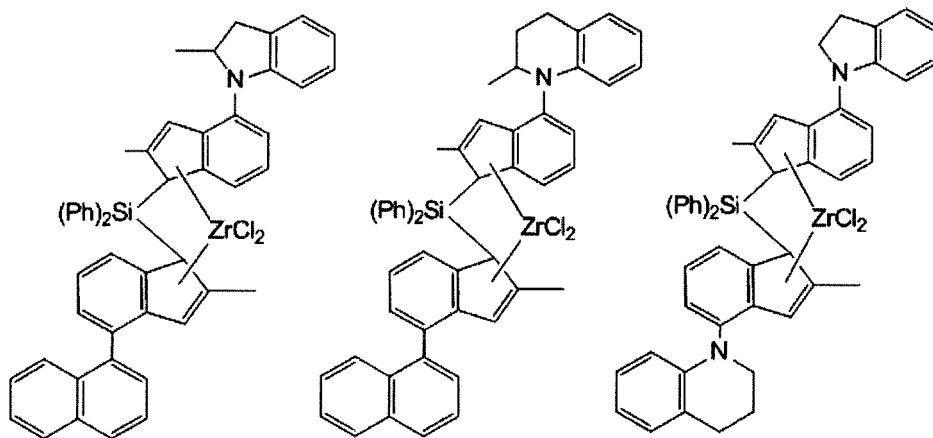
5



10

15

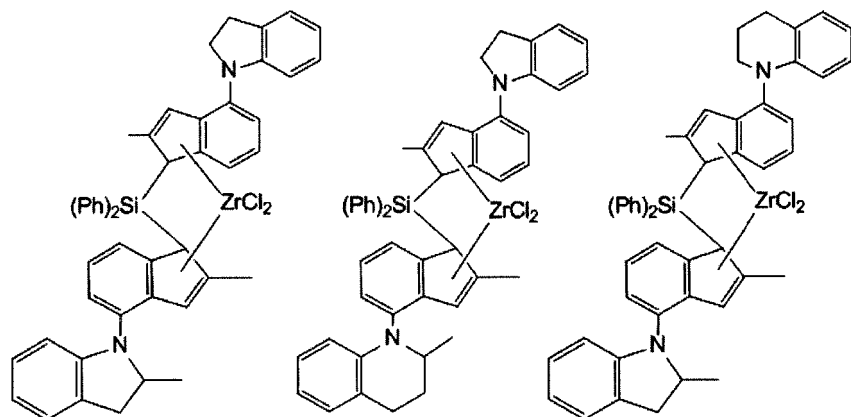
20



25

30

35



40

45

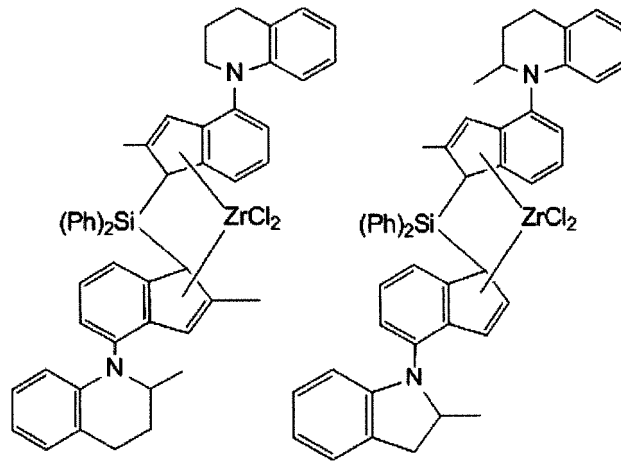
50

55

5

10

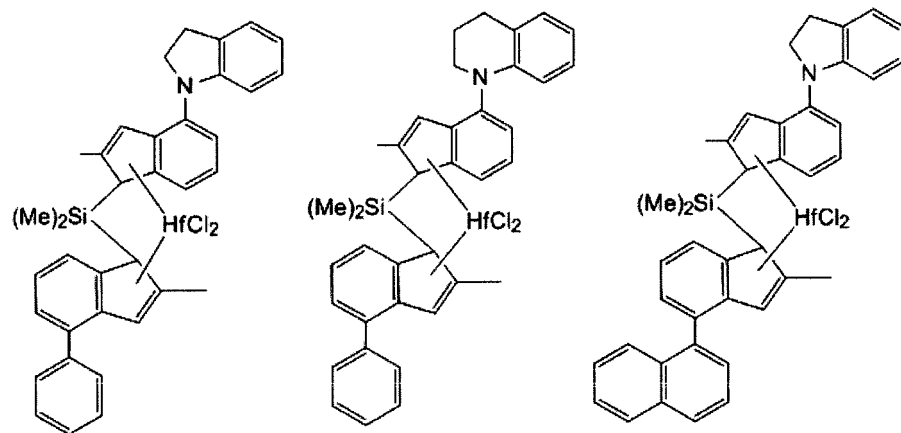
15



20

25

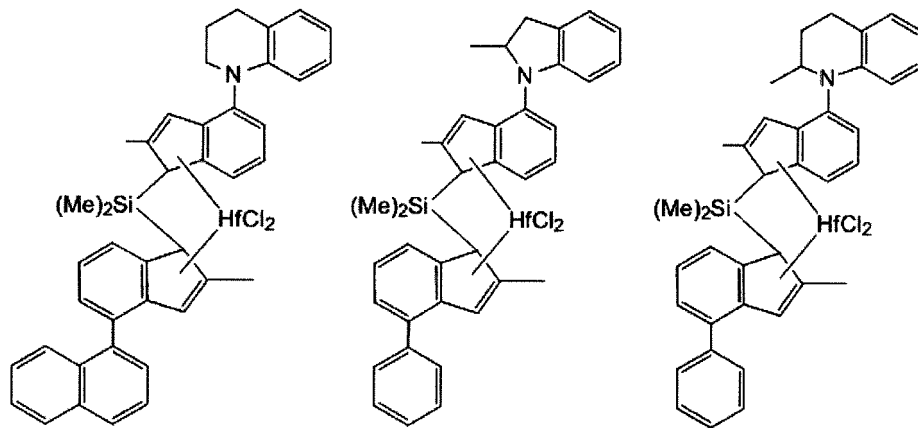
30



35

40

45



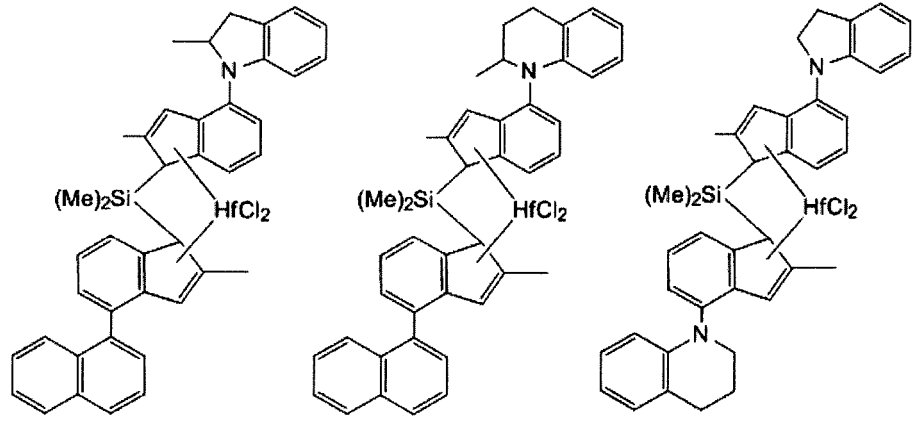
50

55

5

10

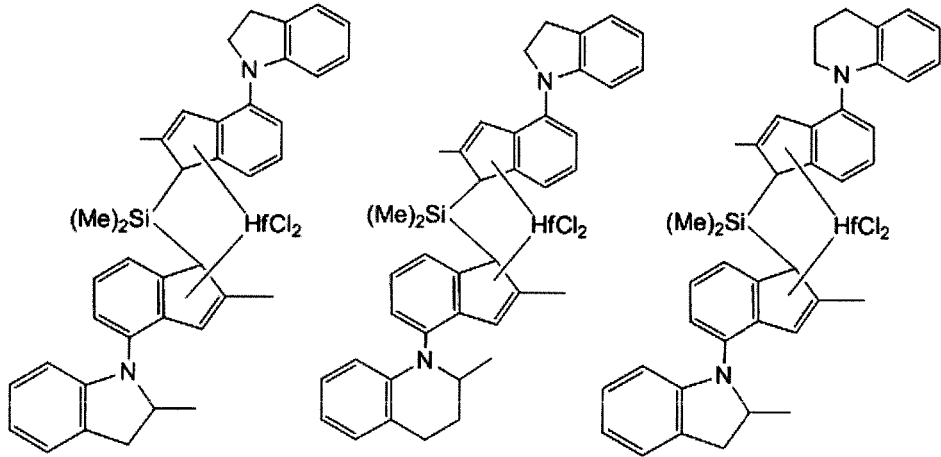
15



20

25

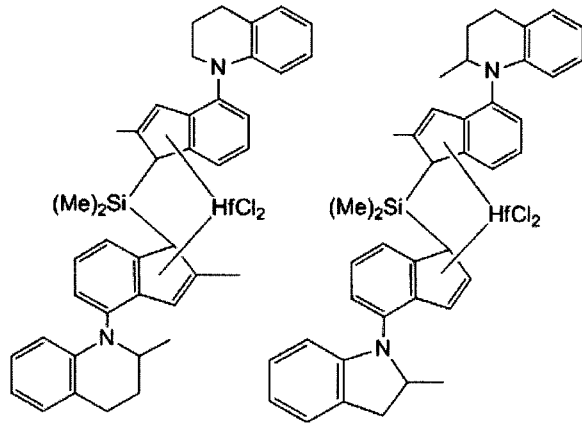
30



35

40

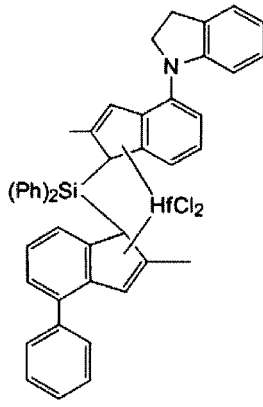
45



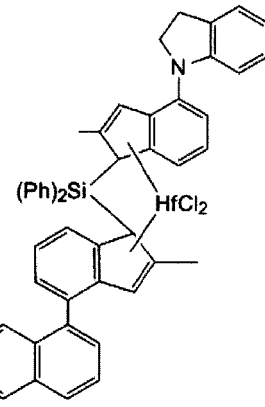
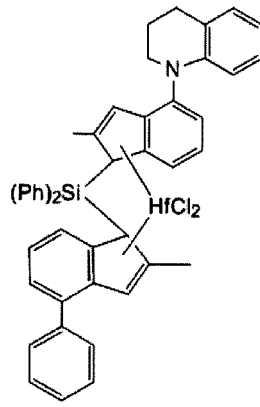
50

55

5

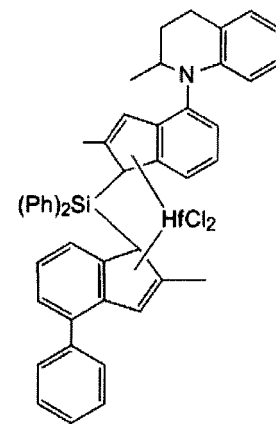
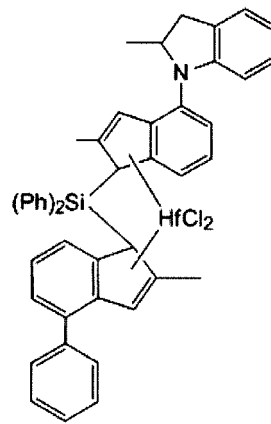
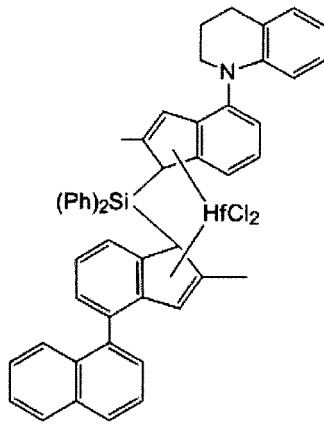


10



15

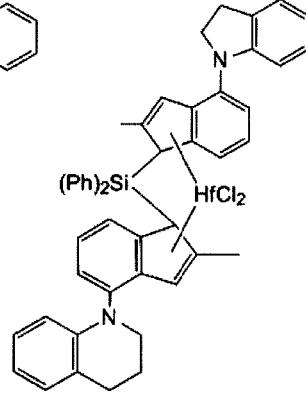
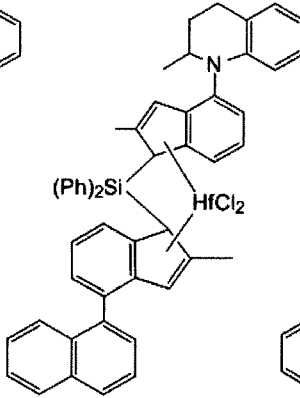
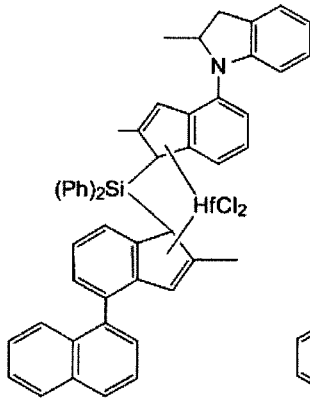
20



25

30

35

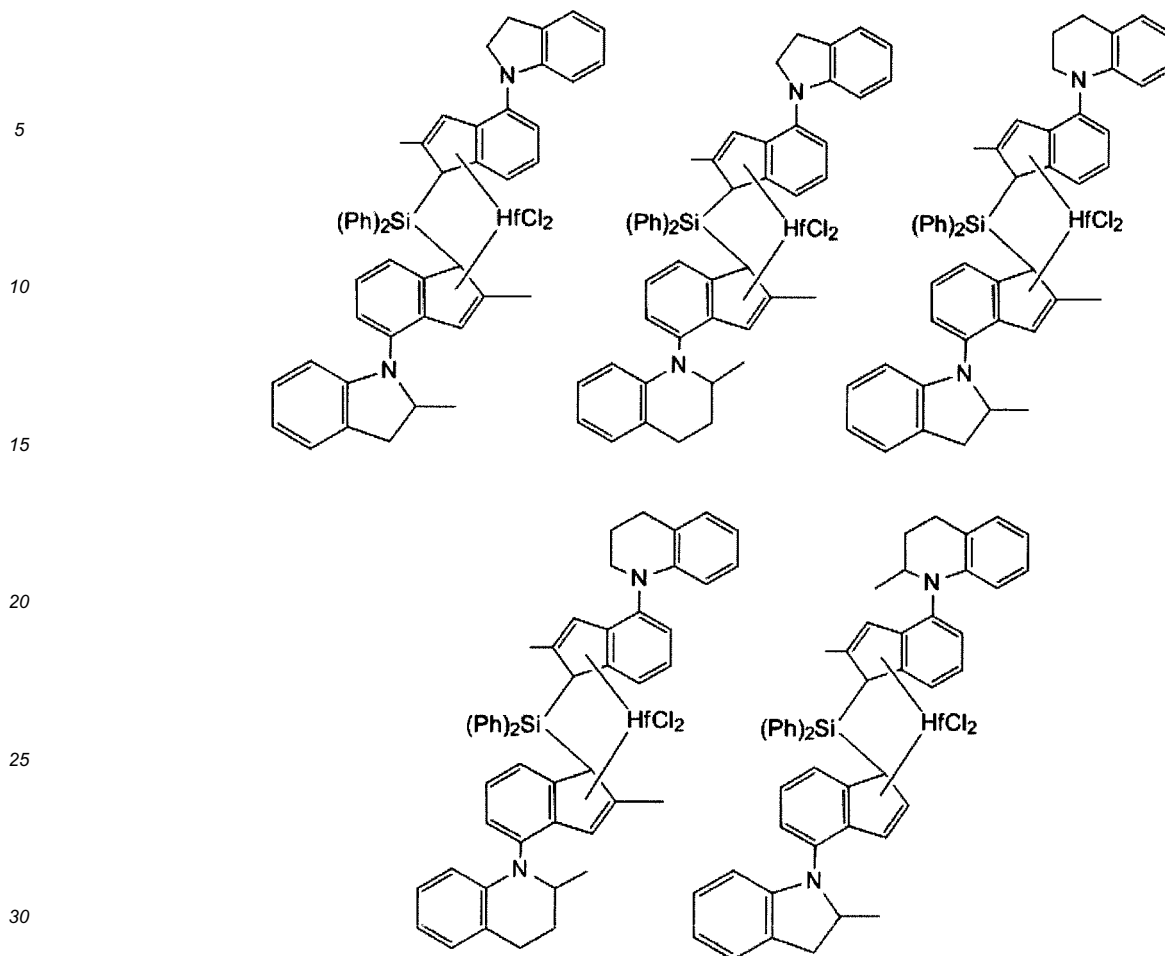


40

45

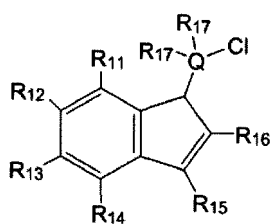
50

55



8. A preparation method of the ligand compound represented by the following Chemical Formula 1, including the step of carrying out the reaction of the compound represented by the following Chemical Formula 3 and the compound represented by the following Chemical Formula 4 or the lithium salt thereof

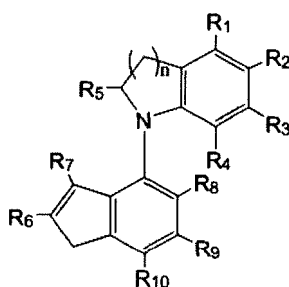
[Chemical Formula 3]



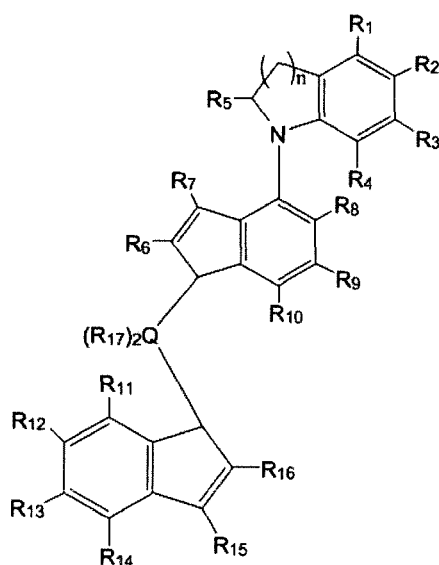
50

55

[Chemical Formula 4]



[Chemical Formula 1]



in Chemical Formulae 1, 3, and 4,
 n is an integer of 1 to 2;

R_1 to R_{16} are equal to or different from each other, and are independently hydrogen, a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_3 - C_{20} cycloalkyl, a C_5 - C_{20} heteroring, or silyl, and 2 or more adjacent groups among R_1 to R_{16} may be connected together via an alkylidene group including a C_1 - C_{20} alkyl group or a C_6 - C_{20} aryl group to form a ring;

R_{17} is hydrogen, a halogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, or a C_1 - C_{20} alkoxy; and
 Q is carbon or silicon.

9. The preparation method according to Claim 8, wherein R_1 to R_{16} are independently hydrogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, or a C_5 - C_{20} heteroring, and R_{17} is a C_1 - C_{20} alkyl or a C_6 - C_{20} aryl.

10. A preparation method of the transition metal compound represented by the following Chemical Formula 2, including the step of carrying out the reaction of the ligand compound represented by the following Chemical Formula 1 and the compound represented by the following Chemical Formula 9:

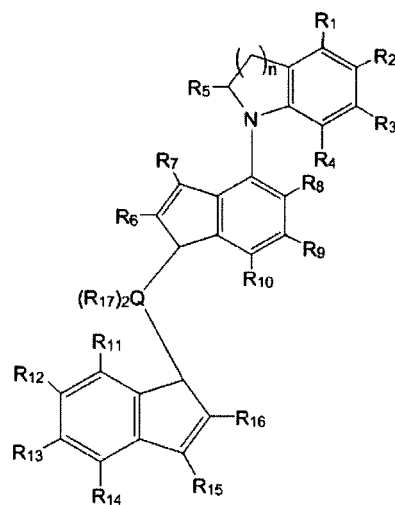
[Chemical Formula 1]

5

10

15

20



[Chemical Formula 9]

 $M(X_1X_2)_2$

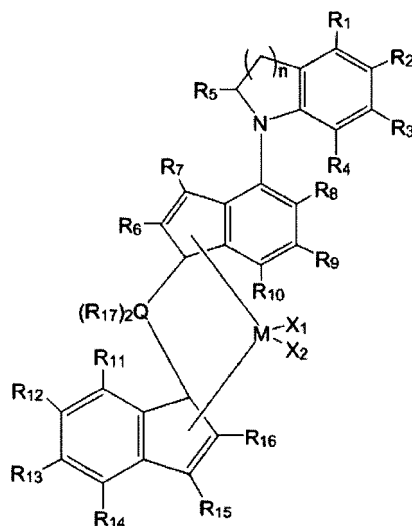
[Chemical Formula 2]

25

30

35

40



45

in Chemical Formulae 1, 2, and 9,
 n is an integer of 1 to 2;

R_1 to R_{16} are equal to or different from each other, and are independently hydrogen, a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_3 - C_{20} cycloalkyl, a C_5 - C_{20} heteroring, or silyl, and 2 or more adjacent groups among R_1 to R_{16} may be connected together via an alkylidene group including a C_1 - C_{20} alkyl group or a C_6 - C_{20} aryl group to form a ring;

50

R_{17} is hydrogen, a halogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, or a C_1 - C_{20} alkoxy;

Q is carbon or silicon;

M is a Group 4 transition metal; and

X_1 and X_2 are equal to or different from each other, and are independently a halogen, a C_1 - C_{20} alkyl, a C_2 - C_{20} alkenyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, a C_1 - C_{20} alkylamino, a C_6 - C_{20} arylamino, or a C_1 - C_{20} alkylidene group.

55

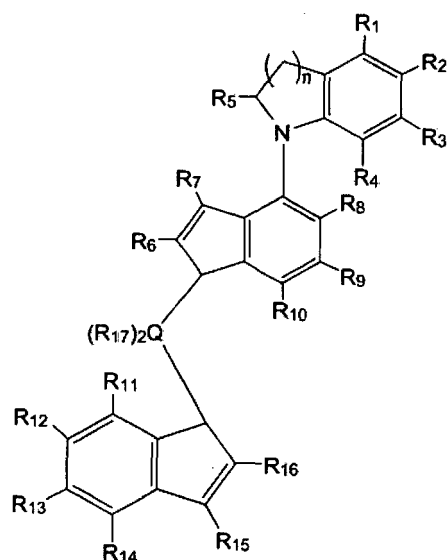
11. The preparation method according to Claim 10, wherein R_1 to R_{16} are independently hydrogen, a C_1 - C_{20} alkyl, a C_6 - C_{20} aryl, a C_7 - C_{20} alkylaryl, a C_7 - C_{20} arylalkyl, or a C_5 - C_{20} heteroring, and R_{17} is a C_1 - C_{20} alkyl or a C_6 - C_{20} aryl.

12. The preparation method according to Claim 10, wherein the M is a metal selected from the group consisting Ti, Zr, and Hf.

5 **Patentansprüche**

1. Ligandenverbindung, dargestellt durch die nachstehende chemische Formel 1:

10 **[Chemische Formel 1]**



in der chemischen Formel 1:

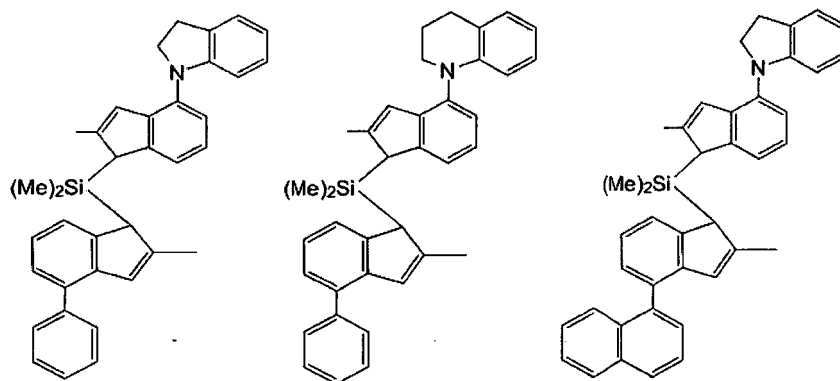
n ist eine ganze Zahl von 1 bis 2;

R₁ bis R₁₆ sind gleich oder voneinander verschieden und sind unabhängig Wasserstoff, C₁₋₂₀-Alkyl, C₁₋₂₀-Alkoxy, C₂₋₂₀-Alkenyl, C₆₋₂₀-Aryl, C₇₋₂₀-Alkylaryl, C₇₋₂₀-Arylalkyl, C₃₋₂₀-cycloalkyl, ein C₅₋₂₀-Heteroring oder Silyl, und zwei oder mehr benachbarte Gruppen von R₁ bis R₁₆ können über eine Alkyldingruppe, einschliesslich einer C₁₋₂₀-Alkylgruppe oder einer C₆₋₂₀-Arylgruppe, miteinander verbunden sein, um einen Ring zu bilden;

R₁₇ ist Wasserstoff, Halogen, C₁₋₂₀-Alkyl, C₆₋₂₀-Aryl oder C₁₋₂₀-Alkoxy; und Q ist Kohlenstoff oder Silicium.

2. Ligandenverbindung gemäss Anspruch 1, worin R₁ bis R₁₆ unabhängig Wasserstoff, C₁₋₂₀-Alkyl, C₆₋₂₀-Aryl, C₇₋₂₀-Alkylaryl, C₇₋₂₀-Arylalkyl oder ein C₅₋₂₀-Heteroring sind und R₁₇ C₁₋₂₀-Alkyl oder C₆₋₂₀-Aryl ist.
3. Ligandenverbindung gemäss Anspruch 1, wobei die Verbindung der chemischen Formel 1 durch irgendeine der nachstehenden Strukturformeln dargestellt ist:

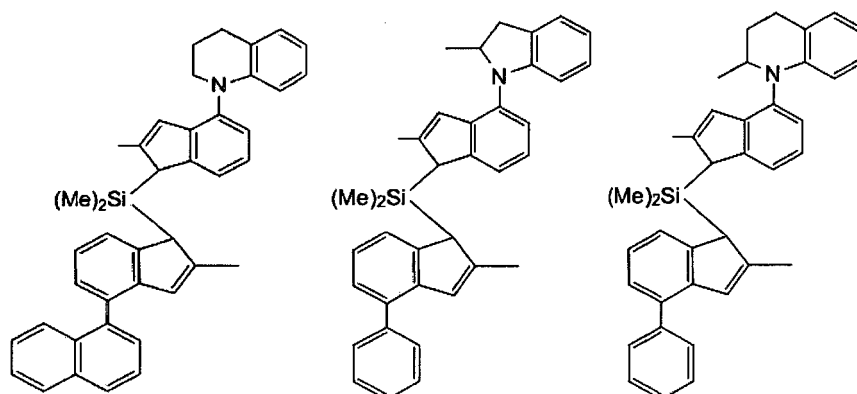
5



10

15

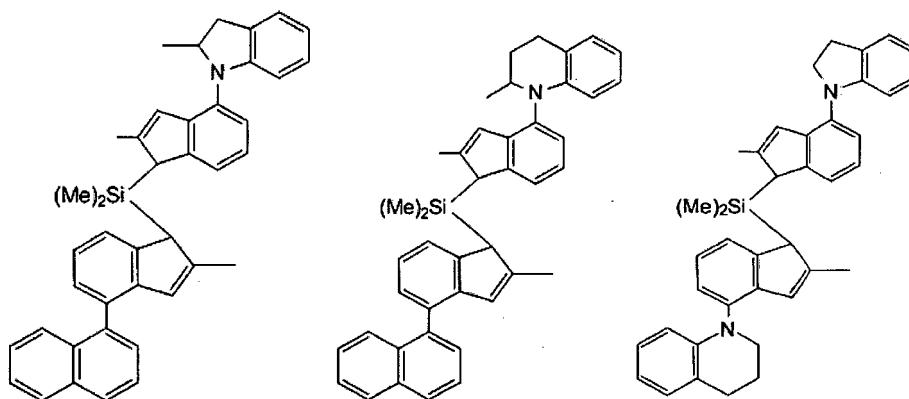
20



25

30

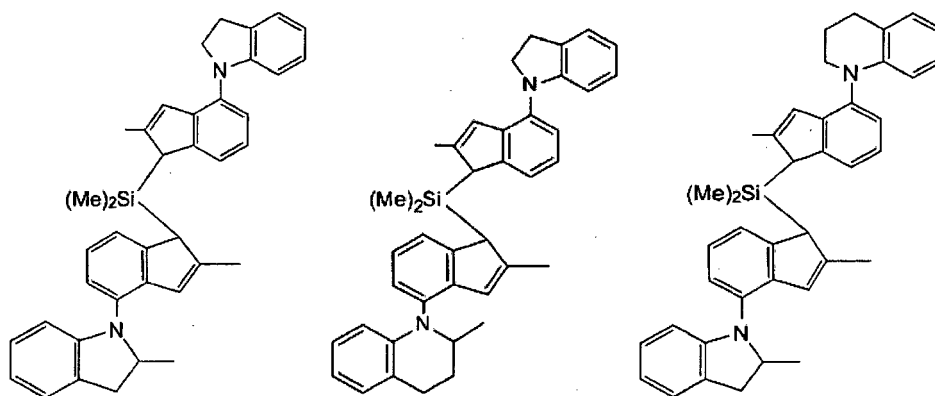
35



40

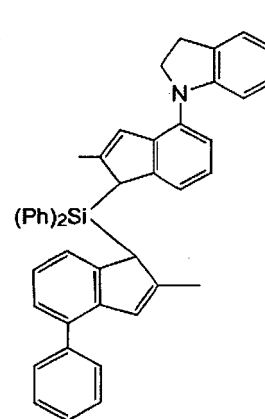
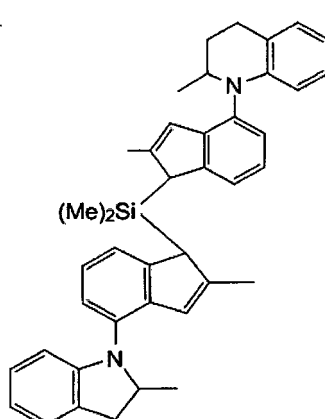
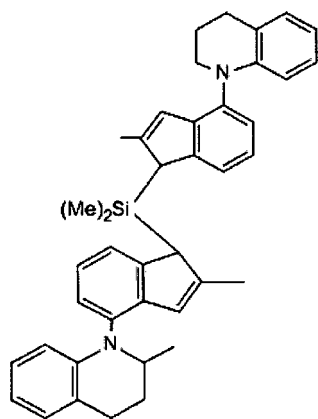
45

50



55

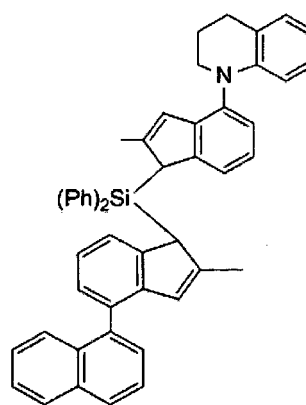
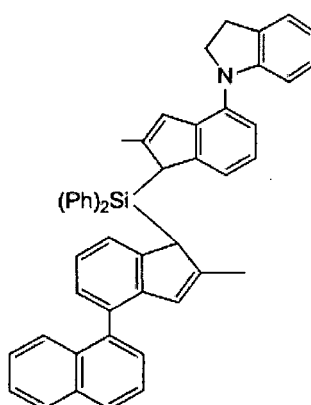
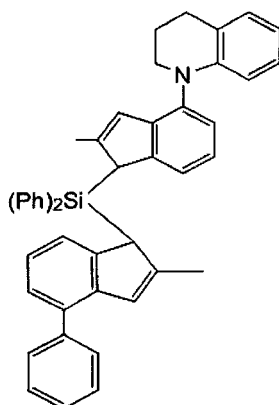
5



10

15

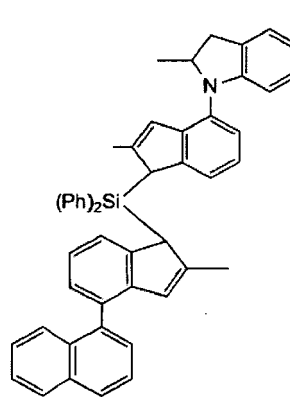
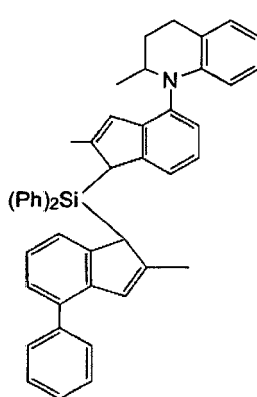
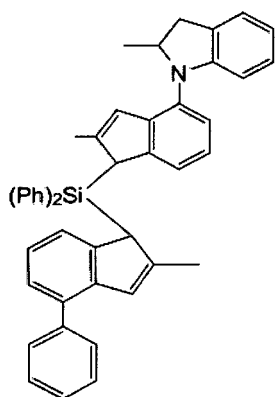
20



25

30

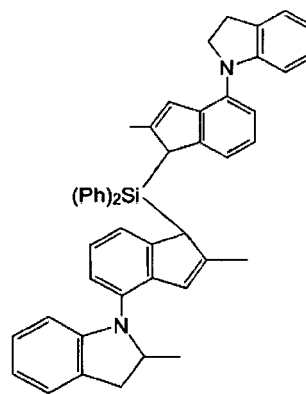
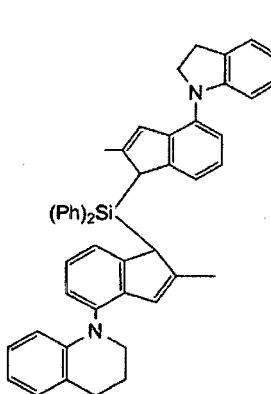
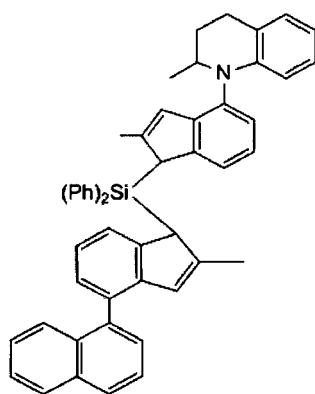
35



40

45

50

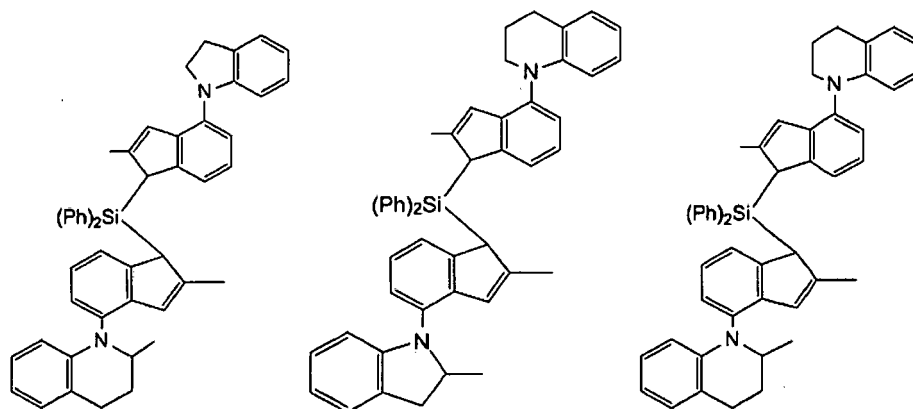


55

5

10

15



4. Übergangsmetallverbindung, dargestellt durch die nachstehende chemische Formel 2:

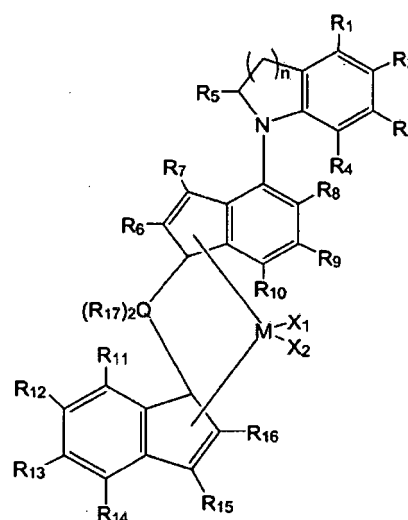
[Chemische Formel 2]

20

25

30

35



in der chemischen Formel 2:

40

n ist eine ganze Zahl von 1 bis 2;

R_1 bis R_{16} sind gleich oder voneinander verschieden und sind unabhängig Wasserstoff, C_{1-20} -Alkyl, C_{1-20} -Alkoxy, C_{2-20} -Alkenyl, C_{6-20} -Aryl, C_{7-20} -Alkylaryl, C_{7-20} -Arylalkyl, C_{3-20} -cycloalkyl, ein C_{5-20} -Heteroring oder Silyl, und zwei oder mehr benachbarte Gruppen von R_1 bis

45 R_{16} können über eine Alkyldingruppe, einschliesslich einer C_{1-20} -Alkylgruppe oder einer C_{6-20} -Arylgruppe, miteinander verbunden sein, um einen Ring zu bilden;

R_{17} ist Wasserstoff, Halogen, C_{1-20} -Alkyl, C_{6-20} -Aryl oder C_{1-20} -Alkoxy;

Q ist Kohlenstoff oder Silicium;

M ist ein Übergangsmetall der Gruppe 4; und

50 X_1 und X_2 sind gleich oder voneinander verschieden und sind unabhängig Halogen, eine C_{1-20} -Alkyl-, C_{2-20} -Alkenyl-, C_{6-20} -Aryl-, C_{7-20} -Alkylaryl-, C_{7-20} -Arylalkyl-, C_{1-20} -Alkylamino-, C_{6-20} -Arylamino- oder C_{1-20} -Alkyldingruppe.

55 5. Übergangsmetallverbindung gemäss Anspruch 4, worin R_1 bis R_{16} unabhängig Wasserstoff, C_{1-20} -Alkyl, C_{6-20} -Aryl, C_{7-20} -Alkylaryl, C_{7-20} -Arylalkyl oder ein C_{5-20} -Heteroring sind und R_{17} C_{1-20} -Alkyl oder C_{6-20} -Aryl ist.

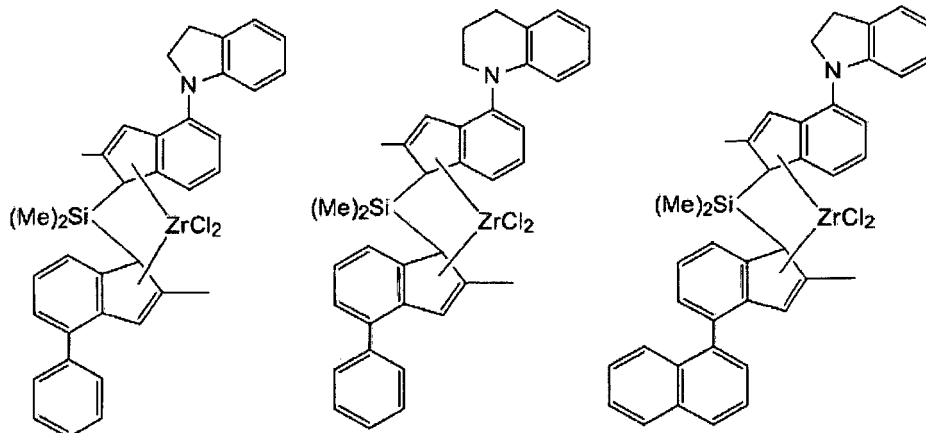
6. Übergangsmetallverbindung gemäss Anspruch 4, worin M ein Metall, ausgewählt aus der Gruppe bestehend aus Ti, Zr und Hf, ist.

7. Übergangsmetallverbindung gemäss Anspruch 4, wobei die Übergangsmetallverbindung der chemischen Formel 2 durch irgendeine der nachstehenden Strukturformeln dargestellt ist:

5

10

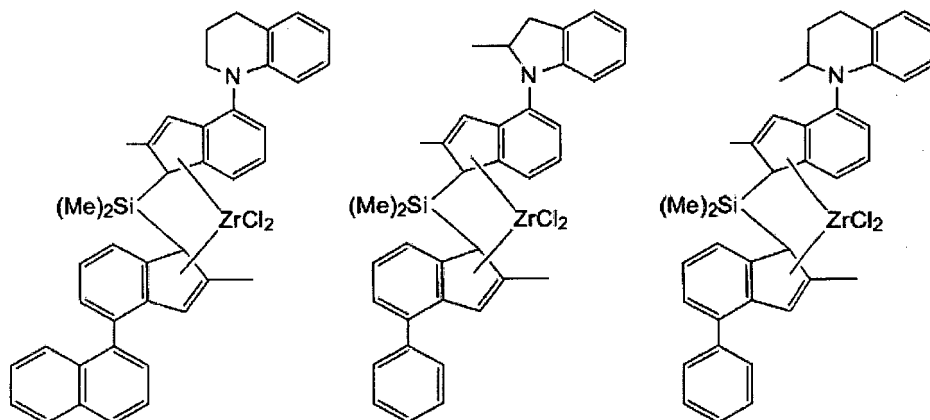
15



20

25

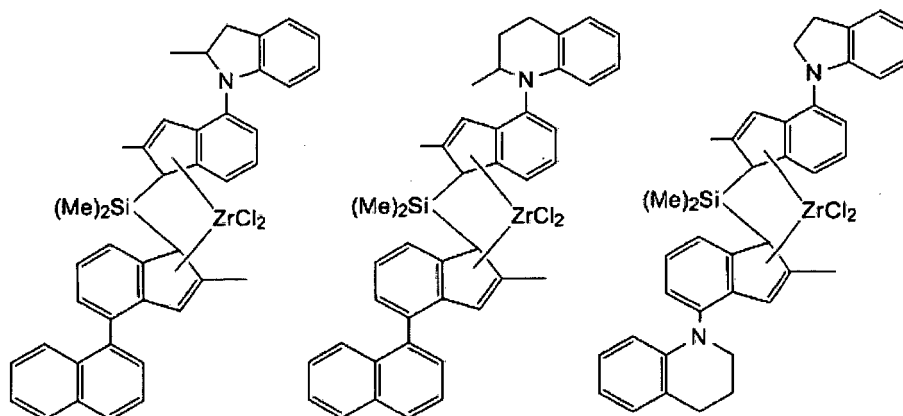
30



35

40

45



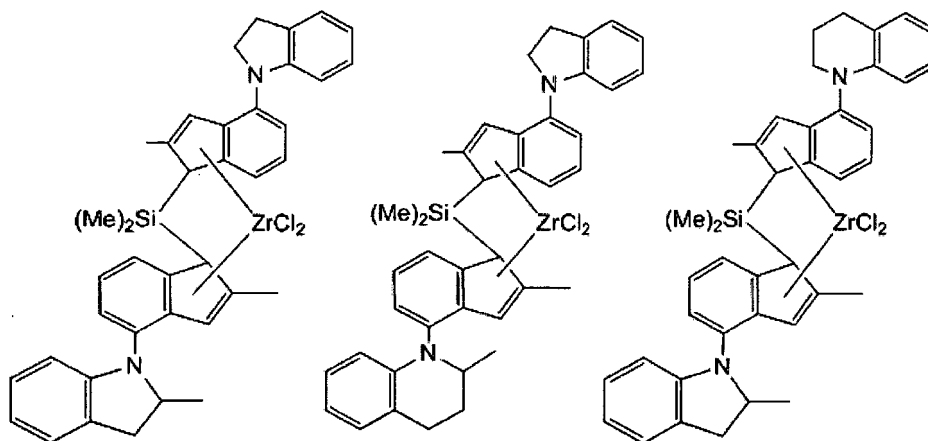
50

55

5

10

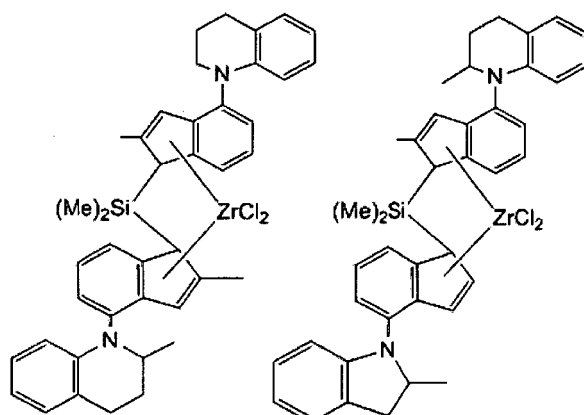
15



20

25

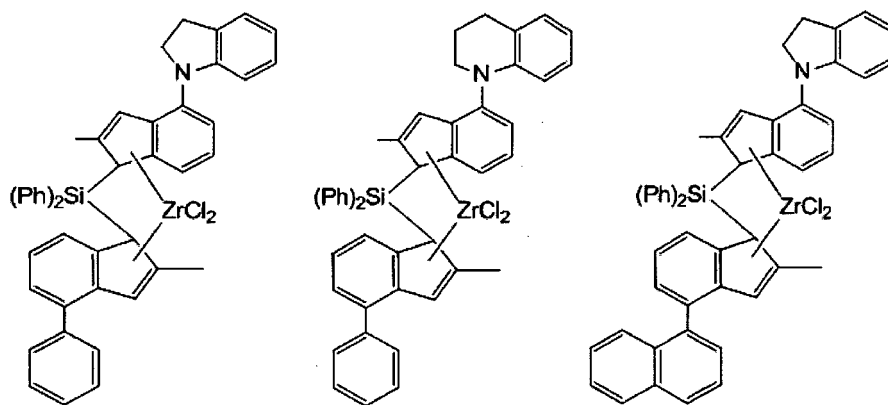
30



35

40

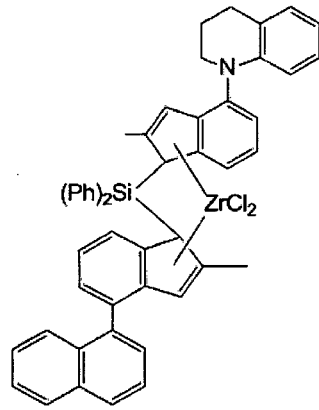
45



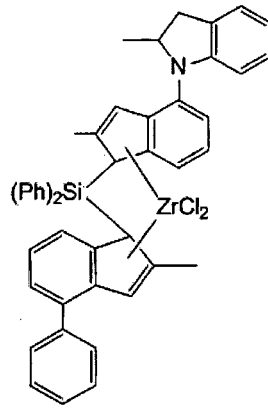
50

55

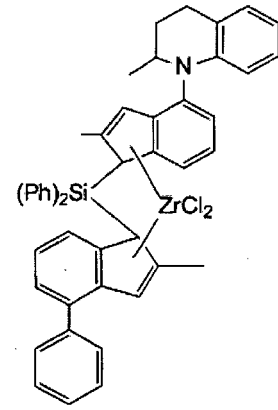
5



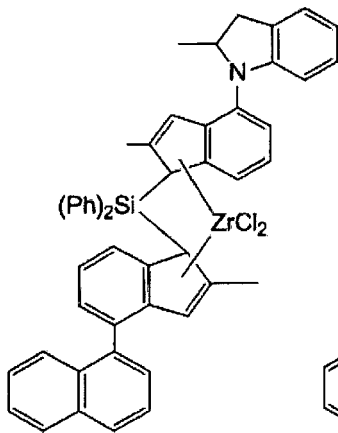
10



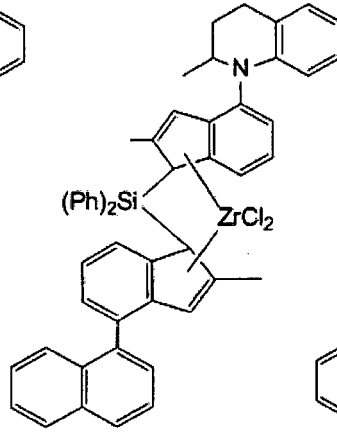
15



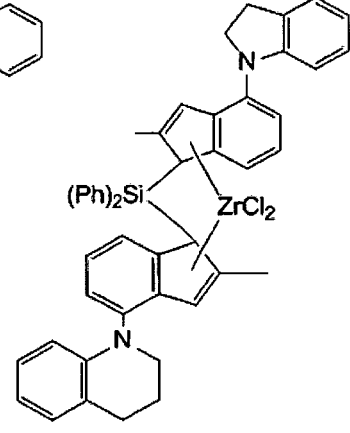
20



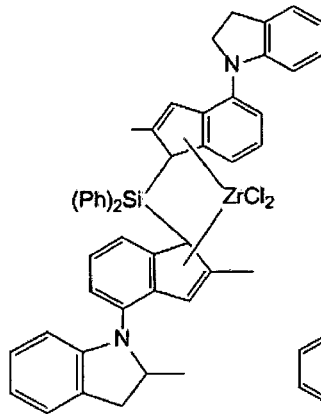
25



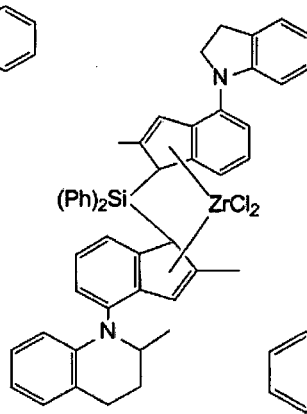
30



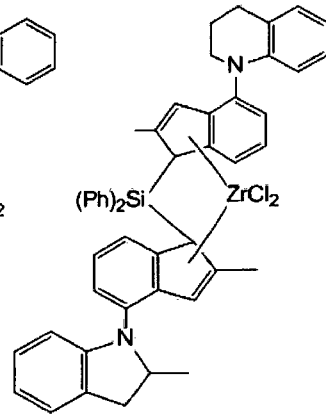
35



40



45



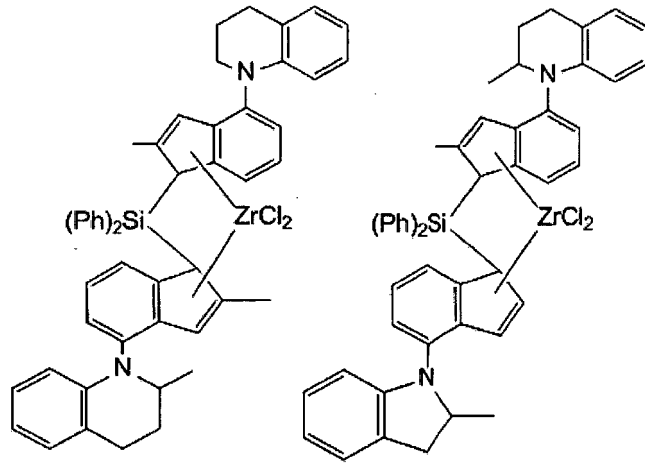
50

55

5

10

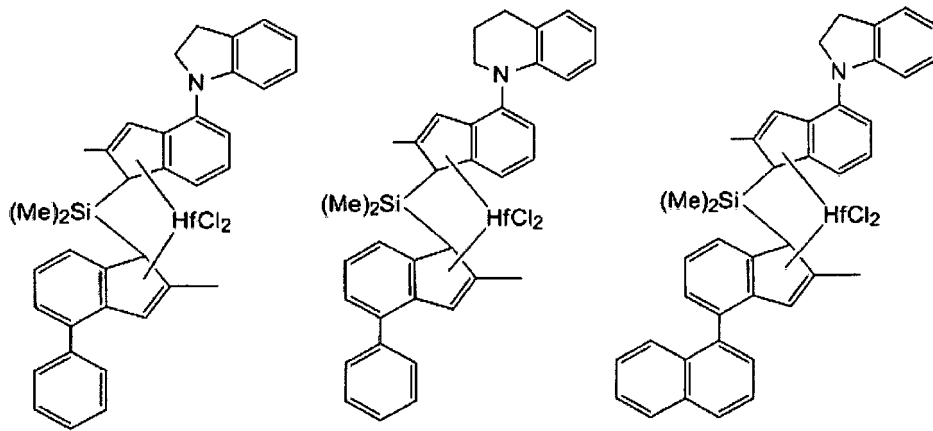
15



20

25

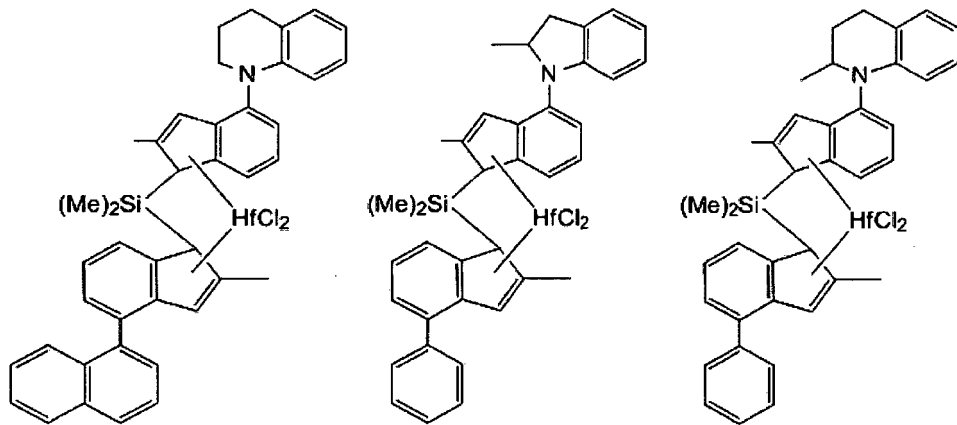
30



35

40

45



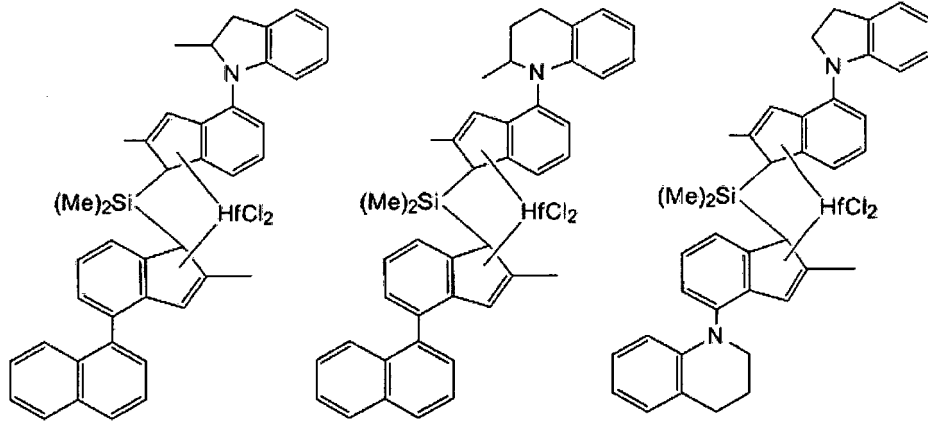
50

55

5

10

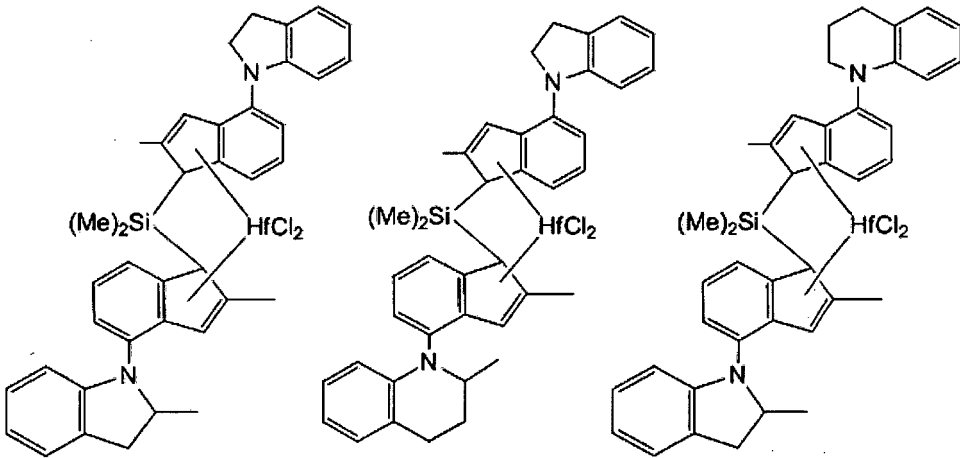
15



20

25

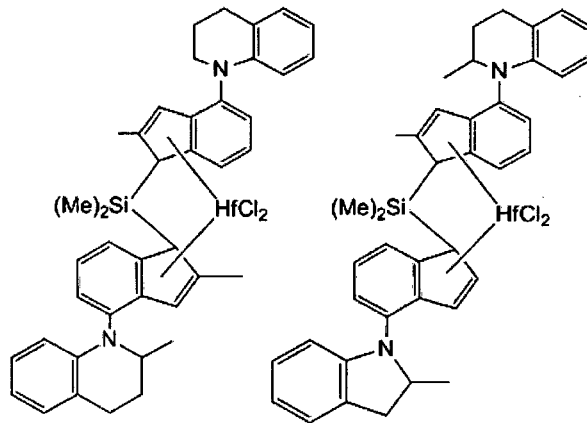
30



35

40

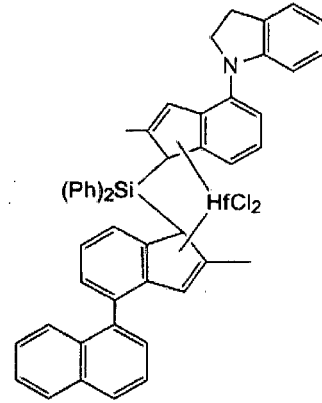
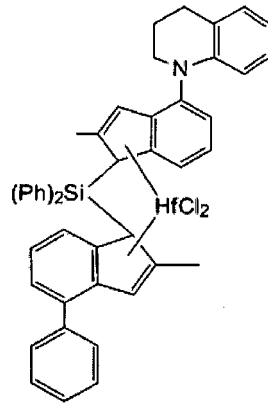
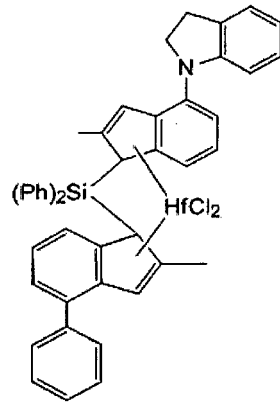
45



50

55

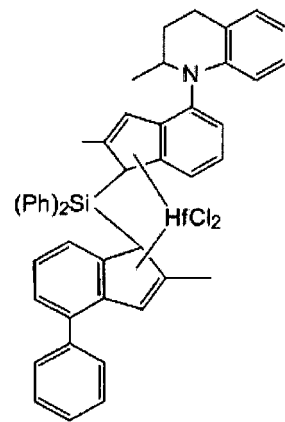
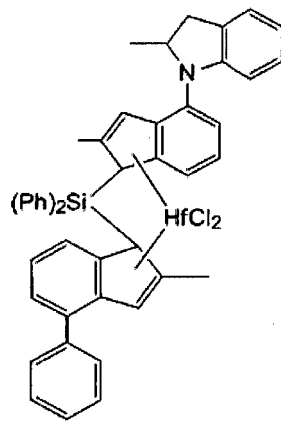
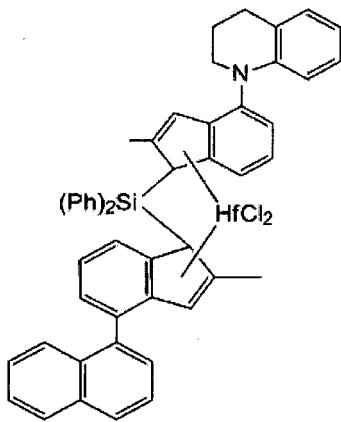
5



10

15

20



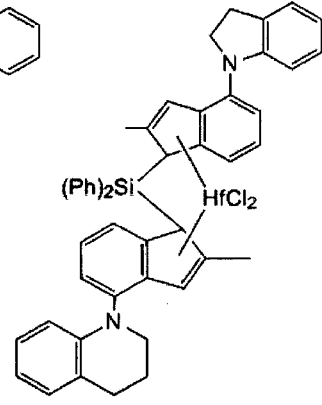
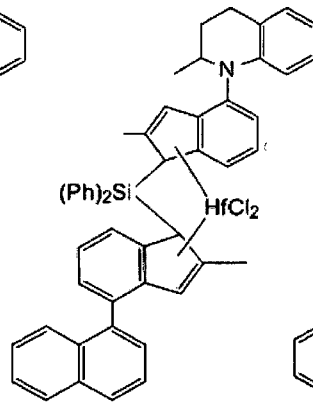
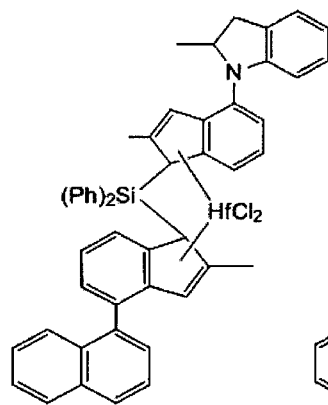
25

30

35

40

45



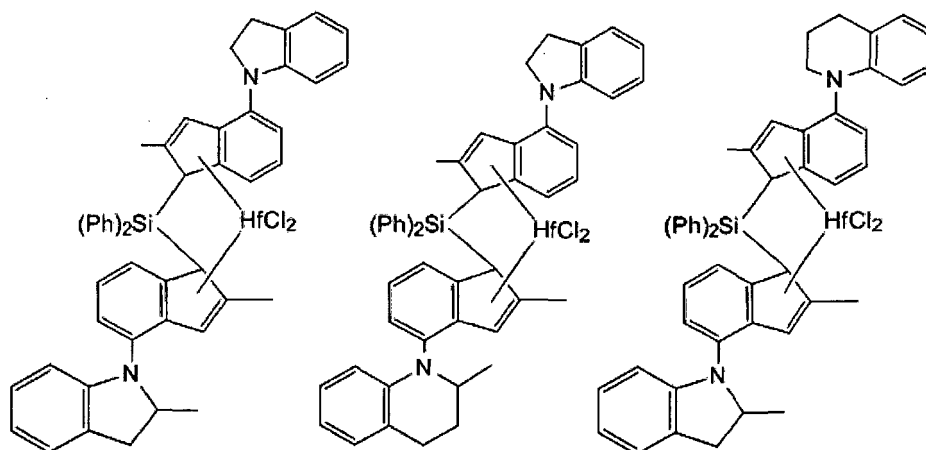
50

55

5

10

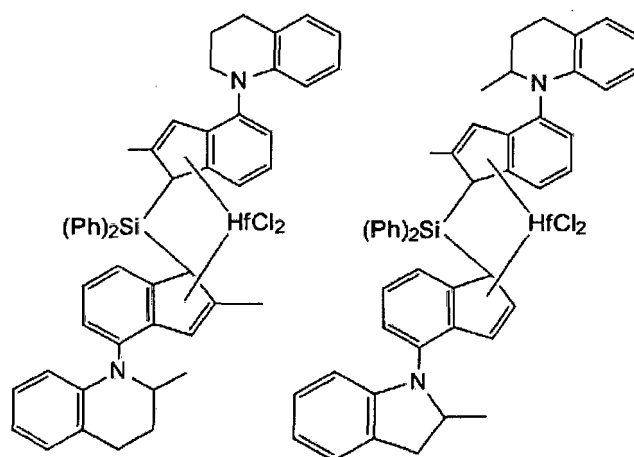
15



20

25

30



35

8. Herstellungsverfahren für eine Ligandenverbindung der nachstehenden chemischen Formel 1, das einen Schritt einschliesst, in dem die durch die nachstehende chemische Formel 3 dargestellte Verbindung und die durch die nachstehende chemische Formel 4 dargestellte Verbindung oder das Lithiumsalz davon umgesetzt werden:

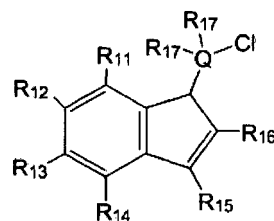
[Chemische Formel 3]

40

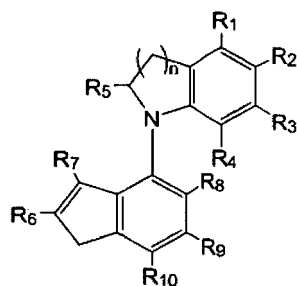
45

50

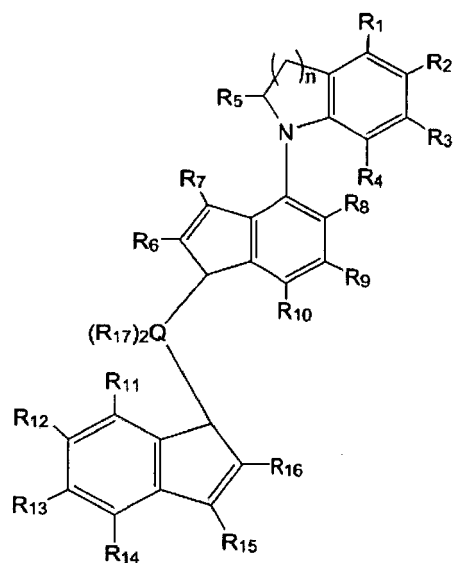
55



[Chemische Formel 4]



[Chemische Formel 1]



in den chemischen Formeln 1, 3 und 4:

n ist eine ganze Zahl von 1 bis 2;

R_1 bis R_{16} sind gleich oder voneinander verschieden und sind unabhängig Wasserstoff, C_{1-20} -Alkyl, C_{1-20} -Alkoxy, C_{2-20} -Alkenyl, C_{6-20} -Aryl, C_{7-20} -Alkylaryl, C_{7-20} -Arylalkyl, C_{3-20} -Cycloalkyl, ein C_{5-20} -Heteroring oder Silyl, und zwei oder mehr benachbarte Gruppen von R_1 bis R_{16} können über eine Alkyldingruppe, einschliesslich einer C_{1-20} -Alkylgruppe oder einer C_{6-20} -Arylgruppe, miteinander verbunden sein, um einen Ring zu bilden;

R_{17} ist Wasserstoff, Halogen, C_{1-20} -Alkyl, C_{6-20} -Aryl oder C_{1-20} -Alkoxy; und

Q ist Kohlenstoff oder Silicium.

- 45
9. Herstellungsverfahren gemäss Anspruch 8, worin R_1 bis R_{16} unabhängig Wasserstoff, C_{1-20} -Alkyl, C_{6-20} -Aryl, C_{7-20} -Alkylaryl, C_{7-20} -Arylalkyl oder ein C_{5-20} -Heteroring sind und R_{17} C_{1-20} -Alkyl oder C_{6-20} -Aryl ist.
- 50
10. Herstellungsverfahren für eine Übergangsmetallverbindung der nachstehenden chemischen Formel 2, das einen Schritt einschliesst, in dem die durch die nachstehende chemische Formel 1 dargestellte Ligandenverbindung und die durch die nachstehende chemische Formel 9 dargestellte Verbindung umgesetzt werden:

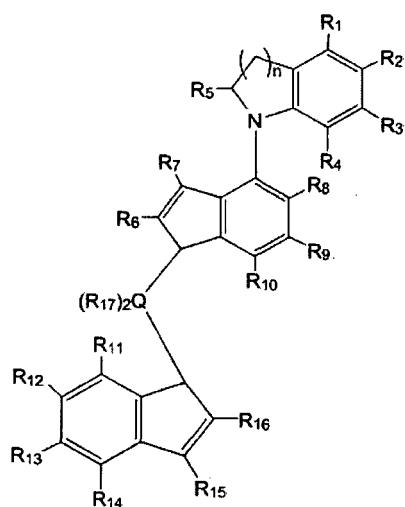
[Chemische Formel 1]

5

10

15

20



[Chemische Formel 9]

 $M(X_1X_2)_2$

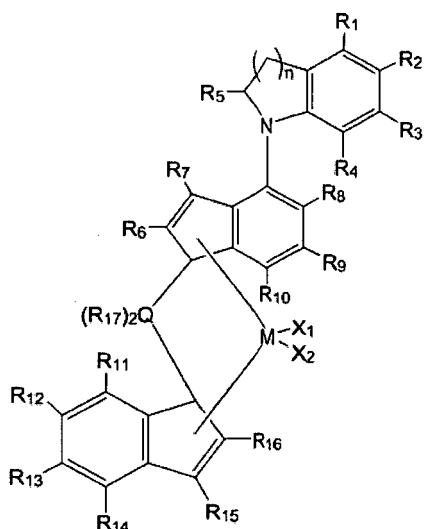
[Chemische Formel 2]

25

30

35

40



in den chemischen Formeln 1, 2 und 9:

45

n ist eine ganze Zahl von 1 bis 2;

R_1 bis R_{16} sind gleich oder voneinander verschieden und sind unabhängig Wasserstoff, C_{1-20} -Alkyl, C_{1-20} -Alkoxo, C_{2-20} -Alkenyl, C_{6-20} -Aryl, C_{7-20} -Alkylaryl, C_{7-20} -Arylalkyl, C_{3-20} -Cycloalkyl, ein C_{5-20} -Heteroring oder Silyl, und zwei oder mehr benachbarte Gruppen von R_1 bis R_{16} können über eine Alkyldingruppe, einschliesslich einer C_{1-20} -Alkylgruppe oder einer C_{6-20} -Arylgruppe, miteinander verbunden sein, um einen Ring zu bilden;

50

R_{17} ist Wasserstoff, Halogen, C_{1-20} -Alkyl, C_{6-20} -Aryl oder C_{1-20} -Alkoxy;

Q ist Kohlenstoff oder Silicium;

M ist ein Übergangsmetall der Gruppe 4; und

55

X_1 und X_2 sind gleich oder voneinander verschieden und sind unabhängig Halogen, eine C_{1-20} -Alkyl-, C_{2-20} -Alkenyl-, C_{6-20} -Aryl-, C_{7-20} -Alkylaryl-, C_{7-20} -Arylalkyl-, C_{1-20} -Alkylamino-, C_{6-20} -Arylamino- oder C_{1-20} -Alkyldingruppe.

11. Herstellungsverfahren gemäss Anspruch 10, worin R_1 bis R_{16} unabhängig Wasserstoff, C_{1-20} -Alkyl, C_{6-20} -Aryl,

C_{7-20} -Alkylaryl, C_{7-20} -Arylalkyl oder ein C_{5-20} -Heteroring sind und R_{17} C_{1-20} -Alkyl oder C_{6-20} -Aryl ist.

12. Herstellungsverfahren gemäss Anspruch 10, worin M ein Metall, ausgewählt aus der Gruppe bestehend aus Ti, Zr und Hf, ist.

5

Revendications

1. Composé de ligand, représenté par la formule chimique 1 suivante :

10

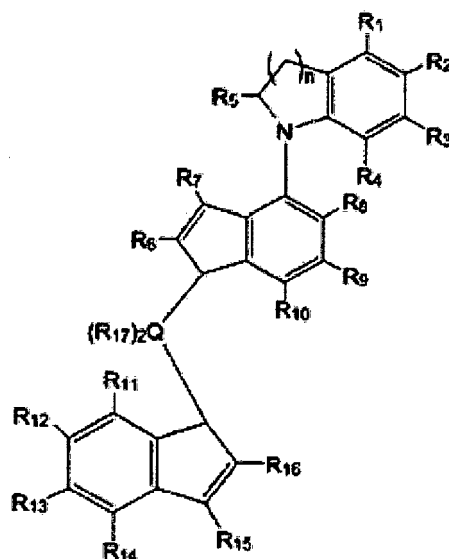
[Formule chimique 1]

15

20

25

30



dans la formule chimique 1,

35

n est un nombre entier allant de 1 à 2 ;

R_1 à R_{16} sont égaux ou différents les uns des autres, et sont indépendamment un hydrogène, un alkyle en C_1 à C_{20} , un alcoxy en C_1 à C_{20} , un alcényle en C_2 à C_{20} , un aryle en C_6 à C_{20} , un alkylaryle en C_7 à C_{20} , un arylalkyle en C_7 à C_{20} , un cycloalkyle en C_3 à C_{20} , un hétérocycle en C_5 à C_{20} , ou un silyle, et 2 groupes adjacents ou plus parmi R_1 à R_{16} peuvent être liés ensemble par l'intermédiaire d'un groupe alkylidine incluant un groupe alkyle en C_1 à C_{20} ou un groupe aryle en C_6 à C_{20} pour former un cycle;

40

R_{17} est un hydrogène, un halogène, un alkyle en C_1 à C_{20} , un aryle en C_6 à C_{20} , ou un alcoxy en C_1 à C_{20} ; et Q est un carbone ou un silicium.

2. Composé de ligand selon la revendication 1, dans lequel R_1 à R_{16} sont indépendamment un hydrogène, un alkyle en C_1 à C_{20} , un aryle en C_6 à C_{20} , un alkylaryle en C_7 à C_{20} , un arylalkyle en C_7 à C_{20} , ou un hétérocycle en C_5 à C_{20} , et R_{17} est un alkyle en C_1 à C_{20} ou un aryle en C_6 à C_{20} .

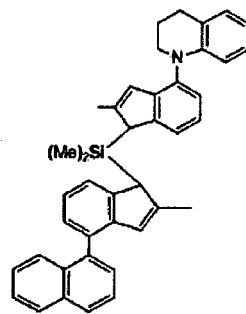
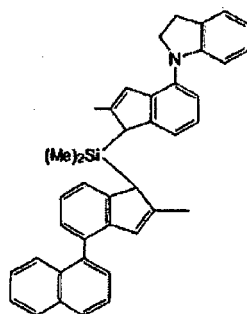
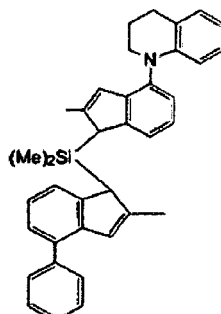
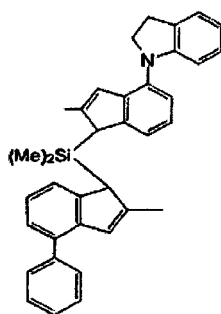
45

3. Composé de ligand selon la revendication 1, dans lequel le composé représenté par la formule chimique 1 est représenté par l'une quelconque des formules structurales suivantes :

50

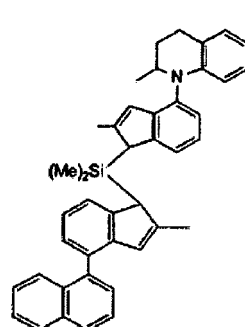
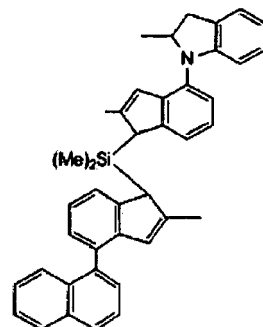
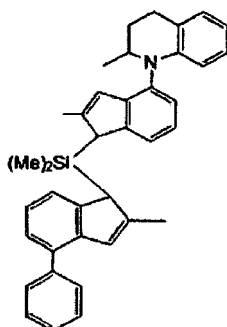
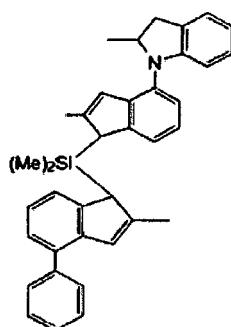
55

5



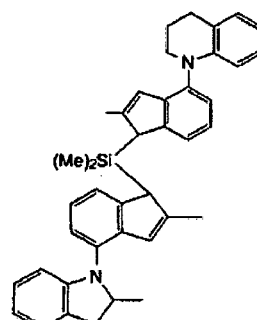
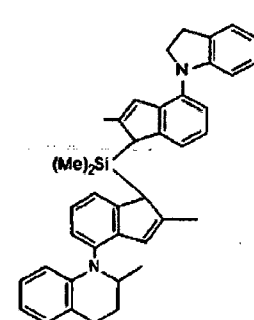
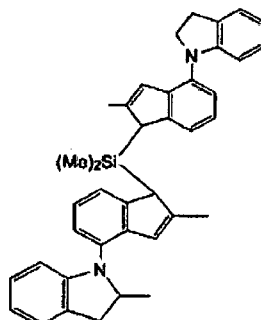
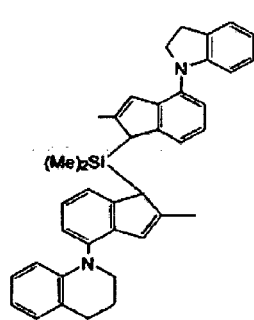
10

15



20

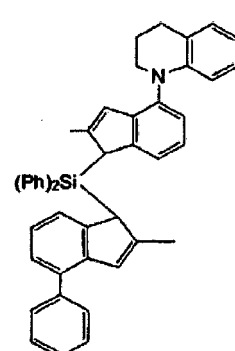
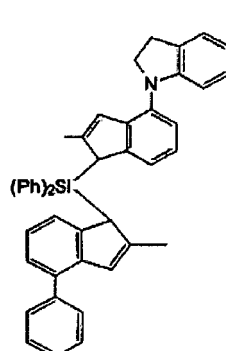
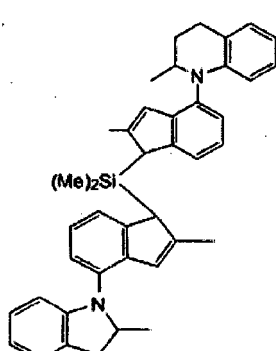
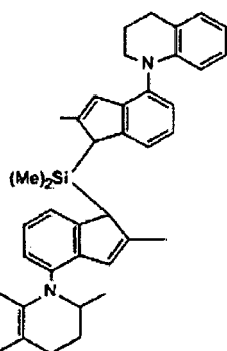
25



30

35

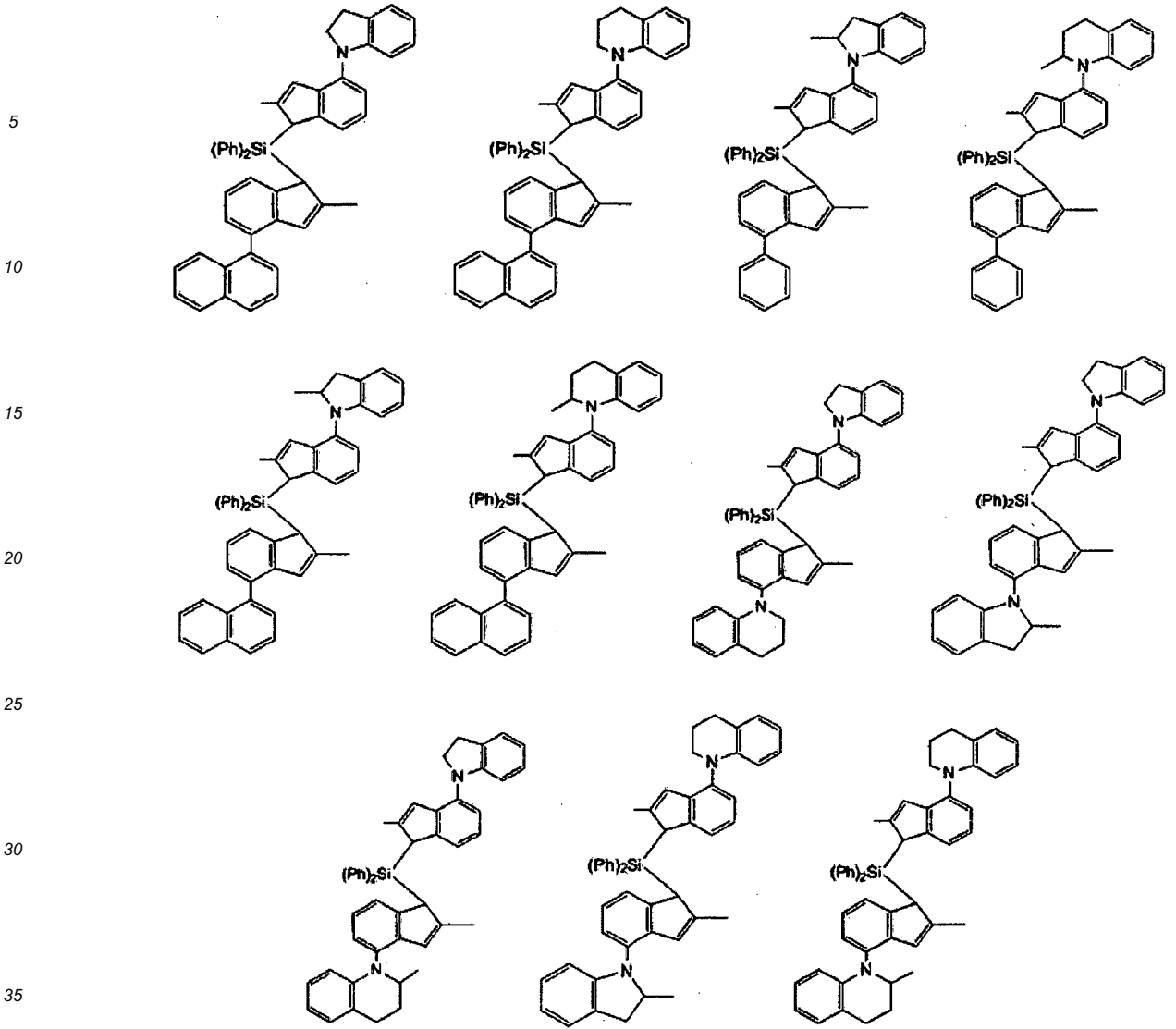
40



45

50

55



4. Composé de métal de transition, représenté par la formule chimique 2 suivante :

40

45

50

55

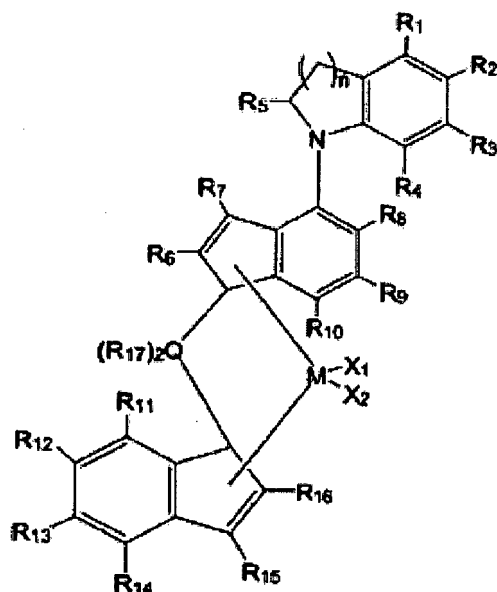
[Formule chimique 2]

5

10

15

20



dans la formule chimique 2,

n est un nombre entier allant de 1 à 2 ;

25

R_1 à R_{16} sont égaux ou différents les uns des autres, et sont indépendamment un hydrogène, un alkyle en C_1 à C_{20} , un alcoxy en C_1 à C_{20} , un alcényle en C_2 à C_{20} , un aryle en C_6 à C_{20} , un alkylaryle en C_7 à C_{20} , un arylalkyle en C_7 à C_{20} , un cycloalkyle en C_3 à C_{20} , un hétérocycle en C_5 à C_{20} , ou un silyle, et 2 groupes adjacents ou plus parmi R_1 à R_{16} peuvent être liés ensemble par l'intermédiaire d'un groupe alkyldine incluant un groupe alkyle en C_1 à C_{20} ou un groupe aryle en C_6 à C_{20} pour former un cycle ;

30

R_{17} est un hydrogène, un halogène, un alkyle en C_1 à C_{20} , un aryle en C_6 à C_{20} , ou un alcoxy en C_1 à C_{20} ;

Q est un carbone ou un silicium ;

M est un métal de transition du groupe 4 ; et

35

X_1 et X_2 sont égaux ou différents l'un de l'autre, et sont indépendamment un halogène, un alkyle en C_1 à C_{20} , un alcényle en C_2 à C_{20} , un aryle en C_6 à C_{20} , un alkylaryle en C_7 à C_{20} , un arylalkyle en C_7 à C_{20} , un alkylamino en C_1 à C_{20} , un arylamino en C_6 à C_{20} , ou un groupe alkyldène en C_1 à C_{20} .

5. Composé de métal de transition selon la revendication 4, dans lequel R_1 à R_{16} sont indépendamment un hydrogène, un alkyle en C_1 à C_{20} , un aryle en C_6 à C_{20} , un alkylaryle en C_7 à C_{20} , un arylalkyle en C_7 à C_{20} , ou un hétérocycle en C_5 à C_{20} , et R_{17} est un alkyle en C_1 à C_{20} ou un aryle en C_6 à C_{20} .

40

6. Composé de métal de transition selon la revendication 4, dans lequel le M est un métal sélectionné dans le groupe constitué de Ti, Zr, et Hf.

7. Composé de métal de transition selon la revendication 4, dans lequel le composé de métal de transition représenté par la formule chimique 2 est représenté par l'une quelconque des formules structurales suivantes :

45

50

55

5

10

15

20

25

30

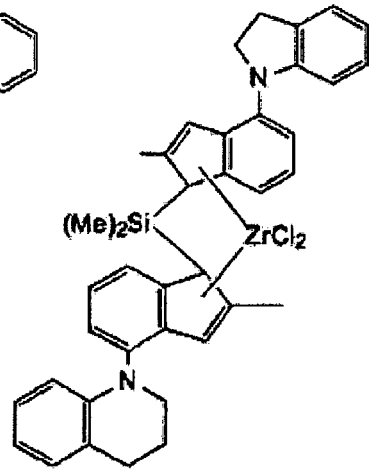
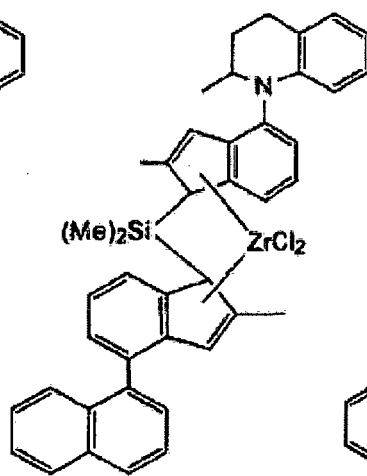
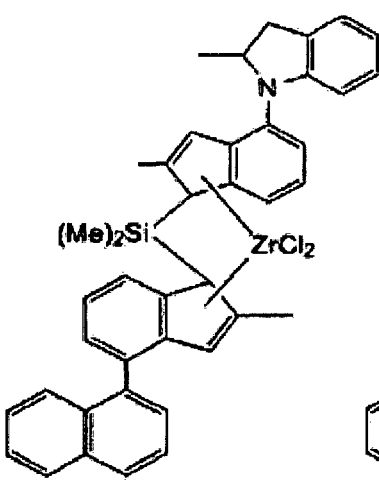
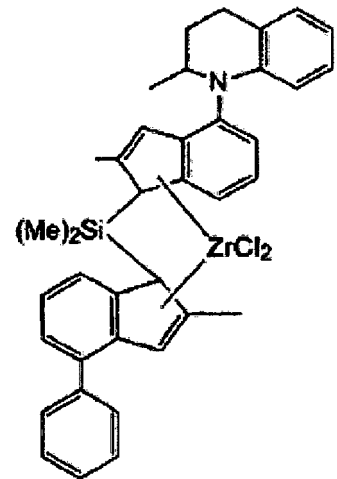
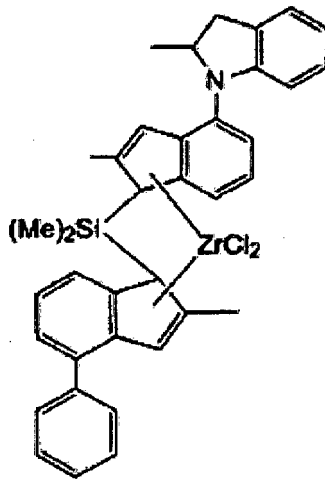
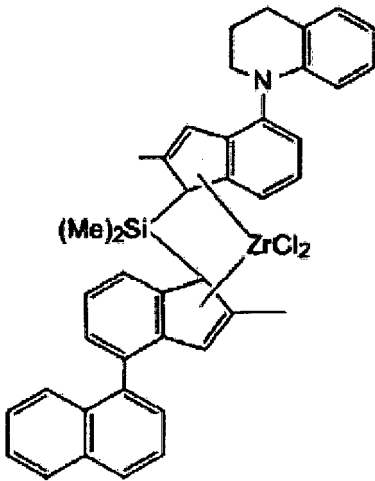
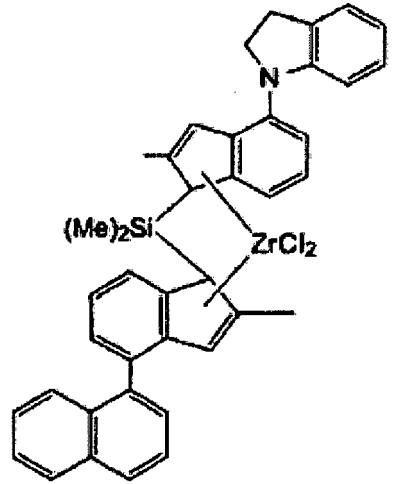
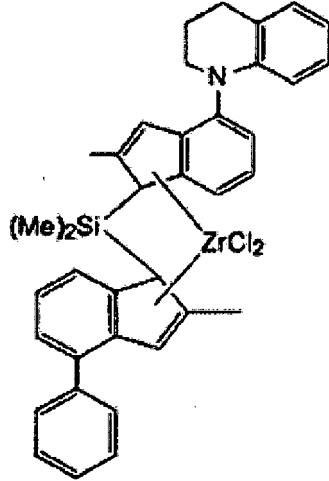
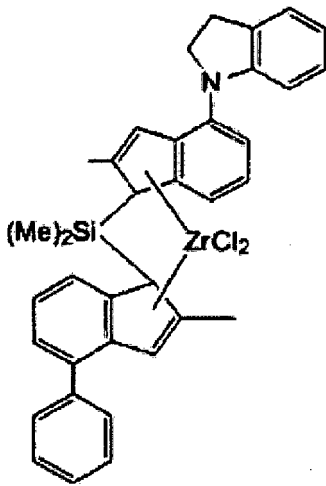
35

40

45

50

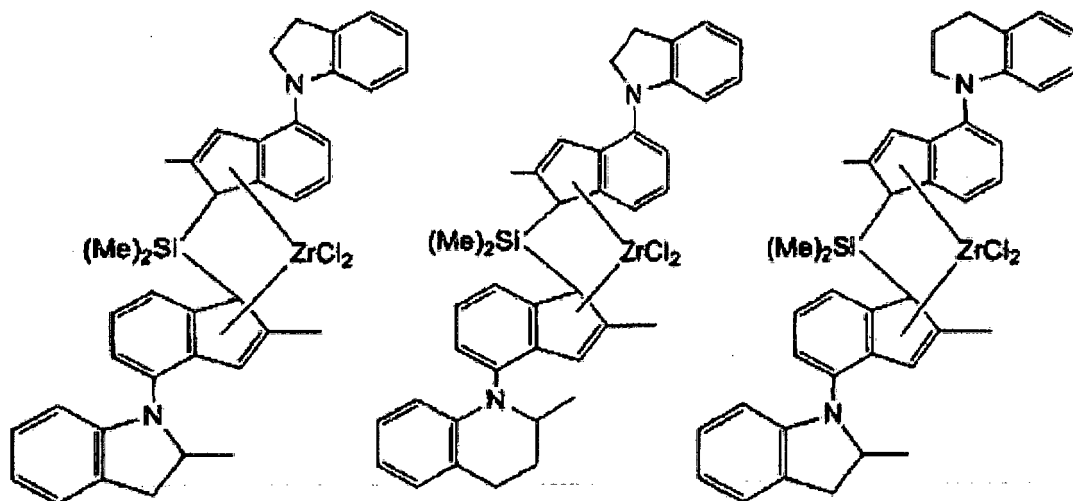
55



5

10

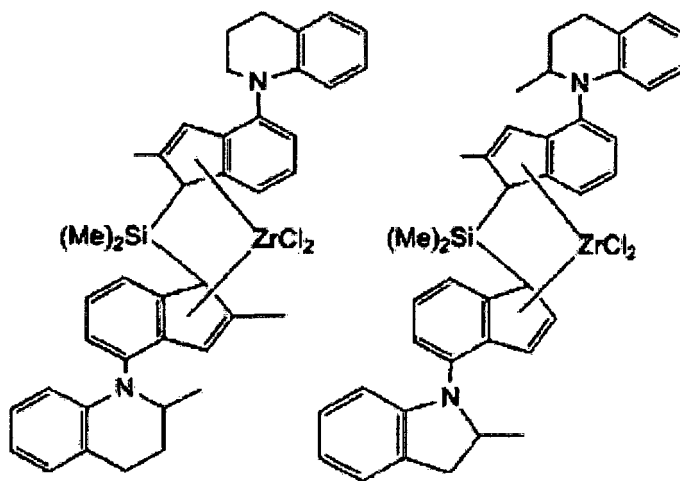
15



20

25

30

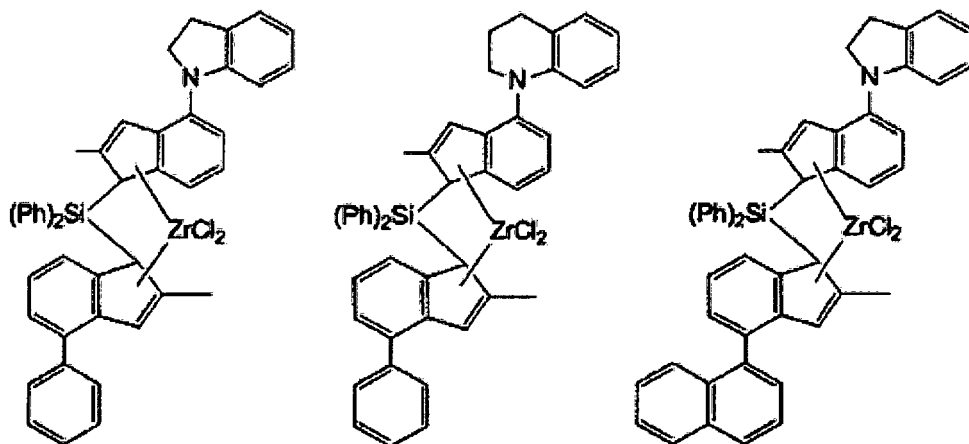


35

40

45

50

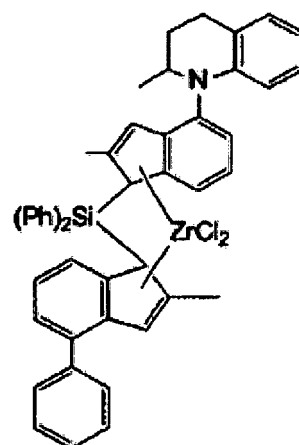
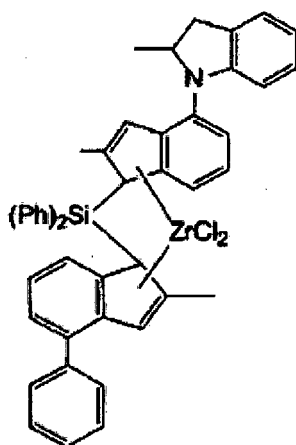
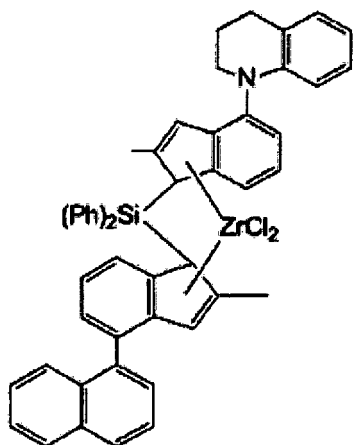


55

5

10

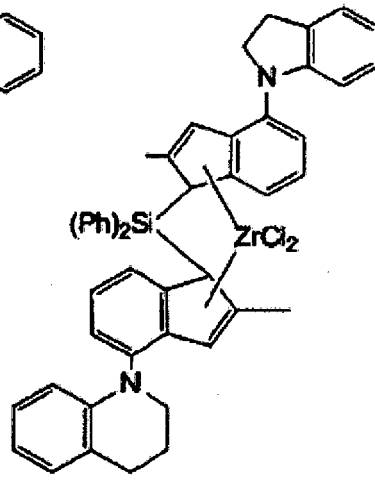
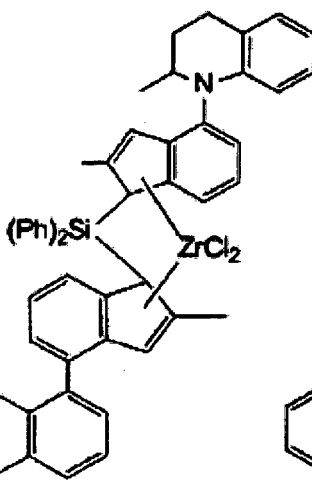
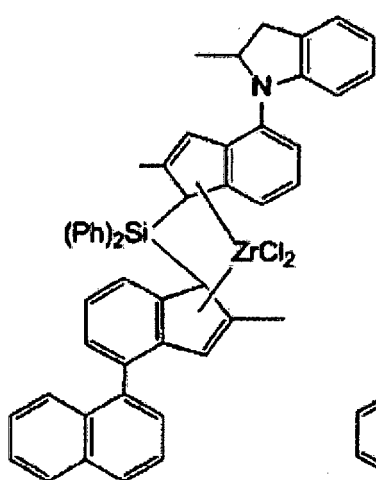
15



20

25

30

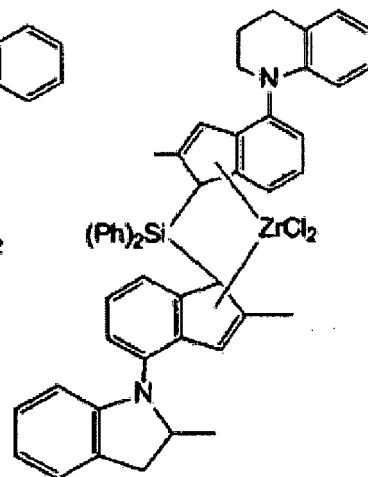
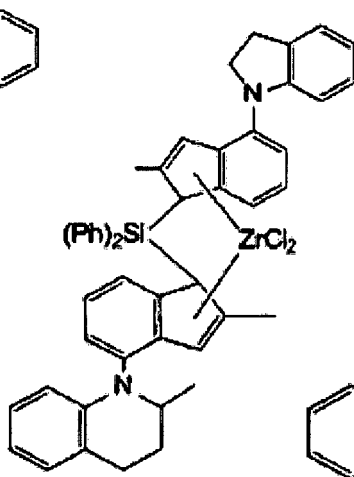
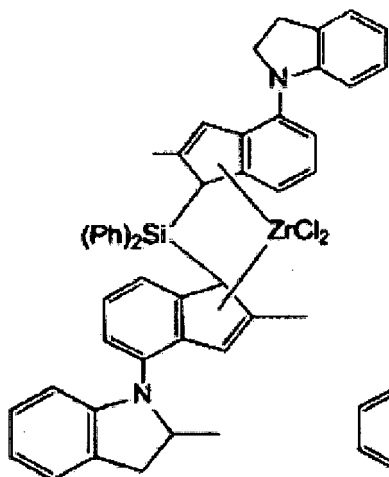


35

40

45

50



55

5

10

15

20

25

30

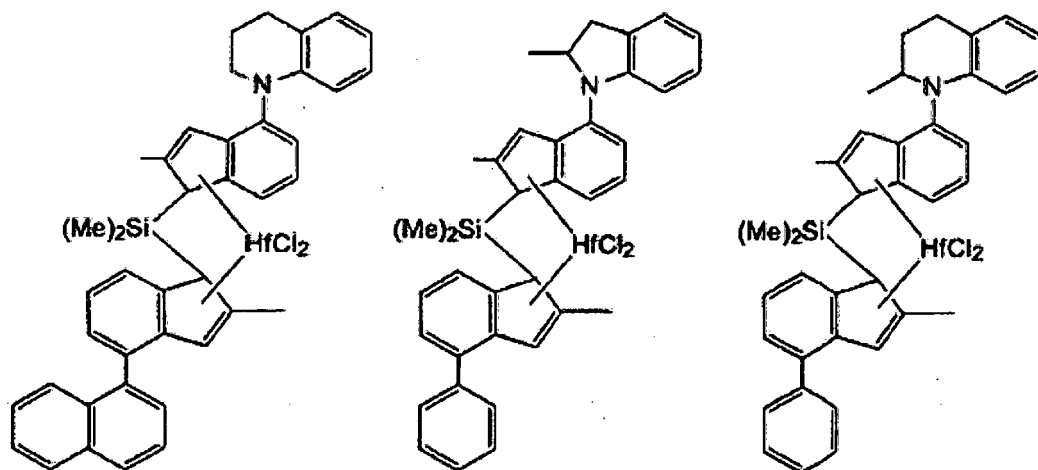
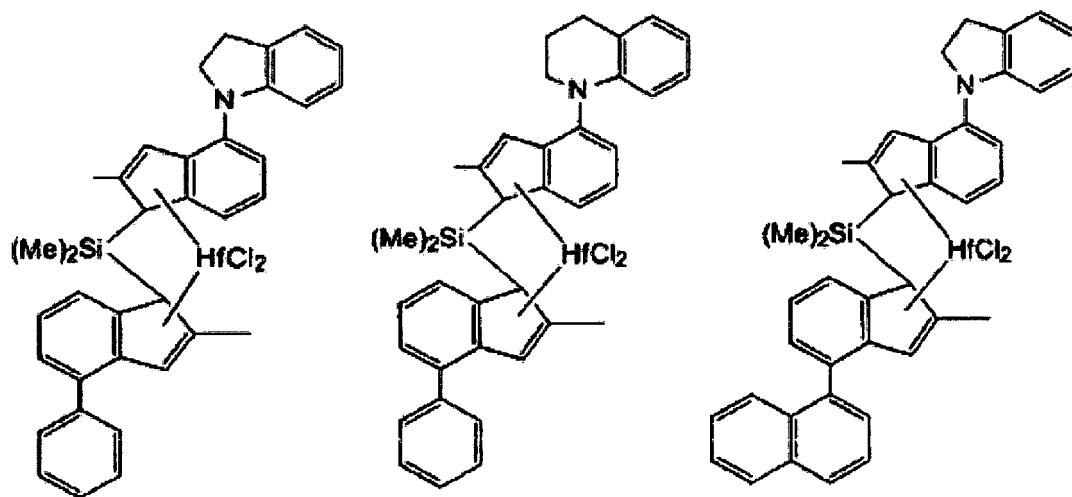
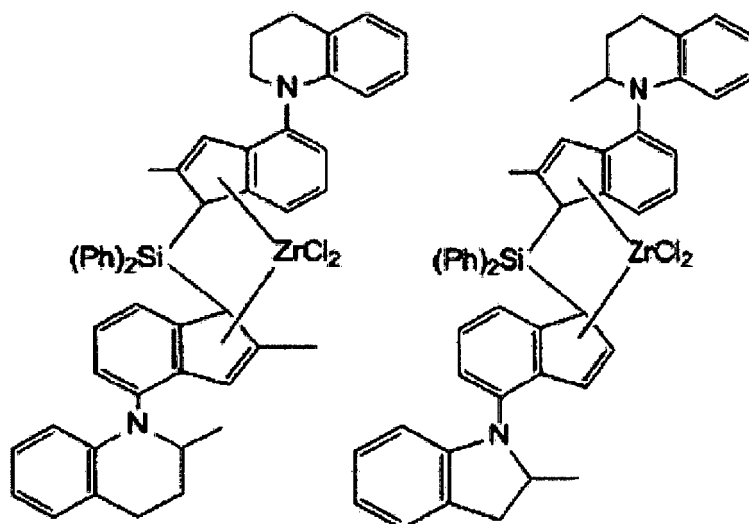
35

40

45

50

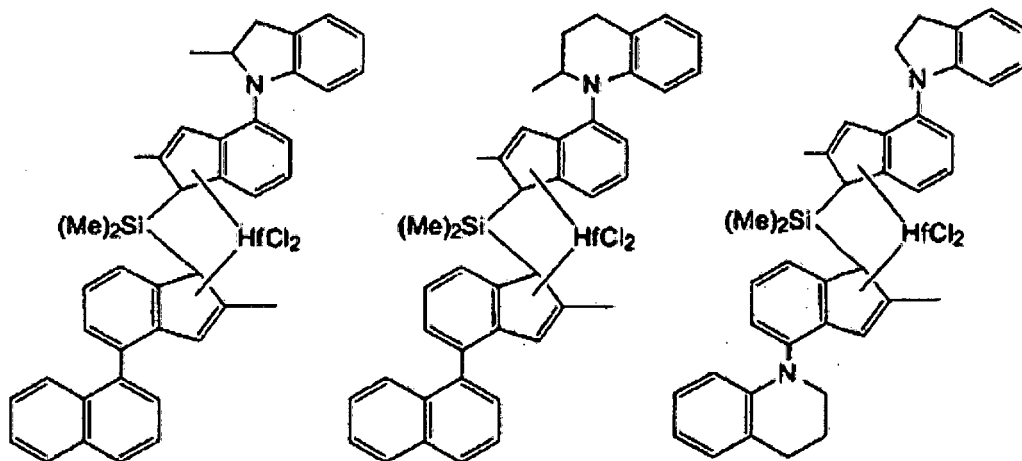
55



5

10

15

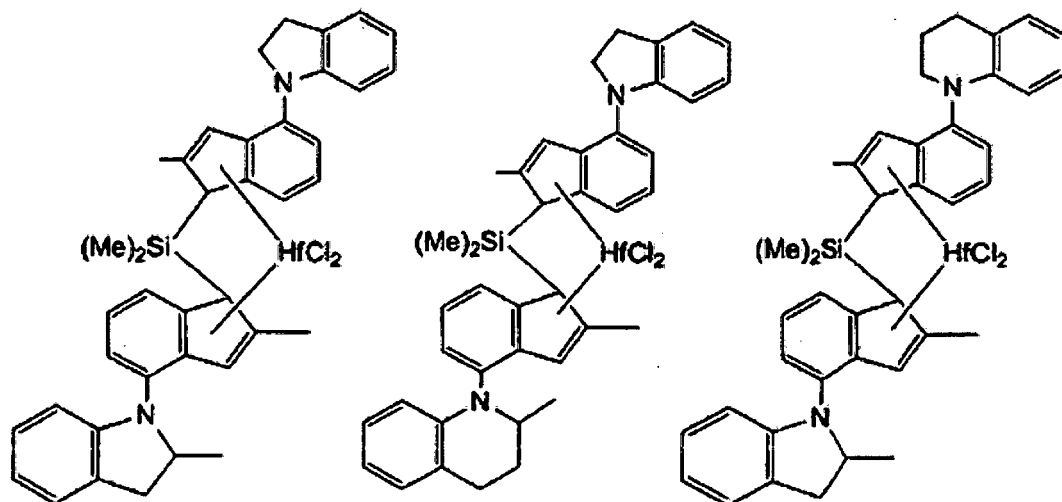


20

25

30

35

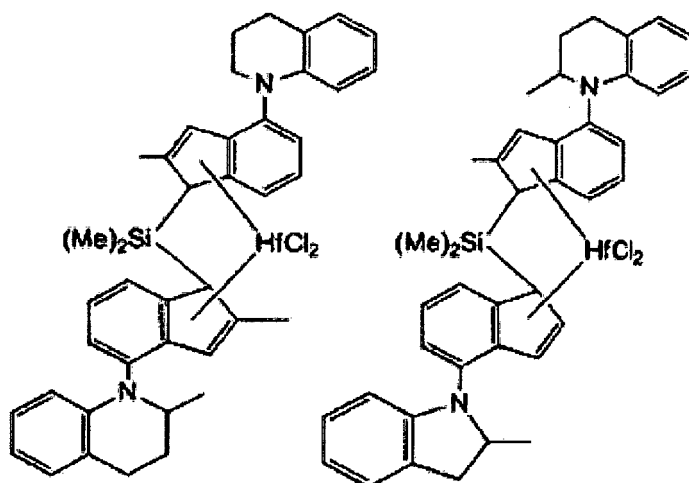


40

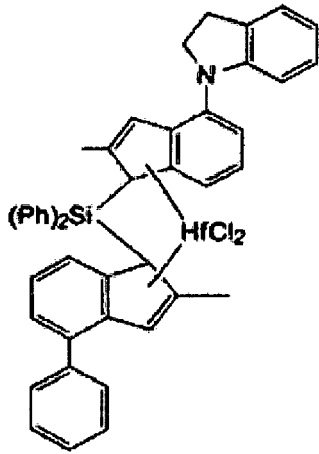
45

50

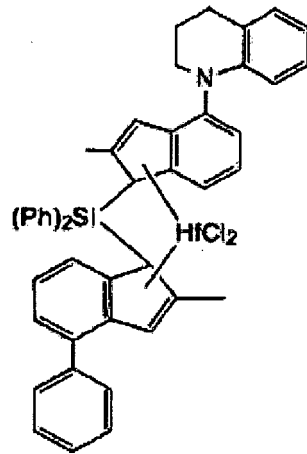
55



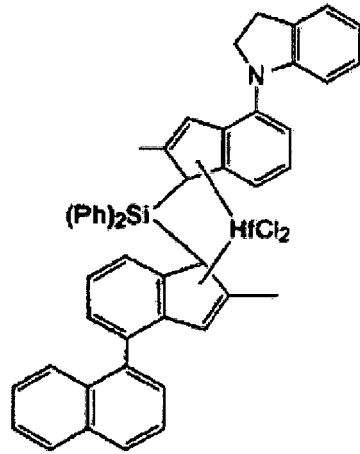
5



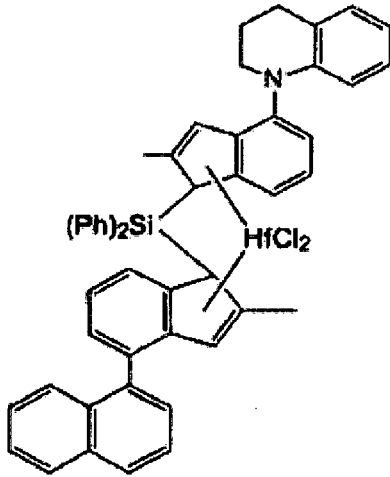
10



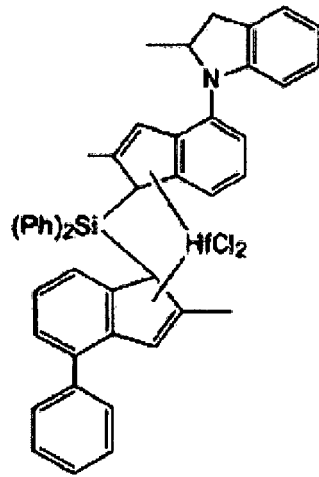
15



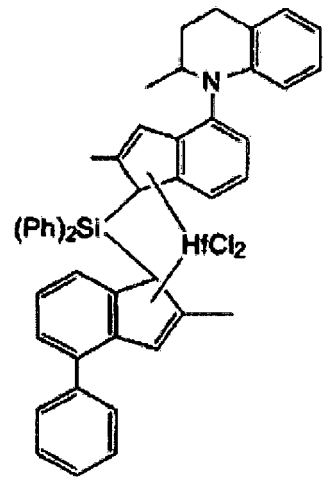
20



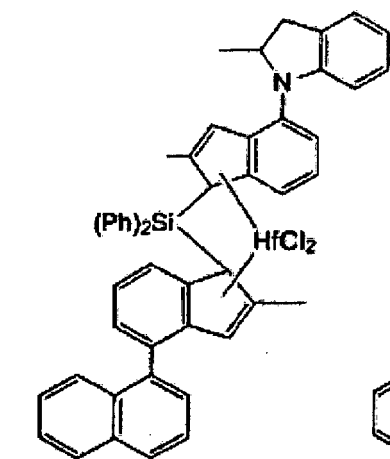
25



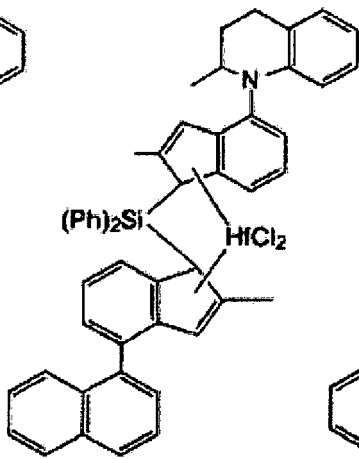
30



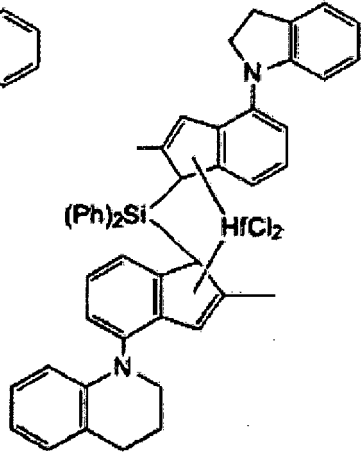
35



40



45



50

55

5

10

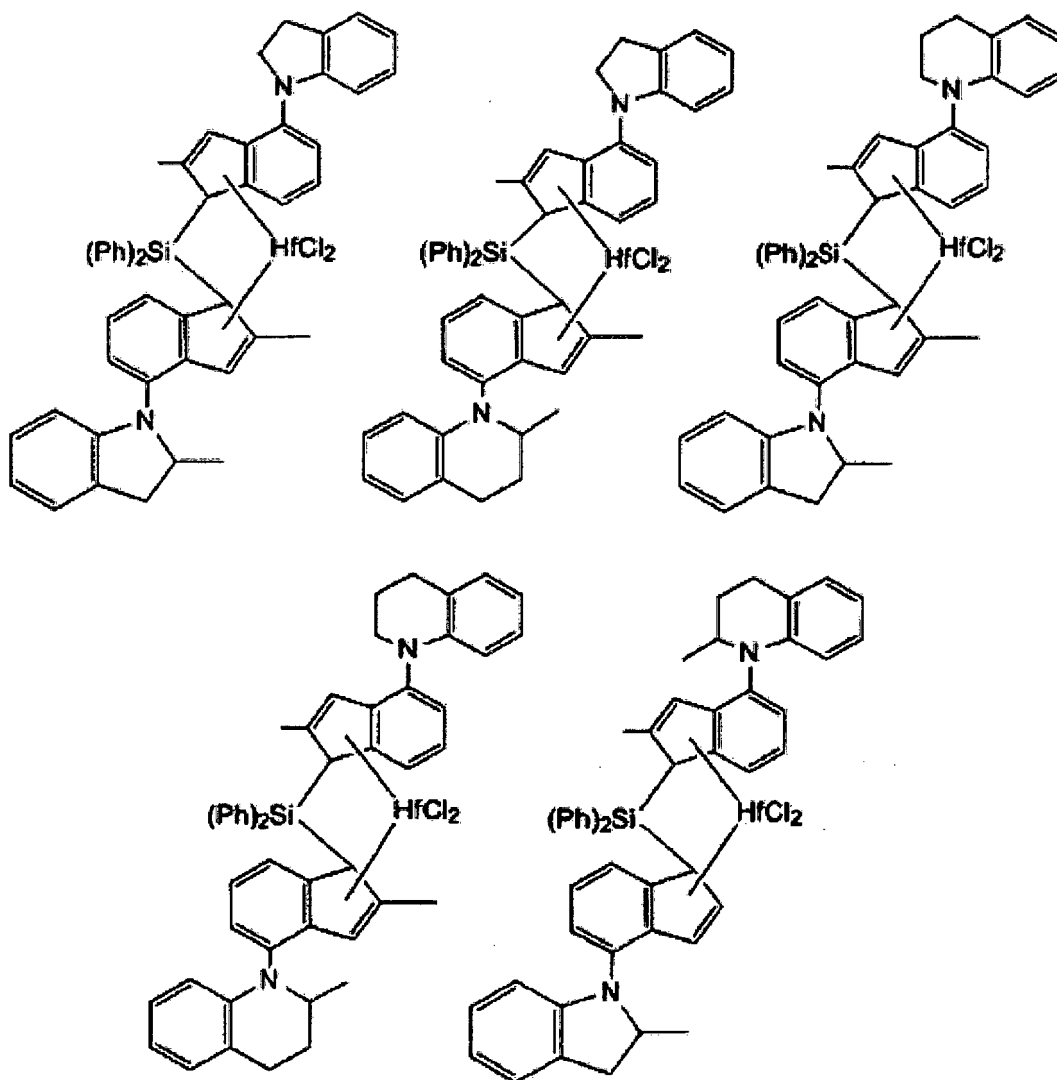
15

20

25

30

35



8. Procédé de préparation du composé de ligand représenté par la formule chimique 1 suivante, incluant l'étape de mise en oeuvre de la réaction du composé représenté par la formule chimique 3 suivante et du composé représenté par la formule chimique 4 suivante ou du sel de lithium de celui-ci

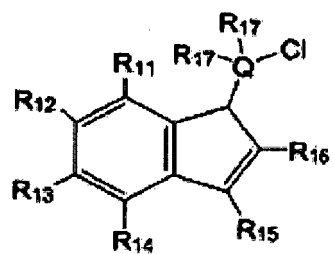
40

[Formule chimique 3]

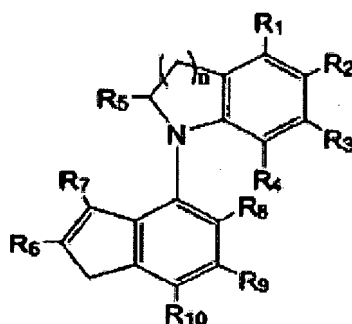
45

50

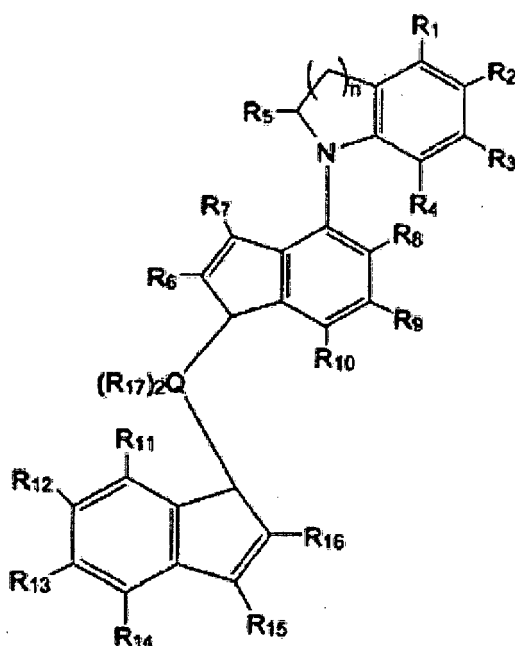
55



[Formule chimique 4]



[Formule chimique 1]



dans les formules chimiques 1, 3 et 4,
 n est un nombre entier allant de 1 à 2 ;

R₁ à R₁₆ sont égaux ou différents les uns des autres, et sont indépendamment un hydrogène, un alkyle en C₁ à C₂₀, un alcoxy en C₁ à C₂₀, un alcényle en C₂ à C₂₀, un aryle en C₆ à C₂₀, un alkylaryle en C₇ à C₂₀, un arylalkyle en C₇ à C₂₀, un cycloalkyle en C₃ à C₂₀, un hétérocycle en C₅ à C₂₀, ou un silyle, et 2 groupes adjacents ou plus parmi R₁ à R₁₆ peuvent être liés ensemble par l'intermédiaire d'un groupe alkylidine incluant un groupe alkyle en C₁ à C₂₀ ou un groupe aryle en C₆ à C₂₀ pour former un cycle;

R₁₇ est un hydrogène, un halogène, un alkyle en C₁ à C₂₀, un aryle en C₆ à C₂₀, ou un alcoxy en C₁ à C₂₀; et Q est un carbone ou un silicium.

9. Procédé de préparation selon la revendication 8, dans lequel R₁ à R₁₆ sont indépendamment un hydrogène, un alkyle en C₁ à C₂₀, un aryle en C₆ à C₂₀, un alkylaryle en C₇ à C₂₀, un arylalkyle en C₇ à C₂₀, ou un hétérocycle en C₅ à C₂₀, et R₁₇ est un alkyle en C₁ à C₂₀ ou un aryle en C₆ à C₂₀.

10. Procédé de préparation du composé de métal de transition représenté par la formule chimique 2 suivante, incluant l'étape de mise en oeuvre de la réaction du composé de ligand représenté par la formule chimique 1 suivante et du composé représenté par la formule chimique 9 suivante :

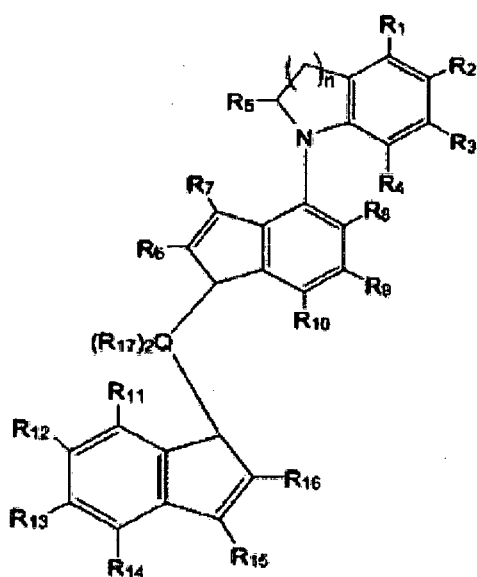
[Formule chimique 1]

5

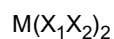
10

15

20



[Formule chimique 9]



25

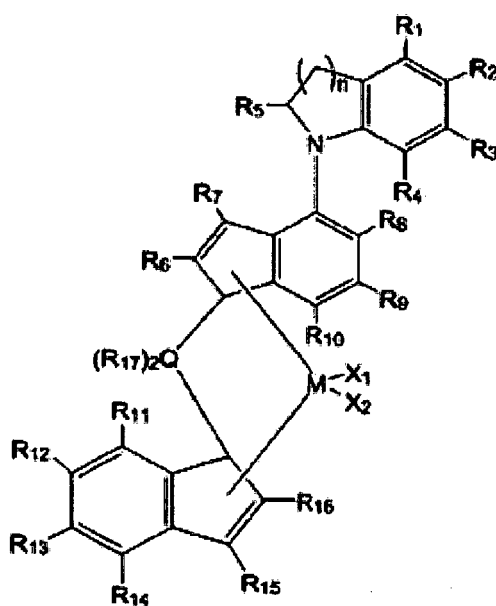
[Formule chimique 2]

30

35

40

45



dans les formules chimiques 1, 2, et 9,
 n est un nombre entier allant de 1 à 2 ;

50

R₁ à R₁₆ sont égaux ou différents les uns des autres, et sont indépendamment un hydrogène, un alkyle en C₁ à C₂₀, un alcoxy en C₁ à C₂₀, un alcényle en C₂ à C₂₀, un aryle en C₆ à C₂₀, un alkylaryle en C₇ à C₂₀, un arylalkyle en C₇ à C₂₀, un cycloalkyle en C₃ à C₂₀, un hétérocycle en C₅ à C₂₀, ou un silyle, et 2 groupes adjacents ou plus parmi R₁ à R₁₆ peuvent être liés ensemble par l'intermédiaire d'un groupe alkyldine incluant un groupe alkyle en C₁ à C₂₀ ou un groupe aryle en C₆ à C₂₀ pour former un cycle ;

55

R₁₇ est un hydrogène, un halogène, un alkyle en C₁ à C₂₀, un aryle en C₆ à C₂₀, ou un alcoxy en C₁ à C₂₀ ;
 Q est un carbone ou un silicium ;

M est un métal de transition du groupe 4 ; et

X₁ et X₂ sont égaux ou différents l'un de l'autre, et sont indépendamment un halogène, un alkyle en C₁ à C₂₀, un alcényle en C₂ à C₂₀, un aryle en C₆ à C₂₀, un alkylaryle en C₇ à C₂₀, un arylalkyle en C₇ à C₂₀, un alkylamino

EP 2 918 591 B1

en C₁ à C₂₀, un arylamino en C₆ à C₂₀, ou un groupe alkylidène en C₁ à C₂₀.

5 11. Procédé de préparation selon la revendication 10, dans lequel R₁ à R₁₆ sont indépendamment un hydrogène, un alkyle en C₁ à C₂₀, un aryle en C₆ à C₂₀, un alkylaryle en C₇ à C₂₀, un arylalkyle en C₇ à C₂₀, ou un hétérocycle en C₅ à C₂₀, et R₁₇ est un alkyle en C₁ à C₂₀ ou un aryle en C₆ à C₂₀.

10 12. Procédé de préparation selon la revendication 10, dans lequel le M est un métal sélectionné dans le groupe constitué de Ti, Zr, et Hf.

10

15

20

25

30

35

40

45

50

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1462464 A [0003]
- KR 820542 [0003]
- US 5064802 A [0004]
- EP 728773 A1 [0007]
- US 5905162 A [0087]

Non-patent literature cited in the description

- *J. Am. Chem. Soc.*, 2000, vol. 122, 10358 [0003]