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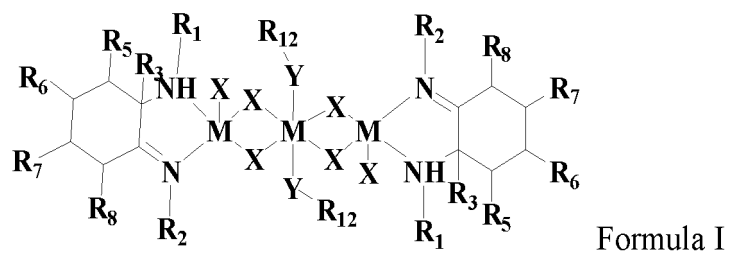
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(54) **AMINO-IMINE METAL COMPLEX AND PREPARATION METHOD THEREFOR AND APPLICATION THEREOF**

(57) The present invention relates to an amino-imine metal complex represented by Formula I and a preparation method and an application thereof. The complex is used as a main catalyst in catalysts for olefin polymerization, and can catalyze the polymerization of ethylene at a relatively high temperature to prepare branched polyethylene having high molecular weight.

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Description

Technical Field

5 **[0001]** The present invention relates to an amino-imine metal complex, a preparation method therefor and application thereof.

Background Art

10 **[0002]** Compared with other resin materials, polyolefin resins have excellent environmental compatibility, and they are therefore widely used in industry and living goods. Polyethylene resins are important polyolefin resins. Commercial polyethylene catalysts include Ziegler-Natta type catalysts (see, for example, DE Pat 889229 (1953); IT Pat 545332 (1956) and IT Pat 536899 (1955); Chem. Rev., 2000, 100, 1169 and related references therein), Phillips type catalysts (see, for example, Belg. Pat. 530617 (1955); Chem. Rev. 1996, 96, 3327), and metallocene type catalysts (see, for example, W. Kaminsky, Metalorganic Catalysts for Synthesis and Polymerization, Berlin: Springer, 1999), as well as late-transition metal complex type high-efficiency ethylene oligomerization and polymerization catalysts that have been rapidly developed in recent years. For example, in 1995, Brookhart et al. reported a class of α -diimine Ni(II) complexes that can polymerize ethylene at a high activity.

20 **[0003]** The α -diimine nickel catalysts have attracted much attention because of their high activity and a great adjustability in molecular weight and branching degree of resulting polymers. Companies including Du Pont have filed multiple patent applications (WO 96/23010, WO 98/03521, WO 98/40374, WO 99/05189, WO 99/62968, WO 00/06620, US 6,103,658, US 6,660,677). Such α -diimine nickel catalysts can catalyze ethylene oligomerization or polymerization at a high activity under the action of methylaluminumoxanes or aluminum alkyls at normal temperature or a low temperature. However, when the reaction temperature is increased to above 50°C, the activity of such α -diimine nickel catalysts generally decreases rapidly, and the molecular weight of the prepared polyethylene decreases rapidly as the polymerization temperature increases.

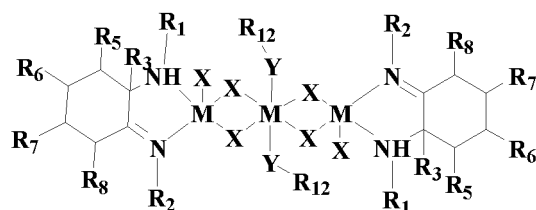
25 **[0004]** Bazan et al. reported that an α -imine amide nickel catalyst can catalyze the living polymerization of ethylene (Macromolecules, 2003, 36, 9731-9735), and on this basis, an α -keto- β -diimine nickel catalyst was synthesized (Chem. Commun. 2009, 6177-6179). This catalyst is used to catalyze the living polymerization of ethylene and propylene at -10°C to obtain an olefin product with a molecular weight distribution below 1.1. Long et al. reported that a large sterically hindered α -diimine nickel catalyst can catalyze the living polymerization of ethylene at 60°C with a molecular weight distribution of 1.11 (ACS Catalysis 2014, 4, 2501-2504). The 2-aminomethylpyridine nickel catalyst developed by Wu Qing's research group at Sun Yat-Sen University can also realize living polymerization of ethylene (Chem. Commun, 2010, 46, 4321-4323).

30 **[0005]** Among the current manners for living polymerization of ethylene using a late-transition metal catalyst, one is to lower the polymerization temperature to inhibit the occurrence of chain transfer at a low temperature (<5 °C) to achieve living polymerization, and another is to inhibit chain transfer by means of increasing the steric hindrance of the ligand to achieve living polymerization at higher temperatures. However, too low temperature is not suitable for the existing industrial reaction equipment, and too large steric hindrance of the ligand makes the design and synthesis of the catalyst more difficult. Therefore, it is of great significance to develop living polymerization catalysts that are relatively simple to synthesize and are resistant to high temperatures.

Disclosures of the invention

45 **[0006]** An object of the present invention is to overcome the shortcomings of the prior art and provide an amino-imine metal complex with good thermal stability, so as to realize the catalytic polymerization of ethylene at a higher temperature to prepare branched polyethylene with high molecular weight.

[0007] In a first aspect, the present invention provides an amino-imine metal complex represented by Formula I:



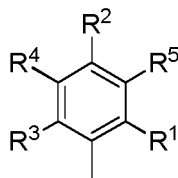
Formula I

wherein, R₁ and R₂ are each independently a C₁-C₃₀ hydrocarbyl with or without a substituent Q; each R₃ is independently

selected from the group consisting of hydrogen and C1-C20 hydrocarbonyl with or without a substituent Q; R₅ to R₈ are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 hydrocarbonyl with or without a substituent Q, and R₅ to R₈ groups are optionally joined to form a ring or ring system; each R₁₂ is independently a C1-C20 hydrocarbonyl with or without a substituent Q; each Y is independently a Group VIA non-metal atom; each M is

independently a Group VIII metal; each X is independently selected from the group consisting of halogen, C1-C10 hydrocarbonyl with or without a substituent Q and C1-C10 hydrocarbonyloxy with or without a substituent Q.

[0008] In some embodiments, in Formula I, R₁ and R₂ are independently selected from the group consisting of C1-C20 alkyl with or without a substituent Q and C6-C20 aryl with or without a substituent Q. Preferably, R₁ and/or R₂ are/is a group represented by Formula A:



Formula A

wherein, R¹-R⁵ are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q, and R¹-R⁵ are optionally joined to form a ring or ring system. Preferably, R¹-R⁵ are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q.

[0009] In some embodiments, each M is independently selected from the group consisting of nickel and palladium.

[0010] In some embodiments, each Y is independently selected from the group consisting of O and S.

[0011] In some embodiments, each X is independently selected from the group consisting of halogen, C1-C10 alkyl with or without a substituent Q and C1-C10 alkoxy with or without a substituent Q, and preferably from the group consisting of halogen, C1-C6 alkyl with or without a substituent Q and C1-C6 alkoxy with or without a substituent Q.

[0012] In some embodiments, in Formula I, each R₁₂ is independently a C1-C20 alkyl with or without a substituent Q, preferably a C1-C10 alkyl with or without a substituent Q, and more preferably a C1-C6 alkyl with or without a substituent Q.

[0013] In some embodiments, in Formula I, each R₃ is selected from the group consisting of C1-C20 alkyl with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q and C7-C20 alkaryl with or without a substituent Q. Preferably, each R₃ is selected from the group consisting of C1-C10 alkyl with or without a substituent Q, C6-C10 aryl with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q and C7-C15 alkaryl with or without a substituent Q. More preferably, each R₃ is a C1-C6 alkyl with or without a substituent Q, such as methyl, ethyl, propyl or butyl.

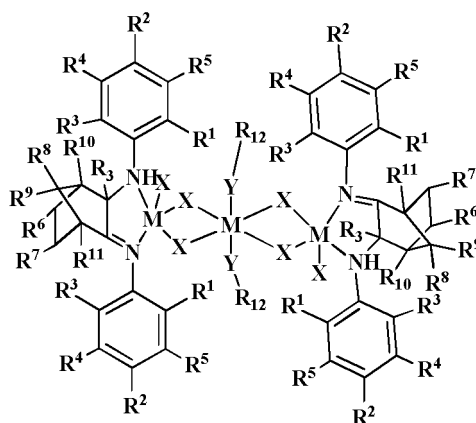
[0014] In some embodiments, the substituent Q is selected from the group consisting of halogen, hydroxy, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy and halogenated C1-C10 alkoxy, and preferably from the group consisting of halogen, hydroxy, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy and halogenated C1-C6 alkoxy.

[0015] Examples of the C1-C6 alkyl include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl and 3,3-dimethylbutyl.

[0016] Examples of the C1-C6 alkoxy include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, n-pentoxy, isopentoxy, n-hexoxy, isohexoxy and 3,3-dimethylbutoxy.

[0017] The term "halogen" as used herein refers to fluorine, chlorine, bromine or iodine.

[0018] In some embodiments, the amino-imine metal complexes according to the present invention are represented by Formula III:



Formula III

wherein, R^1 - R^{11} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q; R_3 , R_{12} , Y, M and X are as defined above for Formula I.

[0019] In some embodiments, the R^1 - R^{11} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q. Preferably, R^1 - R^{11} are each independently selected from the group consisting of hydrogen, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy, halogenated C1-C10 alkoxy and halogen, and more preferably from the group consisting of hydrogen, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy, halogenated C1-C6 alkoxy and halogen.

[0020] In some embodiments, the amino-imine metal complex according to the present invention is selected from the group consisting of

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =methyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =methyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =methyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =methyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =methyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =methyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, $R_{12}=i-Pr$, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein R^1-R^3 =methyl, $R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

5 the complex represented by Formula III, wherein R^1-R^3 =methyl, $R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=Br$, $R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

10 the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=Br$, $R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3=F$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3=Cl$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

15 the complex represented by Formula III, wherein $R^1=R^3=Br$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

20 the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein R^1-R^3 =methyl, $R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

25 the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=Br$, $R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}$ =methyl, R_3 =isopropyl, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3=F$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =isopropyl, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

30 the complex represented by Formula III, wherein $R^1=R^3=Cl$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =isopropyl, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3=Br$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =isopropyl, R_{12} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=CH_3$, R^{11} =bromomethyl, R_3 =isopropyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

35 the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=CH_3$, $R^{11}=CH_2Br$, R_3 =isopropyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9=CH_3$, $R^{11}=CH_2Br$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

40 the complex represented by Formula III, wherein R^1-R^3 =methyl, $R^4-R^7=R^{10}=H$, $R^8=R^9=CH_3$, $R^{11}=CH_2Br$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

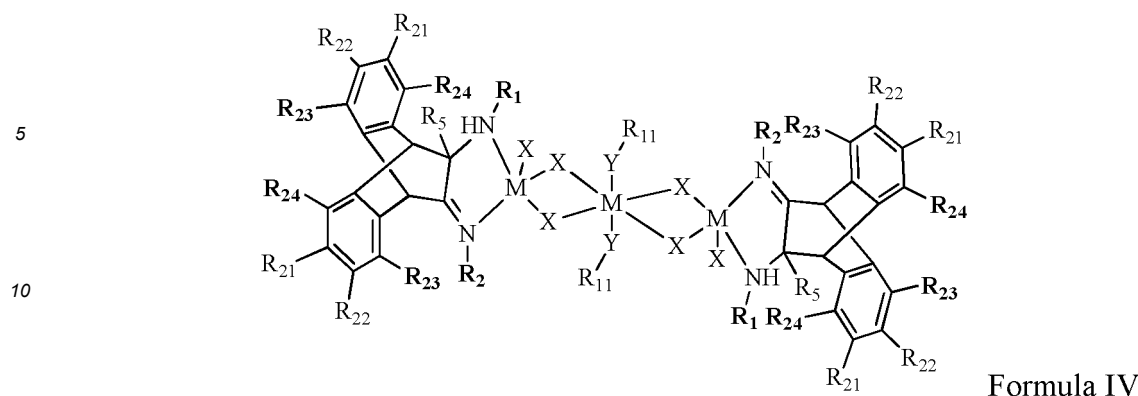
the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=Br$, $R^4-R^7=R^{10}=H$, $R^8=R^9$ =methyl, R_3 =ethyl, $R^{11}=CH_2Br$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3=F$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9$ =methyl, $R^{11}=CH_2Br$, R_3 =isobutyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

45 the complex represented by Formula III, wherein $R^1=R^3=Cl$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9$ =methyl, $R^{11}=CH_2Br$, R_3 =isobutyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

the complex represented by Formula III, wherein $R^1=R^3=Br$, $R^2=R^4-R^7=R^{10}=H$, $R^8=R^9$ =methyl, $R^{11}=CH_2Br$, R_3 =isobutyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$.

50 **[0021]** In a sub-aspect, the amino-imine metal complex according to the present invention has a structure as shown by Formula IV:



15 wherein, R_1 and R_2 are each independently a C1-C30 hydrocarbonyl with or without a substituent Q; R_{21} - R_{24} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 hydrocarbonyl with or without a substituent Q and C1-C20 hydrocarbonyloxy with or without a substituent Q, and R_{21} - R_{24} are optionally joined to form a ring or ring system, preferably a substituted or unsubstituted benzene ring; each R_5 is independently selected from the group consisting of hydrogen and C1-C20 hydrocarbonyl with or without a substituent Q; each R_{11} is independently a C1-C20 hydrocarbonyl with or without a substituent Q; each Y is independently a Group VIA non-metal atom; each M is independently a Group VIII metal; each X is independently selected from the group consisting of halogen, C1-C10 hydrocarbonyl with or without a substituent Q and C1-C10 hydrocarbonyloxy with or without a substituent Q.

[0022] The term "substituted" as used herein refers to substitution by a substituent Q, for example.

20 [0023] In some embodiments of this subaspect, the R_1 and R_2 are independently selected from the group consisting of C1-C20 alkyl with or without a substituent Q and C6-C20 aryl with or without a substituent Q. Preferably, R_1 and/or R_2 are/is a group represented by Formula A:



35 wherein, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q, and R^1 - R^5 are optionally joined to form a ring or ring system. Preferably, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q. More preferably, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C6 alkyl with or without a substituent Q, C2-C6 alkenyl with or without a substituent Q, C2-C6 alkynyl with or without a substituent Q, C1-C6 alkoxy with or without a substituent Q, C2-C6 alkenyloxy with or without a substituent Q, C2-C6 alkynyloxy with or without a substituent Q, C6-C10 aryl with or without a substituent Q, C7-C10 aralkyl group with or without a substituent Q, C7-C10 alkaryl with or without a substituent Q, C6-C10 aryloxy with or without a substituent Q, C7-C10 aralkyloxy with or without a substituent Q, and C7-C10 alkaryloxy with or without a substituent Q.

[0024] In some embodiments of this subaspect, each M is independently selected from the group consisting of nickel and palladium.

55 [0025] In some embodiments of this subaspect, each Y is independently selected from the group consisting of O and S.

[0026] In some embodiments of this subaspect, each X is independently selected from the group consisting of halogen, C1-C10 alkyl with or without a substituent Q and C1-C10 alkoxy with or without a substituent Q, and preferably from the group consisting of halogen, C1-C6 alkyl with or without a substituent Q and C1-C6 alkoxy with or without a substituent Q.

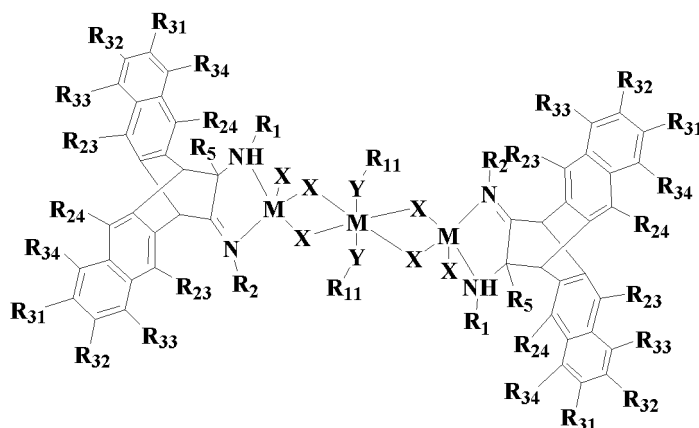
[0027] In some embodiments of this subaspect, each R_{11} is independently a C1-C20 alkyl with or without a substituent Q, preferably a C1-C10 alkyl with or without a substituent Q, and more preferably a C1-C6 alkyl with or without a substituent Q.

[0028] In some embodiments of this subaspect, each R_5 is independently selected from the group consisting of C1-C20 alkyl with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q and C7-C20 alkaryl with or without a substituent Q. Preferably, each R_5 is independently selected from the group consisting of C1-C10 alkyl with or without a substituent Q, C6-C10 aryl with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q and C7-C15 alkaryl with or without a substituent Q. More preferably, each R_5 is independently a C1-C6 alkyl with or without a substituent Q, such as methyl, ethyl, propyl or butyl.

[0029] In some embodiments of this subaspect, the substituent Q is selected from the group consisting of halogen, hydroxy, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy and halogenated C1-C10 alkoxy, and preferably from the group consisting of halogen, hydroxy, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy and halogenated C1-C6 alkoxy. Preferably, the C1-C6 alkyl is selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl and 3,3-dimethylbutyl. Preferably, the C1-C6 alkoxy is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, n-pentoxy, isopentoxy, n-hexyloxy, isohexyloxy and 3,3-dimethylbutoxy.

[0030] In some embodiments of this subaspect, R_{21} - R_{24} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q and C7-C20 alkarylxy with or without a substituent Q, and R_{21} - R_{24} are optionally joined to form a ring or ring system. Preferably, R_{21} - R_{24} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q and C7-C15 alkarylxy with or without a substituent Q. More preferably, R_{21} - R_{24} are each independently selected from the group consisting of hydrogen, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy, halogenated C1-C10 alkoxy and halogen, and more preferably from the group consisting of hydrogen, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy, halogenated C1-C6 alkoxy and halogen.

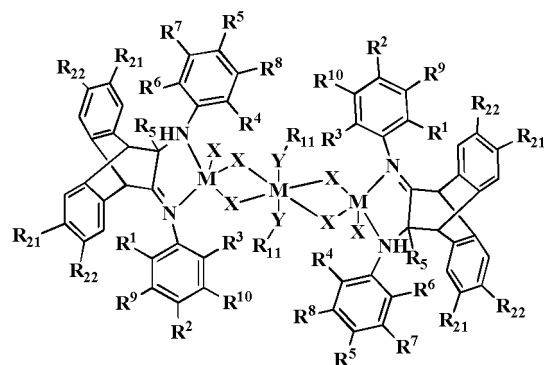
[0031] In some embodiments of this subaspect, the amino-imine metal complex according to the present invention has a structure as shown by Formula IVa:



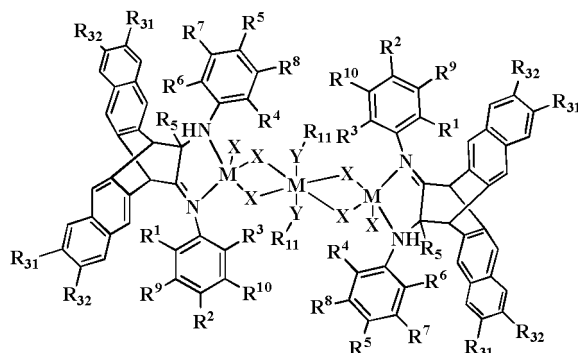
Formula IVa

wherein R_{31} - R_{34} have the same meanings as R_{21} - R_{24} in Formula IV, preferably R_{33} and R_{34} are hydrogen, and R_1 , R_2 , R_5 , R_{11} , Y, M and X are as defined above for Formula IV.

[0032] In some embodiments of this subaspect, the amino-imine metal complex according to the present invention is represented by the following Formula V or Formula V':



Formula V



Formula V'

wherein the individual symbols are as defined above.

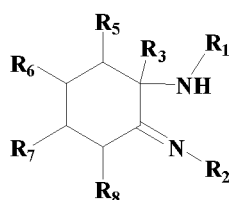
[0033] In some embodiments of this subaspect, the amino-imine metal complex according to the present invention is selected from the group consisting of

- 1) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 2) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 3) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 4) the complex represented by Formula V, wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 5) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =Br, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 6) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =Cl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 7) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =F, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, R_5 =CH₃, R_{11} =ethyl, M=Ni, Y=O, X=Br;
- 8) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;
- 9) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;
- 10) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;
- 11) the complex represented by Formula V, wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;
- 12) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =Br, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;
- 13) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =Cl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;
- 14) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =F, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}$ =H, $R_5=R_{11}$ =ethyl, M=Ni, Y=O, X=Br;

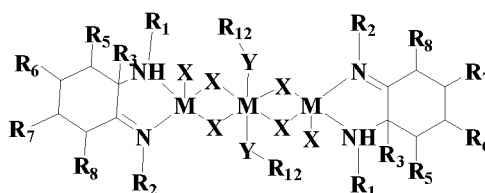
- 15) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 16) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 5 17) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 18) the complex represented by Formula V, wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 19) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 10 20) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 21) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 15 22) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 23) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 24) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 20 25) the complex represented by Formula V, wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 26) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 25 27) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 28) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 29) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 30 30) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 31) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 35 32) the complex represented by Formula V, wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 33) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 34) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 40 35) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;
- 36) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 45 37) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 38) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 39) the complex represented by Formula V', wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 50 40) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 41) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 55 42) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 43) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

- 44) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}$ =H, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 45) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}$ =H, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 46) the complex represented by Formula V', wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{31}=R_{32}$ =H, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 47) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =Br, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}$ =H, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 48) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =Cl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}$ =H, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 49) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =F, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}$ =H, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 50) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 51) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 52) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 53) the complex represented by Formula V', wherein R^1-R^6 =methyl, R^7-R^{10} =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 54) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =Br, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 55) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =Cl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 56) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =F, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 57) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}=R_{11}$ =ethyl, R_5 =CH₃, M=Ni, Y=O, X=Br;
- 58) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}$ =ethyl, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 59) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}$ =ethyl, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 60) the complex represented by Formula V', wherein R^1-R^6 =methyl, R^7-R^{10} =H, $R_{31}=R_{32}$ =ethyl, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 61) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =Br, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}$ =ethyl, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 62) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =Cl, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}$ =ethyl, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br;
- 63) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =F, $R^2=R^5=R^7-R^{10}$ =H, $R_{31}=R_{32}$ =ethyl, R_5 =CH₃, R_{11} =isobutyl, M=Ni, Y=O, X=Br.

[0034] In a second aspect, the present invention provides a method for preparing the amino-imine metal complex, comprising step 1) reacting an amino-imine compound represented by Formula VI with MX_n and $R_{12}YH$ to generate the amino-imine metal complex represented by Formula I,



Formula VI



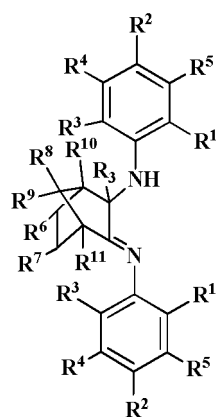
Formula I

wherein R_1 , R_2 , R_3 and R_5 - R_8 in Formula VI have the same definitions as in Formula I;

M and X in MX_n have the same definitions as in Formula I, and n is the number of X satisfying the valence state of M;

Y and R₁₂ in R₁₂YH have the same definitions as in Formula I.

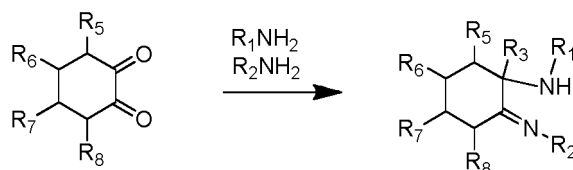
[0035] According to some embodiments of the present invention, the amino-imine compound represented by Formula VI is as shown by the following Formula VIa:



Formula VIa

wherein, R¹-R¹¹ and R₃ have the same meanings as defined for Formula III.

[0036] According to some embodiments of the present invention, the preparation of the amino-imine compound represented by Formula VI comprises step 2) reacting a diketone compound represented by Formula VII with A(R₃)_a and an amine compound, to generate the amino-imine compound represented by Formula VI, with the amine compound being R₁NH₂ and R₂NH₂;

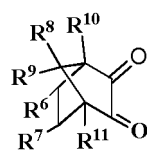


Formula VII

Formula VI

wherein, R₁, R₂, R₃, and R₅-R₈ have the same definitions as in Formula I, A is one or more selected from aluminum, zinc, lithium and magnesium. Preferably, a molar ratio of A(R₃)_a to the amine compound is greater than or equal to 2.0, preferably from 2.0 to 6.0, and more preferably from 3.0 to 6.0.

[0037] According to some embodiments of the present invention, the diketone compound represented by Formula VII is represented by the following Formula VIIa:



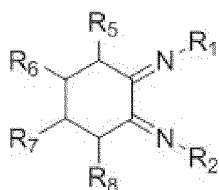
Formula VIIa

wherein R⁶-R¹¹ have the same definitions as in Formula III.

[0038] According to some embodiments of the present invention, the reaction in step 1) is carried out in an organic solvent, and the organic solvent is preferably a halogenated alkane, more preferably the organic solvent is one or more selected from dichloromethane, trichloromethane and 1,2-dichloroethane.

[0039] According to some embodiments of the present invention, the reaction in step 2) is carried out in an aprotic solvent. Preferably, the aprotic solvent is one or more of toluene, benzene, and xylenes.

[0040] According to some embodiments of the present invention, the preparation of the amino-imine compound represented by Formula VI comprises contacting and reacting a diimine compound represented by Formula VIII with A(R₃)_a or a Grignard reagent to generate the amino-imine compound represented by Formula VI,

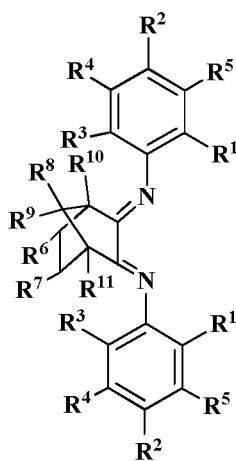


Formula VIII

wherein R_1 , R_2 , and R_5 - R_8 in Formula VIII have the same definitions as in Formula I;

in the $A(R_3)_a$, A is one or more selected from aluminum, zinc, lithium and magnesium, R_3 has the same definitions as in Formula I, a is the number of R_3 that satisfies the valence state of A; and the Grignard reagent has a general formula of R_3MgX , wherein R_3 has the same definitions as in Formula I, and X is a halogen, and preferably bromine and/or chlorine.

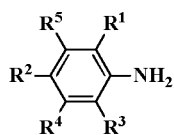
[0041] According to some embodiments of the present invention, the diimine compound represented by Formula VIII is represented the following Formula VIIIa:



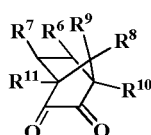
Formula VIIIa

wherein R^1 - R^{11} have the same definition as in Formula III.

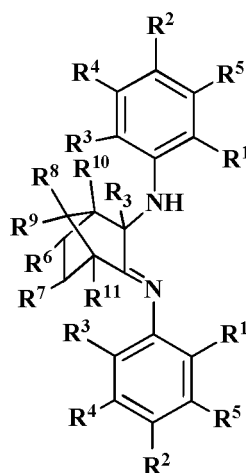
[0042] According to some embodiments of the present invention, the preparation method comprises a first reflux reaction of an amine compound represented by Formula (a) with $A(R_3)_a$ in a solvent, and then a second reflux reaction with a diketone compound represented by Formula VIIa to form a compound represented by Formula VIa,



Formula (a)



Formula VIIa



Formula VIa

[0043] According to a preferred embodiment of the present invention, examples of the amine compound may include 2,6-dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, 2,4,6-trimethylaniline, 2,4,6-triethylaniline, 2,4,6-triisopropylaniline, 2,6-difluoroaniline, 2,6-dibromoaniline, 2,6-dichloroaniline, and 2,6-dimethyl-4-bromoaniline.

[0044] According to a preferred embodiment of the present invention, the amine compound and the $A(R_3)_a$ are refluxed in toluene as a solvent.

[0045] According to a preferred embodiment of the present invention, the conditions of the first reflux reaction include: a reaction temperature of from 10 to 120°C, and a reaction time of from 2 to 12 hours.

[0046] According to a preferred embodiment of the present invention, the time for the second reflux reaction is from 2 to 12 hours, and preferably from 4 to 12 hours.

[0047] In the preparation of the aminoimine ligand by the above method, after the first reflux reaction, the product does not need to be post-treated, and the diketone can be directly added to perform the second reflux reaction so that the operation is simple.

[0048] According to a preferred embodiment of the present invention, the $A(R_3)_a$ encompasses aluminum alkyls, zinc alkyls and lithium alkyls, preferably is selected from aluminum C1-C6 alkyls, zinc C1-C6 alkyls and lithium C1-C6 alkyls, and more preferably is one or more selected from tri-C1-C6-alkyl aluminum, di-C1-C6-alkyl zinc and C1-C6-alkyl lithium, such as trimethyl aluminum, triethyl aluminum, tripropyl aluminum, diethyl zinc and butyl lithium.

[0049] In some embodiments of the present invention, the MXn includes nickel halides, such as nickel bromide and nickel chloride, and derivatives of MXn include 1,2-dimethoxyethane nickel halides, such as 1,2-dimethoxyethane nickel bromide and 1,2-dimethoxyethane nickel chloride.

[0050] In a third aspect, the present invention also provides the use of the above-described aminoimine metal complex in olefin polymerization. Preferably, the olefin includes ethylene and α -olefins with a polar group.

[0051] In a fourth aspect, the present invention also provides a catalyst for olefin polymerization, the catalyst comprising the above-described aminoimine metal complex.

[0052] According to some embodiments of the present invention, the catalyst further comprises a cocatalyst selected from the group consisting of organoaluminum compounds and/or organoboron compounds; the organoaluminum compounds are selected from the group consisting of alkylaluminoxanes or organoaluminum compounds of general formula $AlR_nX^{1}_{3-n}$ (alkylaluminums or alkyl aluminum halides), in which R is H, a C_1 - C_{20} hydrocarbyl or a C_1 - C_{20} hydrocarbyloxy, preferably a C_1 - C_{20} alkyl, a C_1 - C_{20} alkoxy, a C_7 - C_{20} aralkyl or a C_6 - C_{20} aryl; X^1 is a halogen, preferably chlorine or bromine; and $0 < n \leq 3$.

[0053] According to some embodiments of the present invention, specific examples of the organoaluminum compound include, but are not limited to, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, trioctylaluminum, diethyl aluminum hydride, diisobutyl aluminum hydride, diethyl aluminum chloride, diisobutyl aluminum chloride, ethyl aluminum sesquichloride, ethyl aluminum dichloride, methylaluminoxane (MAO), and modified methyl aluminoxane (MMAO). Preferably, the organoaluminum compound is methylaluminoxane (MAO).

[0054] According to some embodiments of the present invention, the organoboron compound is selected from the group consisting of aromatic hydrocarbyl boron compounds and borates. The aromatic hydrocarbyl boron compounds are preferably substituted or unsubstituted phenyl boron, and more preferably tris(pentafluorophenyl)boron. The borates are preferably N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and/or triphenylcarbonium tetrakis(pentafluorophenyl)borate.

[0055] According to some embodiments of the present invention, when the cocatalyst is an organoaluminum compound, a molar ratio of aluminum in the cocatalyst to M in the main catalyst is $(10^{-10} - 10^7):1$, for example, 10:1, 20:1, 50:1, 100:1, 200:1, 300:1, 500:1, 700:1, 800:1, 1,000:1, 2,000:1, 3,000:1, 5,000:1, 10,000:1, 100,000:1, 1,000,000:1, 10,000,000:1, and any value therebetween, preferably $(10^{-1} - 100,000):1$, and more preferably $(100 - 10,000):1$; when the cocatalyst is an organoboron compound, a molar ratio of boron in the cocatalyst to M in the main catalyst is $(0.1 - 1,000):1$, for example, 0.1:1, 0.2:1, 0.5:1, 1:1, 2:1, 3:1, 5:1, 8:1, 10:1, 20:1, 50:1, 100:1, 200:1, 300:1, 500:1, 700:1, 800:1, 1,000:1, and any value therebetween, preferably $(0.1 - 500):1$.

[0056] According to some embodiments of the present invention, the olefin polymerized by means of the catalyst of the present invention is a C2-C16 olefin. Preferably, the olefin is ethylene or an α -olefin having 3-16 carbon atoms.

[0057] According to some embodiments of the present invention, the catalyst further comprises a chain transfer agent, which is one or more selected from aluminum alkyls, magnesium alkyls, boron alkyls and zinc alkyls, and a molar ratio of the chain transfer agent to M in the main catalyst is $(0.1 - 5,000):1$.

[0058] In a fifth aspect, the present invention also provides an olefin polymerization process comprising performing an olefin polymerization reaction such as homopolymerization or copolymerization in the presence of the above-described amino-imine metal complex or the above-described catalyst. Preferably, the temperature for the polymerization reaction ranges from -78°C to 200°C, and preferably from -20°C to 150°C, and the pressure for the polymerization ranges from 0.01 to 10.0 MPa, and preferably from 0.01 to 2.0 MPa.

[0059] According to some embodiments of the present invention, the olefin includes a C2-C16 olefin.

[0060] According to some embodiments of the present invention, the olefin includes a C2-C16 α -olefin.

[0061] According to some embodiments of the present invention, the olefin includes ethylene.

[0062] According to some embodiments of the present invention, the polymerization temperature ranges from -78°C to 200°C, and preferably from -20°C to 150°C.

5 **[0063]** According to some embodiments of the present invention, the polymerization pressure ranges from 0.01 to 10.0 MPa, and preferably from 0.01-2.0 MPa.

[0064] According to some embodiments of the present invention, the polymerization is performed by using an olefin monomer in a solvent, and the solvent for polymerization is one or more selected from alkanes, aromatic hydrocarbons and halogenated hydrocarbons.

10 **[0065]** According to some specific embodiments of the present invention, the solvent for polymerization is one or more selected from hexane, pentane, heptane, benzene, toluene, dichloromethane, chloroform and dichloroethane, and preferably one or more of hexane, toluene and heptane.

[0066] In the present disclosure, the symbols used in different general formulae or structural formulae, such as R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R₁₂, R₃, X, M, A, Y, etc. have the same definitions in each general formula or structural formula, unless specifically indicated.

15 **[0067]** In the present invention, the term "alkyl" refers to straight chain alkyl, branched chain alkyl or cycloalkyl. For example, C₁-C₂₀ alkyl group refers to a C₁-C₂₀ straight chain alkyl group, a C₃-C₂₀ branched chain alkyl group, or a C₃-C₂₀ cycloalkyl group. Examples include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, tert-pentyl, neopentyl, n-hexyl, n-heptyl, n-octyl, and n-decyl. Examples of C₃-C₂₀ cycloalkyl include, but are not limited to, cyclopropyl, cyclopentyl, cyclohexyl, 4-methylcyclohexyl, 4-ethylcyclohexyl, 4-n-propylcyclohexyl and 4-n-butylcyclohexyl.

20 **[0068]** Examples of C₆-C₂₀ aryl group include, but are not limited to, phenyl, 4-methylphenyl, 4-ethylphenyl, dimethylphenyl, vinylphenyl.

[0069] In the present invention, the term "alkenyl" refers to straight chain alkenyl, branched alkenyl or cycloalkenyl. For example, C₂-C₂₀ alkenyl group refers to a C₂-C₂₀ straight chain alkenyl group, a C₃-C₂₀ branched chain alkenyl group, or a C₃-C₂₀ cycloalkenyl group. Examples include, but are not limited to, vinyl, allyl, butenyl.

25 **[0070]** Examples of C₇-C₂₀ aralkyl group include, but are not limited to, phenylmethyl, phenylethyl, phenyl-n-propyl, phenyl-isopropyl, phenyl-n-butyl, and phenyl-t-butyl.

[0071] Examples of C₇-C₂₀ alkaryl group include, but are not limited to, tolyl, ethylphenyl, n-propylphenyl, isopropylphenyl, n-butylphenyl, and tert-butylphenyl.

30 **[0072]** Compared with the prior art, the present invention has the following advantages:

1. The synthesis method of the complexes of the present invention is simple and easy to implement, whereby the trinuclear complexes can be directly prepared from the ligands.

35 2. The catalyst of the present invention can catalyze, under the action of the organoaluminum or organoboron cocatalyst, the polymerization of ethylene at a high activity, and especially can maintain high polymerization activity at a higher polymerization temperature (above 90 degrees). (The activity of diimine nickel catalysts reported in the previous literatures or patents is greatly attenuated above 50 degrees, and the molecular weight is greatly reduced).

3. The catalyst of the present invention has better copolymerization performance with α -olefin or polar monomer.

40 Examples

[0073] The present invention will be described in detail below in conjunction with examples, but the present invention are not limited to these examples.

[0074] The analytical characterization instruments and test methods used in the present invention are as follows:

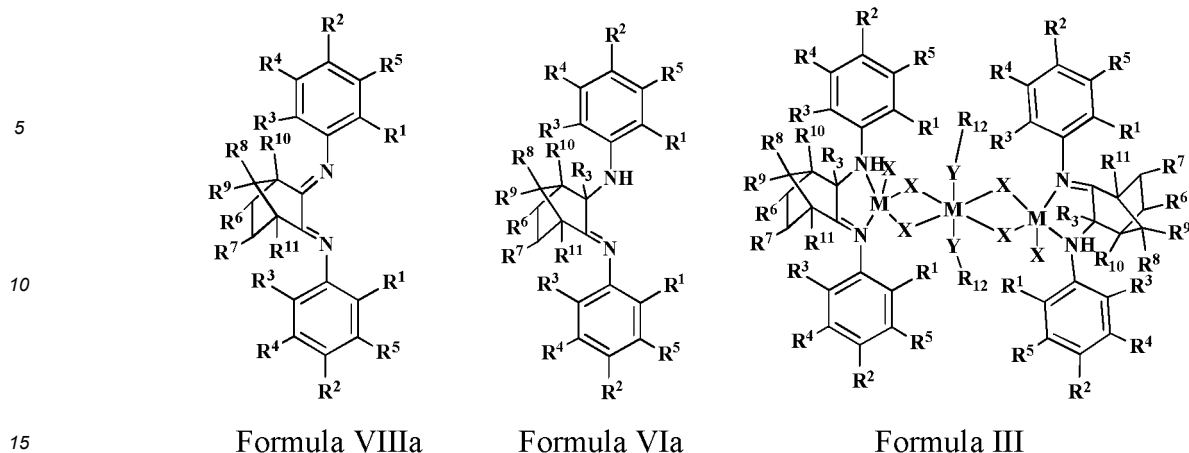
45 Nuclear magnetic resonance instrument: Bruker DMX 300 (300MHz), with tetramethyl silicon (TMS) as an internal standard.

50 Molecular weight and molecular weight distribution PDI (PDI=Mw/Mn) of polymer: measured by PL-GPC220 chromatograph, with trichlorobenzene as a solvent, at 150°C (standards: PS; flow rate: 1.0mL/min; Column: 3×PLgel 10um M1×ED-B 300×7.5nm).

Activity measurement method: gravimetric method, with activity being expressed as polymer weight (g) / nickel (mol) × 2.

[0075] The following compounds, ligands and complexes are involved in the following examples:

55



Diimine compound A1: α -diimine compound represented by Formula VIIIa, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$;

Diimine compound A2: α -diimine compound represented by Formula VIIIa, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$;

Ligand L1: amino-imine compound represented by Formula VIa, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$;

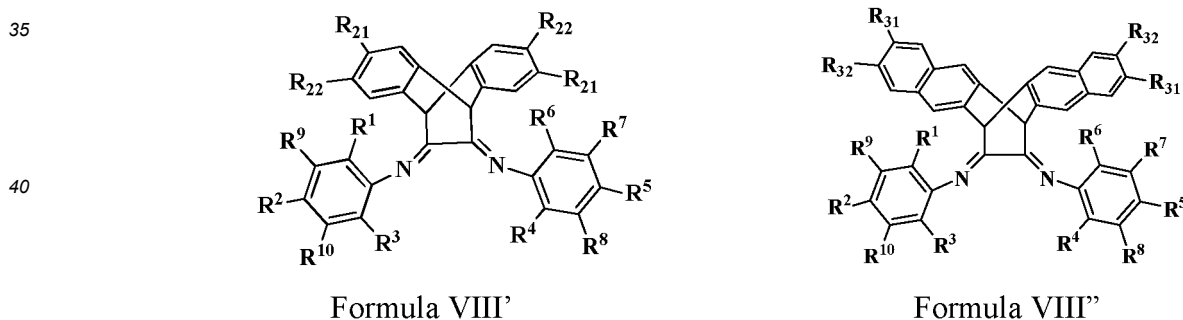
Ligand L2: amino-imine compound represented by Formula VIa, wherein $R^1=R^3$ =i-Pr, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl;

Ligand L3: amino-imine compound represented by Formula VIa, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$;

Complex Ni1: the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

Complex Ni2: the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, R_3 =ethyl, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$;

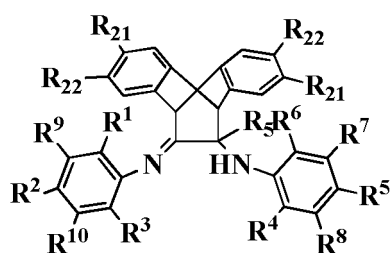
Complex Ni3: the complex represented by Formula III, wherein $R^1=R^3$ =methyl, $R^2=R^4=R^5=R^6=R^7=R^{10}=H$, $R^8=R^9=R^{11}=CH_3$, $R_3=CH_3$, R_{12} =ethyl, $M=Ni$, $Y=O$, $X=Br$.



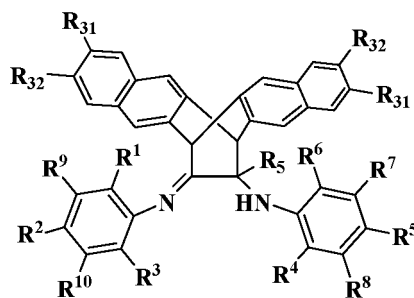
Diimine compound A3: α -diimine compound represented by Formula VIII', wherein $R^1=R^3=R^4=R^6=CH_3$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$;

Diimine compound A4: α -diimine compound represented by Formula VIII', wherein $R^1=R^3=R^4=R^6=i-Pr$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$;

Diimine compound A5: α -diimine compound represented by Formula VIII'', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$;



Formula IX



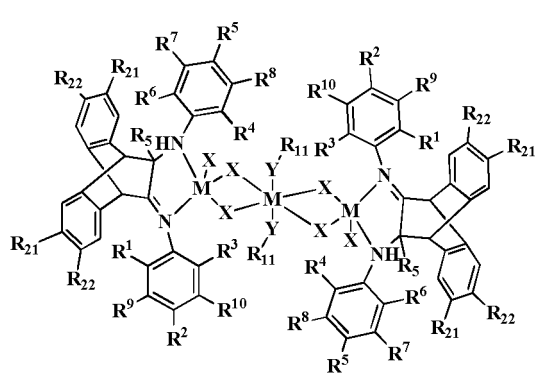
Formula IX'

Ligand L4: amino-imine compound represented by Formula IX, wherein $R^1=R^3=R^4=R^6=CH_3$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$;

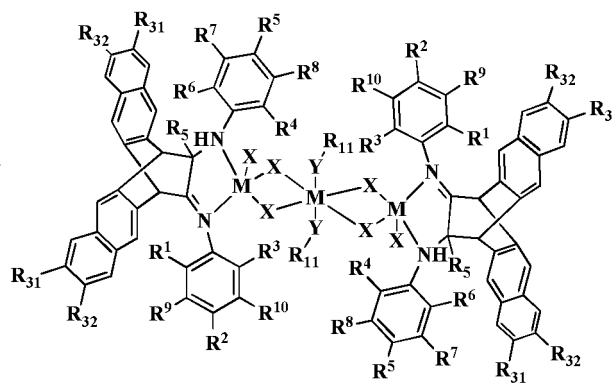
Ligand L5: amino-imine compound represented by Formula IX, wherein $R^1=R^3=R^4=R^6=$ isopropyl, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$;

Ligand L6: amino-imine compound represented by Formula IX, wherein $R^1=R^3=R^4=R^6=CH_3$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$, $R_5=$ ethyl;

Ligand L7: amino-imine compound represented by Formula IX', wherein $R^1=R^3=R^4=R^6=$ methyl, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$;



Formula V



Formula V'

Complex Ni4: the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=CH_3$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, $R_{11}=$ ethyl, $M=Ni$, $Y=O$, $X=Br$;

Complex Ni5: the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=$ isopropyl, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$; $R_5=CH_3$, $R_{11}=$ ethyl, $M=Ni$, $Y=O$, $X=Br$;

Complex Ni6: the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=$ isopropyl, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$; $R_5=CH_3$, $R_{11}=$ isobutyl, $M=Ni$, $Y=O$, $X=Br$;

Complex Ni7: the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=CH_3$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{21}=R_{22}=H$; $R_5=$ ethyl, $R_{11}=$ ethyl, $M=Ni$, $Y=O$, $X=Br$;

Complex Ni8: the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=CH_3$, $R^2=R^5=R^7=R^8=R^9=R^{10}=R_{31}=R_{32}=H$; $R_5=$ methyl, $R_{11}=$ ethyl, $M=Ni$, $Y=O$, $X=Br$.

Example 1

[0076]

1) Preparation of ligand L1:

To a reaction flask were successively charged with 3.88 g (8 mmol) of α -diimine compound A1, 30ml of toluene, and 1M trimethylaluminum (16 ml, 16 mmol), and the contents were allowed to react under reflux for 8 hours. The reaction was terminated with sodium hydroxide/ice water and extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L1 as colorless crystals in a yield of 84.2%. 1H NMR

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δ (ppm) 7.19-7.06 (m, 6H, Ar-H), 3.42 (s, 1H, NH), 2.98 (m, 2H, CH(CH₃)₂), 2.88 (m, 2H, CH(CH₃)₂), 2.32 (m, 1H, CH), 1.81 (m, 4H, CH₂), 1.50(s, 3H, CH₃), 1.21 (m, 24H, CH₃), 0.92 (s, 3H, CH₃), 0.75 (s, 3H, CH₃), 0.72 (s, 3H, CH₃).

2) Preparation of complex Ni1:

5 A solution of (DME)NiBr₂ (277 mg, 0.9 mmol) in ethanol (10mL) was added dropwise to a solution of ligand L1 (300 mg, 0.6 mmol) in dichloromethane (10mL), and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford red powdery solids. Yield: 78%. Elemental analysis (calculated for C₇₄H₁₁₄Br₆N₄Ni₃O₂): C, 50.87; H, 6.58; N, 3.21; experimental value (%): C, 50.57; H, 6.73; N, 3.04.

3) 10 atm Ethylene Polymerization:

10 After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.4 mg (2.5 μ mol) of the complex Ni1 was added. The reaction was vigorously stirred at 30 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 1 below.

Example 2

20 **[0077]** Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 1, except that the polymerization temperature was 60 °C. The results are shown in Table 1 below.

Example 3

25 **[0078]** Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 1, except that the polymerization temperature was 60 °C and the polymerization time was 10 min. The results are shown in Table 1 below.

Example 4

30 **[0079]** Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 1, except that the polymerization temperature was 60 °C and the polymerization time was 20 min. The results are shown in Table 1 below.

Example 5

35 **[0080]** Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 1, except that the polymerization temperature was 60 °C and the polymerization time was 60 min. The results are shown in Table 1 below.

Example 6

40 **[0081]** Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 1, except that the polymerization temperature was 90 °C. The results are shown in Table 1 below.

Example 7

45 **[0082]** 10 atm Ethylene Polymerization: After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 0.8 ml of diethyl aluminum chloride (2.0 mol/l solution in toluene) was added, and 4.4 mg (2.5 μ mol) of the complex Ni1 was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 1 below.

Example 8

55 **[0083]** After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was

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charged into the polymerization autoclave, and at the same time 4.4 mg (2.5 μ mol) of the complex Ni1, 6 mL of 10-undecen-1-ol, 30 mL of triethylaluminum (1.0 mol/L solution in hexane), 5.0 mL of MAO (1.53 mol/L solution in toluene) were added thereto. The reaction was stirred at 30 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was finally neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polymer. The results are shown in Table 1 below.

Example 9

[0084] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, and at the same time 4.4 mg (2.5 μ mol) of the complex Ni1, 5.52g of 10-undecenoic acid, 30 mL of triethylaluminum (1.0 mol/L solution in hexane), 5.0 mL of MAO (1.53 mol/L solution in toluene) were added thereto. The reaction was stirred at 30 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was finally neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polymer. The results are shown in Table 1 below.

Example 10

[0085]

1) Preparation of ligand L2:

To a reaction flask were successively charged with 3.88 g (8 mmol) of α -diimine compound A1, 30ml of diethyl ether, and 2M diethylzinc (4ml, 8 mmol), and the contents were stirred at room temperature for 3 hours. The reaction was terminated with ice water, the reaction mixture was extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L2 as colorless crystals in a yield of 52.1%. ¹HNMR δ (ppm) 7.17-7.06 (m, 6H, Ar-H), 4.44 (s, 1H, NH), 2.98 (m, 2H, CH(CH₃)₂), 2.87 (m, 2H, CH(CH₃)₂), 2.33 (m, 1H), 1.86 (m, 2H, CH₂), 1.81 (m, 4H, CH₂), 1.21 (m, 24H, CH₃), 1.08 (t, 3H, CH₃), 0.93 (s, 3H, CH₃), 0.75 (s, 3H, CH₃), 0.72 (s, 3H, CH₃).

2) Preparation of complex Ni2:

A solution of (DME)NiBr₂ (277 mg, 0.9 mmol) in ethanol (10 mL) was added dropwise to a solution of ligand L2 (309 mg, 0.6 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford red powdery solids. Yield: 72%. Elemental analysis (calculated for C₇₆H₁₁₈Br₆N₄Ni₃O₂): C, 51.42; H, 6.70; N, 3.16; experimental value (%): C, 51.29; H, 6.98; N, 3.04.

3) 10 atm Ethylene Polymerization:

After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminumoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.4 mg (2.5 μ mol) of the complex Ni2 was added. The reaction was vigorously stirred at 30 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 1 below.

Example 11

[0086] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 10, except that the polymerization temperature was 60 °C. The results are shown in Table 1 below.

Example 12

[0087]

1) Preparation of ligand L3:

1.5 mL of 2,6-dimethylaniline (12 mmol) was reacted with 57 ml of 1M trimethylaluminum in toluene under refluxing for 3h. Then, camphorquinone (1.05 g, 5 mmol) was added thereto, and the reaction mixture was refluxed for 8 hours. After cooling, the reaction was terminated with sodium hydroxide/ice water, the reaction mixture was extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L3 as colorless crystals in a yield of 70.2%. ¹HNMR δ (ppm) 7.00-6.89 (m, 6H, Ar-H), 3.57 (s, 1H, NH), 2.18(s, 6H, CA-

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CH₃), 2.05(s, 6H, CH₃), 1.74 (m, 4H, CH₂), 1.44 (s, 3H, CH₃), 1.35 (m, 1H, CH), 1.21 (s, 3H, CH₃), 1.01 (s, 3H, CH₃), 0.87 (s, 3H, CH₃).

2) Preparation of complex Ni3:

A solution of (DME)NiBr₂ (277 mg, 0.9 mmol) in ethanol (10 mL) was added dropwise to a solution of ligand L3 (233 mg, 0.6 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford red powdery solids. Yield: 70 %. Elemental analysis (calculated for C₅₈H₈₂Br₆N₄Ni₃O₂): C, 45.75; H, 5.43; N, 3.68; experimental value (%): C, 45.56; H, 5.83; N, 3.46.

3) 10 atm Ethylene Polymerization:

After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 3.8 mg (2.5 μmol) of the complex Ni3 was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 1 below.

Example 13

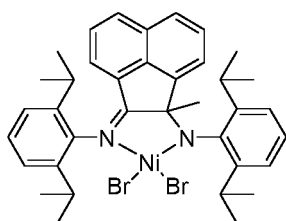
[0088] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 3.8 mg (2.5 μmol) of the complex Ni3 and 10ml of 1-hexene were added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polymer. The results are shown in Table 1 below.

Comparative Example 1

[0089] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 5.5 mg (7.5 μmol) of Comparative Catalyst A was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polymer. The results are shown in Table 1 below.

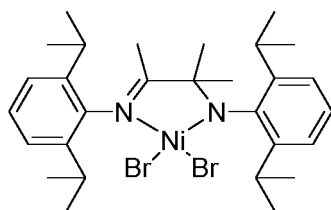
Comparative Example 2

[0090]



Comparative Catalyst A

[0091] Ethylene polymerization was carried out according to the procedure described in Comparative Example 1, except that 4.8 mg (7.5 μmol) of Comparative Catalyst B was used to replace for the Comparative Catalyst A. The results are shown in Table 1 below.



Comparative Catalyst B

Table 1

Example No.	Complex	Activity ($10^6\text{g/mol cat}\cdot\text{h}$)	Mw ($\times 10^4$)	Mw/Mn
Example 1	Ni1	7.62	51.0	1.02
Example 2	Ni1	8.33	38.4	1.05
Example 3	Ni1	8.62	14.2	1.02
Example 4	Ni1	8.42	30.4	1.03
Example 5	Ni1	7.67	62.4	1.02
Example 6	Ni1	4.27	13.2	1.07
Example 7	Ni1	6.24	27.2	1.23
Example 8	Ni1	4.72	37.2	1.53
Example 9	Ni1	4.60	14.2	1.11
Example 10	Ni2	4.08	15.4	1.03
Example 11	Ni2	4.28	8.4	1.03
Example 12	Ni3	3.21	9.3	1.05
Example 13	Ni3	3.54	10.1	1.04
Comp. Ex. 1	A	0.78	21.3	1.54
Comp. Ex. 2	B	0.43	18.4	1.43

[0092] It can be seen from Table 1 that the complexes of the present invention can catalyze the polymerization of ethylene with high activity at a higher temperature, with the ethylene polymerization activity of the catalyst of the invention being up to $8.62 \times 10^6 \text{g}\cdot\text{mol}^{-1}(\text{Ni})\cdot\text{h}^{-1}$. Also, the complexes of the present invention can catalyze the copolymerization of ethylene and higher α -olefin with high activity, and the resulting copolymers have a narrow molecular weight distribution. When used as a main catalyst, the complexes of the invention have much higher polymerization activities under high temperature polymerization conditions, compared with the complexes used in Comparative Examples 1-2, and the obtained polymers have a narrower molecular weight distribution.

Example 14

[0093]

1) Preparation of ligand L4:

To a reaction flask were successively charged with 3.52 g (8 mmol) of α -diimine compound A3, 30ml of toluene, and 1M trimethylaluminum (16mL, 16 mmol), and the reaction mixture was refluxed for 8 hours. The reaction was terminated with sodium hydroxide/ice water, the reaction mixture was extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L4 as colorless crystals in a yield of 85.2%. $^1\text{H NMR}$ δ (ppm) 7.23-6.88 (m, 14H), 4.84 (s, 1H), 4.73(s, 1H), 3.85 (s, 1H, NH), 2.02 (s, 3H, CH_3), 1.87 (s, 6H, CH_3), 1.75 (s, 6H, CH_3).

2) Preparation of complex Ni4:

10 mL solution of $(\text{DME})\text{NiBr}_2$ (277 mg, 0.9 mmol) in ethanol was added dropwise to 10 mL solution of ligand L4

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(274 mg, 0.6 mmol) in dichloromethane, and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford Ni4 as red powdery solids. Yield: 74 %. Elemental analysis (calculated for $C_{70}H_{74}Br_6N_4Ni_3O_2$): C, 50.68; H, 4.50; N, 3.38; experimental value (%): C, 50.53; H, 4.73; N, 3.21.

3) Ethylene Polymerization:

After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N_2 gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.1 mg (2.5 μ mol) of the complex Ni4 was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Example 15

[0094] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 14, except that the polymerization temperature was 100 °C. The results are shown in Table 2 below.

Example 16

[0095] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 14, except that 0.75 mL of diethyl aluminum monochloride (2.0 mol/L solution in toluene) was used instead of the methylaluminoxane. The results are shown in Table 2 below.

Example 17

[0096]

1) Preparation of ligand L5:

To a reaction flask were successively charged with 4.42 g (8 mmol) of α -diimine compound A4, 30ml of toluene, and 1M trimethylaluminum (16 mL, 16 mmol), and the reaction mixture was refluxed for 8 hours. The reaction was terminated with sodium hydroxide/ice water, the reaction mixture was extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L5 as colorless crystals in a yield of 76.2%. 1H NMR δ (ppm) 7.21-6.95 (m, 14H), 4.96(s, 1H), 4.87(s, 1H), 3.85 (s, 1H, NH), 2.51 (m, 4H, $CH(CH_3)_2$), 2.02(s, 3H, CH_3), 1.18 (d, 3H, CH_3), 1.11 (d, 3H, CH_3), 1.05 (d, 6H, CH_3), 0.98 (d, 6H, CH_3), 0.60 (d, 6H, CH_3).

2) Preparation of complex Ni5:

10 mL solution of $(DME)NiBr_2$ (277 mg, 0.9 mmol) in ethanol was added dropwise to 10 mL solution of ligand L5 (341 mg, 0.6 mmol) in dichloromethane, and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford Ni5 as red powdery solids. Yield: 76 %. Elemental analysis (calculated for $C_{86}H_{106}Br_6N_4Ni_3O_2$): C, 54.85; H, 5.67; N, 2.97; experimental value (%): C, 54.61; H, 5.73; N, 3.14.

3) Ethylene Polymerization:

After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N_2 gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.7 mg (2.5 μ mol) of the complex Ni5 was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Example 18

[0097] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 17, except that the polymerization time was 10 min. The results are shown in Table 2 below.

Example 19

[0098] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 17, except that the polymerization time was 20 min. The results are shown in Table 2 below.

Example 20

[0099] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 17, except that the polymerization time was 60 min. The results are shown in Table 2 below.

Example 21

[0100] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 17, except that the polymerization temperature was 100 °C. The results are shown in Table 2 below.

Example 22

[0101] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane and 10mL of 1-hexene were charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.7 mg (2.5 μmol) of the complex Ni5 was added. Next, the autoclave was evacuated and then filled with ethylene 3 times. The reaction was then vigorously stirred at 100 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Example 23

[0102] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization system, and at the same time 6 mL of 10-undecen-1-ol, 30 mL of triethylaluminum (1.0 mol/L solution in hexane), 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene), and 4.7 mg (2.5 μmol) of the complex Ni5 were added thereto. The reaction was stirred at 30 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was finally neutralized with an ethanol solution acidified with 5 vol.% hydrochloric acid to obtain a polymer. The results are shown in Table 2 below.

Example 24

[0103] Ethylene copolymerization was carried out according to the procedure for ethylene copolymerization described in Example 23, except that the polymerization temperature was 60 °C. The results are shown in Table 2 below.

Example 25

[0104] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization system, and at the same time 5.52 g of 10-undecenoic acid, 30 mL of triethylaluminum (1.0 mol/L solution in hexane), 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene), and 4.7 mg (2.5 μmol) of the complex Ni5 were added thereto. The reaction was stirred at 30 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was finally neutralized with an ethanol solution acidified with 5 vol.% hydrochloric acid to obtain a polymer. The results are shown in Table 2 below.

Example 26

[0105] Ethylene copolymerization was carried out according to the procedure for ethylene copolymerization described in Example 25, except that the polymerization temperature was 60 °C. The results are shown in Table 2 below.

Example 27

[0106] Preparation of complex Ni6:

A solution of 277 mg (0.9 mmol) of (DME)NiBr₂ in 2-methyl-1-propanol (10mL) was added slowly dropwise to a solution of 341 mg (0.6 mmol) of ligand L5 in dichloromethane (10mL). The color of the solution immediately changed to deep red, and a large quantity of precipitants was formed. The reaction was stirred at room temperature for 6h, and then anhydrous diethyl ether was added to perform precipitation. A filtration was performed to afford a filter cake, and the filter cake was washed with anhydrous diethyl ether and dried in vacuum to afford Ni6 as brownish-red powdery solids.

Yield: 84.0%. Elemental analysis (calculated for $C_{90}H_{114}Br_6N_4Ni_3O_2$): C, 55.74; H, 5.92; N, 2.89; experimental value (%): C, 56.08; H, 6.12; N, 3.08.

[0107] 3) Ethylene Polymerization:

After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N_2 gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.8 mg (2.5 μ mol) of the complex Ni6 was added. The reaction was vigorously stirred at 100 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Example 28

[0108]

1) Preparation of ligand L6:

To a reaction flask were successively charged with 3.52 g (8 mmol) of α -diimine compound A3, 30ml of diethyl ether, and 2M diethylzinc (4 mL, 8 mmol), and the reaction mixture was stirred at room temperature for 3 hours. The reaction was terminated with ice water, the reaction mixture was extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L3 as colorless crystals in a yield of 50.1%. 1H NMR δ (ppm) 7.22-6.86 (m, 14H), 4.82 (s, 1H), 4.73(s, 1H), 3.85(s, 1H, NH), 2.04 (m, 2H, CH_2CH_3), 1.89 (s, 6H, CH_3), 1.74 (s, 6H, CH_3), 0.89 (t, 3H, CH_3).

2) Preparation of complex Ni7:

10 mL solution of $(DME)NiBr_2$ (277 mg, 0.9 mmol) in ethanol was added dropwise to 10 mL solution of ligand L6 (282 mg, 0.6 mmol) in dichloromethane, and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford Ni7 as red powdery solids. Yield: 73 %. Elemental analysis (calculated for $C_{72}H_{78}Br_6N_4Ni_3O_2$): C, 51.26; H, 4.66; N, 3.32; experimental value (%): C, 51.39; H, 4.93; N, 3.24.

3) Ethylene Polymerization:

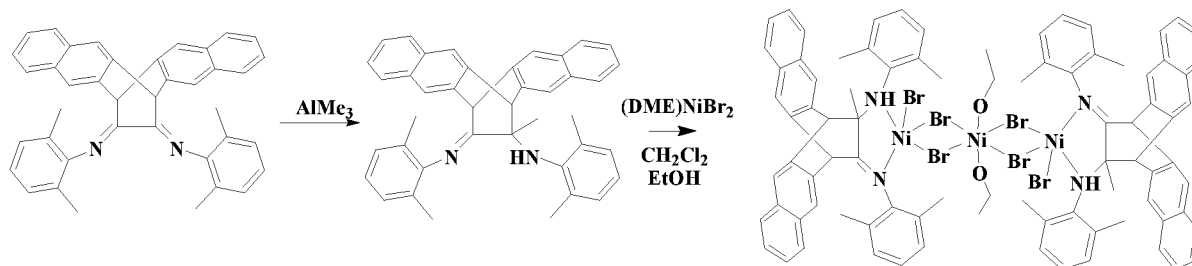
After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N_2 gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.2 mg (2.5 μ mol) of the complex Ni7 was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Example 29

[0109] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 28, except that the polymerization temperature was 100 °C. The results are shown in Table 2 below.

Example 30

[0110]



A5

1) Preparation of ligand L7:

To a reaction flask were successively charged with 4.32 g (8 mmol) of α -diimine compound A5, 30ml of toluene, and 1M trimethylaluminum (16 mL, 16 mmol), and the reaction mixture was stirred at room temperature for 3 hours. The reaction was terminated with ice water, the reaction mixture was extracted with ethyl acetate, and organic phases were combined and dried over anhydrous magnesium sulfate. The product was separated by column chromatography with petroleum ether/ethyl acetate as an eluent to obtain ligand L7 as colorless crystals in a yield of 72.1%. $^1\text{H NMR}$ δ (ppm) 7.68-7.54 (m, 8H), 7.37 (m, 4H), 7.11-7.04 (m, 6H), 5.16 (s, 1H), 5.08(s, 1H), 4.05(s, 1H, NH), 1.94 (s, 3H, CH₃), 1.89 (s, 6H, CH₃), 1.73 (s, 6H, CH₃).

2) Preparation of complex Ni8:

10 mL solution of (DME)NiBr₂ (277 mg, 0.9 mmol) in ethanol was added dropwise to 10 mL solution of ligand L7 (334 mg, 0.6 mmol) in dichloromethane, and the resulting mixture was stirred at room temperature for 6h, with precipitants being generated. After filtering, the filter cake was washed with diethyl ether and dried to afford red powdery solids. Yield: 72 %. Elemental analysis (calculated for C₈₆H₈₂Br₆N₄Ni₃O₂): C, 55.56; H, 4.45; N, 3.01; experimental value (%): C, 55.74; H, 4.73; N, 3.14.

3) Ethylene Polymerization:

After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 4.6 mg (2.5 μ mol) of the complex Ni8 was added. The reaction was vigorously stirred at 60 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Example 31

[0111] Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Example 30, except that the polymerization temperature was 100 °C. The results are shown in Table 2 below.

Example 32

[0112] After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) and 10mL of 1-hexene were added, and 4.6 mg (2.5 μ mol) of the complex Ni8 was added. The reaction was vigorously stirred at 100 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polymer. The results are shown in Table 2 below.

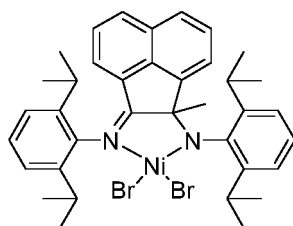
Comparative Example 3

[0113] Comparative Catalyst C was prepared by following patent application CN102250152A.

[0114] Ethylene Polymerization: After having been continuously dried at 130°C for 6hrs, a 1L stainless steel polymerization autoclave equipped with mechanical stirring was evacuated while it was hot and then filled with N₂ gas 3 times. 500 mL of hexane was charged into the polymerization autoclave, then 5.0 mL of methylaluminoxane (MAO) (1.53 mol/l solution in toluene) was added, and 5.5 mg (7.5 μ mol) of Comparative Catalyst C was added. The reaction was vigorously stirred at 100 °C for 30 minutes, with ethylene pressure being maintained at 10 atm. The reaction mixture was neutralized with an ethanol solution acidified with 10 wt% hydrochloric acid to obtain a polyethylene. The results are shown in Table 2 below.

Comparative Example 4

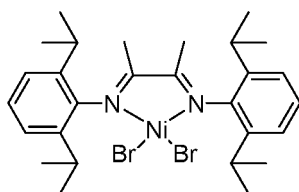
[0115]



Comparative Catalyst C

[0116] Comparative Catalyst D was prepared by following patent application CN102250152A.

[0117] Ethylene Polymerization: Ethylene polymerization was carried out according to the procedure for ethylene polymerization described in Comparative Example 3, except that 4.8 mg (7.5 μ mol) of Comparative Catalyst D was used instead of Comparative Catalyst C. The results are shown in Table 2 below.



Comparative Catalyst D

Table 2

Example	Complex	Activity (10 ⁵ g/molcat.h)	Mw $\times 10^{-4}$	Mw/Mn
Example 14	Ni4	4.32	2.27	1.05
Example 15	Ni4	3.09	0.96	1.68
Example 16	Ni4	3.94	1.80	1.10
Example 17	Ni5	8.12	50.6	1.05
Example 18	Ni5	8.11	17.3	1.03
Example 19	Ni5	8.14	36.1	1.02
Example 20	Ni5	8.00	70.2	1.08
Example 21	Ni5	6.44	20.1	1.63
Example 22	Ni5	6.82	21.3	1.62
Example 23	Ni5	5.27	50.2	1.26
Example 24	Ni5	4.86	21.7	1.32
Example 25	Ni5	4.72	17.3	1.03
Example 26	Ni5	4.08	10.2	1.16
Example 27	Ni6	5.33	18.3	1.72
Example 28	Ni7	2.17	1.42	1.06
Example 29	Ni7	1.04	0.67	1.69
Example 30	Ni8	4.82	2.52	1.07
Example 31	Ni8	3.67	1.76	1.80
Example 32	Ni8	3.88	1.82	1.72
Comp. Ex. 3	C	Trace amount		
Comp. Ex. 4	D	Trace amount		

[0118] It can be seen from Table 2 that when used as a main catalyst, the amino-imine metal complexes of the present invention have higher polymerization activities under high temperature polymerization conditions, compared with the catalysts used in Comparative Examples 3 and 4, and the obtained polymers have a higher molecular weight and a narrower molecular weight distribution than that of the polymers obtained in the comparative examples.

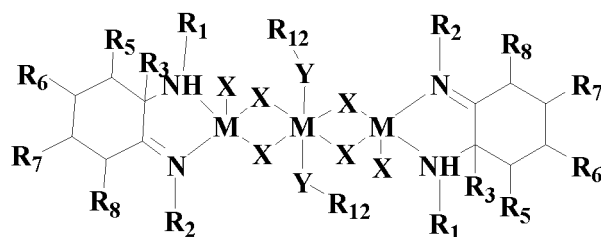
[0119] It should be noted that the above-described examples are used only to illustrate the present invention and do not constitute any limitation to the present invention. The present invention has been described with reference to typical examples, but it should be understood that the words used therein are descriptive and explanatory words, rather than restrictive words. The present invention may be modified within the scope of the claims of the present invention as stipulated, and the present invention may be revised without departing from the scope and spirit of the present invention. Although the present invention described therein relates to specific methods, materials and embodiments, it does not mean that the present invention is limited to the specific examples disclosed therein. On the contrary, the present invention can be extended to all other methods and applications with the same function.

Claims

1. An amino-imine metal complex represented by Formula I:

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Formula I

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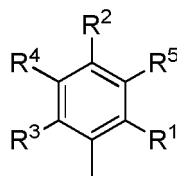
wherein, R_1 and R_2 are each independently a C1-C30 hydrocarbyl with or without a substituent Q; each R_3 is independently selected from the group consisting of hydrogen and C1-C20 hydrocarbyl with or without a substituent Q; R_5 - R_8 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 hydrocarbyl with or without a substituent Q, and R_5 - R_8 groups are optionally joined to form a ring or ring system; each R_{12} is independently a C1-C20 hydrocarbyl with or without a substituent Q; each Y is independently a Group VIA non-metal atom; each M is independently a Group VIII metal; each X is independently selected from the group consisting of halogen, C1-C10 hydrocarbyl with or without a substituent Q and C1-C10 hydrocarbyloxy with or without a substituent Q.

2. The amino-imine metal complex as claimed in claim 1, having at least one of the following features:

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- R_1 and R_2 are independently selected from the group consisting of C1-C20 alkyl with or without a substituent Q and C6-C20 aryl with or without a substituent Q, and preferably R_1 and/or R_2 are/is a group represented by Formula A:

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Formula A

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wherein, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q, and R^1 - R^5 are optionally joined to form a ring or ring system; preferably, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q;

- each M is independently selected from the group consisting of nickel and palladium;

- each Y is independently selected from the group consisting of O and S;

- each X is independently selected from the group consisting of halogen, C1-C10 alkyl with or without a substituent Q and C1-C10 alkoxy with or without a substituent Q, and preferably from the group consisting of halogen, C1-C6 alkyl with or without a substituent Q and C1-C6 alkoxy with or without a substituent Q;

- each R_{12} is independently a C1-C20 alkyl with or without a substituent Q, preferably a C1-C10 alkyl with or without a substituent Q, and more preferably a C1-C6 alkyl with or without a substituent Q;

- each R_3 is selected from the group consisting of C1-C20 alkyl with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q and C7-C20 alkaryl with or without

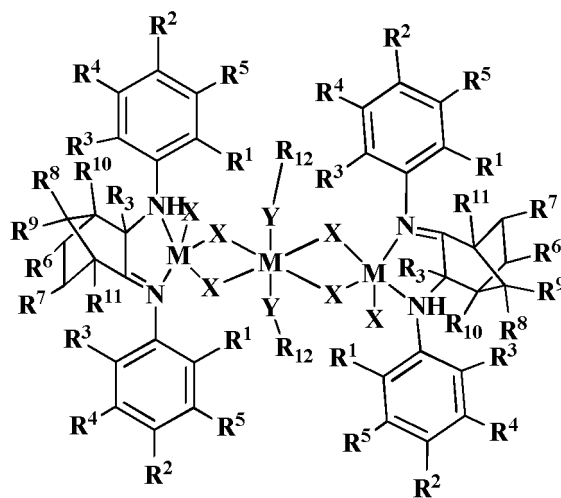
a substituent Q; preferably, each R_3 is selected from the group consisting of C1-C10 alkyl with or without a substituent Q, C6-C10 aryl with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q and C7-C15 alkaryl with or without a substituent Q; and more preferably, each R_3 is a C1-C6 alkyl with or without a substituent Q, such as methyl, ethyl, propyl or butyl;

- the substituent Q is selected from the group consisting of halogen, hydroxy, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy and halogenated C1-C10 alkoxy, and preferably from the group consisting of halogen, hydroxy, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy and halogenated C1-C6 alkoxy;

preferably, the C1-C6 alkyl is selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl and 3,3-dimethylbutyl;

preferably, the C1-C6 alkoxy is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, n-pentoxy, isopentoxy, n-hexyloxy, isohexyloxy and 3,3-dimethylbutoxy.

3. The amino-imine metal complex as claimed in claim 1 or 2, which is represented by Formula III:



Formula III

wherein, R^1 - R^{11} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q; R_3 , R_{12} , Y, M and X are as defined in claim 1.

4. The amino-imine metal complex as claimed in claim 3, wherein R^1 - R^{11} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 aralkyloxy with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q; preferably, R^1 - R^{11} are each independently selected from the group consisting of hydrogen, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy, halogenated C1-C10 alkoxy and halogen, and more preferably from the group consisting of hydrogen, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy, halogenated C1-C6 alkoxy and halogen.

5. The amino-imine metal complex as claimed in any one of claims 1 to 4, which is selected from the group consisting of:

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}$ =H, $R^8=R^9=R^{11}$ =CH₃, R_3 =CH₃, R_{12} =methyl, M=Ni, Y=O, X=Br;

the complex represented by Formula III, wherein $R^1=R^3$ =isopropyl, $R^2=R^4=R^5=R^6=R^7=R^{10}$ =H, $R^8=R^9=R^{11}$ =CH₃, R_3 =ethyl, R_{12} =methyl, M=Ni, Y=O, X=Br;

the complex represented by Formula III, wherein $R^1=R^3$ =ethyl, $R^2=R^4=R^5=R^6=R^7=R^{10}$ =H, $R^8=R^9=R^{11}$ =CH₃,

R_{12} =ethyl, M =Ni, Y =O, X =Br;

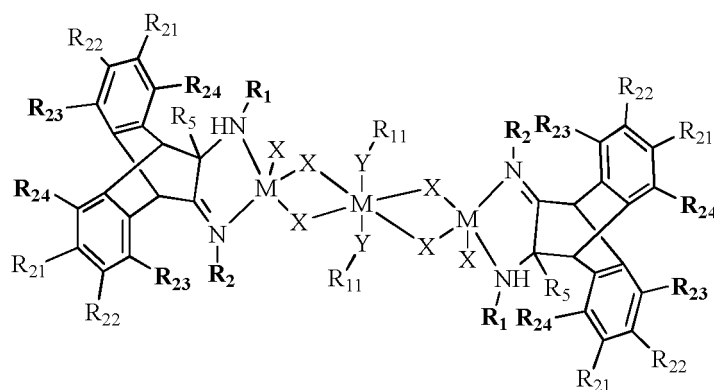
the complex represented by Formula III, wherein $R^1=R^3$ =methyl, R^2 =Br, R^4 - R^7 = R^{10} =H, R^8 = R^9 =methyl, R_3 =ethyl, R^{11} = CH_2Br , R_{12} =ethyl, M =Ni, Y =O, X =Br;

the complex represented by Formula III, wherein $R^1=R^3$ =F, $R^2=R^4$ - R^7 = R^{10} =H, R^8 = R^9 =methyl, R^{11} = CH_2Br , R_3 =isobutyl, R_{12} =ethyl, M =Ni, Y =O, X =Br;

the complex represented by Formula III, wherein $R^1=R^3$ =Cl, $R^2=R^4$ - R^7 = R^{10} =H, R^8 = R^9 =methyl, R^{11} = CH_2Br , R_3 =isobutyl, R_{12} =ethyl, M =Ni, Y =O, X =Br;

the complex represented by Formula III, wherein $R^1=R^3$ =Br, $R^2=R^4$ - R^7 = R^{10} =H, R^8 = R^9 =methyl, R^{11} = CH_2Br , R_3 =isobutyl, R_{12} =ethyl, M =Ni, Y =O, X =Br.

6. The amino-imine metal complex as claimed in claim 1, which has a structure represented by Formula IV:

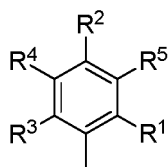


Formula IV

wherein, R_1 and R_2 are each independently a C1-C30 hydrocarbyl with or without a substituent Q; R_{21} - R_{24} are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 hydrocarbyl with or without a substituent Q and C1-C20 hydrocarbyloxy with or without a substituent Q, and R_{21} - R_{24} are optionally joined to form a ring or ring system, preferably a substituted or unsubstituted benzene ring; each R_5 is independently selected from the group consisting of hydrogen and C1-C20 hydrocarbyl with or without a substituent Q; each R_{11} is independently a C1-C20 hydrocarbyl with or without a substituent Q; each Y is independently a Group VIA nonmetal atom; each M is independently a Group VIII metal; each X is independently selected from the group consisting of halogen, C1-C10 hydrocarbyl with or without a substituent Q and C1-C10 hydrocarbyloxy with or without a substituent Q.

7. The amino-imine metal complex as claimed in claim 6, having at least one of the following features:

- R_1 and R_2 are independently selected from the group consisting of C1-C20 alkyl with or without a substituent Q and C6-C20 aryl with or without a substituent Q, and preferably R_1 and/or R_2 are/is a group represented by Formula A:



Formula A

wherein, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q, and R^1 - R^5 are optionally joined to form a ring or ring system;

preferably, R^1 - R^5 are each independently selected from the group consisting of hydrogen, halogen, hydroxy,

C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q;

more preferably, R¹-R⁵ are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C6 alkyl with or without a substituent Q, C2-C6 alkenyl with or without a substituent Q, C2-C6 alkynyl with or without a substituent Q, C1-C6 alkoxy with or without a substituent Q, C2-C6 alkenyloxy with or without a substituent Q, C2-C6 alkynyloxy with or without a substituent Q, C6-C10 aryl with or without a substituent Q, C7-C10 aralkyl group with or without a substituent Q, C7-C10 alkaryl with or without a substituent Q, C6-C10 aryloxy with or without a substituent Q, C7-C10 aralkyloxy with or without a substituent Q, and C7-C10 alkaryloxy with or without a substituent Q;

- each M is independently selected from the group consisting of nickel and palladium;
- each Y is independently selected from the group consisting of O and S;
- each X is independently selected from the group consisting of halogen, C1-C10 alkyl with or without a substituent Q and C1-C10 alkoxy with or without a substituent Q, and preferably from the group consisting of halogen, C1-C6 alkyl with or without a substituent Q and C1-C6 alkoxy with or without a substituent Q;
- each R₁₁ is independently a C1-C20 alkyl with or without a substituent Q, preferably a C1-C10 alkyl with or without a substituent Q, and more preferably a C1-C6 alkyl with or without a substituent Q;
- each R₅ is independently selected from the group consisting of C1-C20 alkyl with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q and C7-C20 alkaryl with or without a substituent Q; preferably, each R₅ is independently selected from the group consisting of C1-C10 alkyl with or without a substituent Q, C6-C10 aryl with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q and C7-C15 alkaryl with or without a substituent Q, and more preferably each R₅ is a C1-C6 alkyl with or without a substituent Q, such as methyl, ethyl, propyl or butyl; and
- the substituent Q is selected from the group consisting of halogen, hydroxy, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy and halogenated C1-C10 alkoxy, preferably from the group consisting of halogen, hydroxy, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy and halogenated C1-C6 alkoxy; preferably, the C1-C6 alkyl is selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl and 3,3-dimethylbutyl; preferably, the C1-C6 alkoxy is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, n-pentoxy, isopentoxy, n-hexyloxy, isohexyloxy and 3,3-dimethylbutoxy;
- R₂₁-R₂₄ are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C20 alkyl with or without a substituent Q, C2-C20 alkenyl with or without a substituent Q, C2-C20 alkynyl with or without a substituent Q, C1-C20 alkoxy with or without a substituent Q, C2-C20 alkenoxy with or without a substituent Q, C2-C20 alkynoxy with or without a substituent Q, C6-C20 aryl with or without a substituent Q, C7-C20 aralkyl with or without a substituent Q, C7-C20 alkaryl with or without a substituent Q, C6-C20 aryloxy with or without a substituent Q, C7-C20 aralkyloxy with or without a substituent Q and C7-C20 alkaryloxy with or without a substituent Q, and R₂₁-R₂₄ are optionally joined to form a ring or ring system;

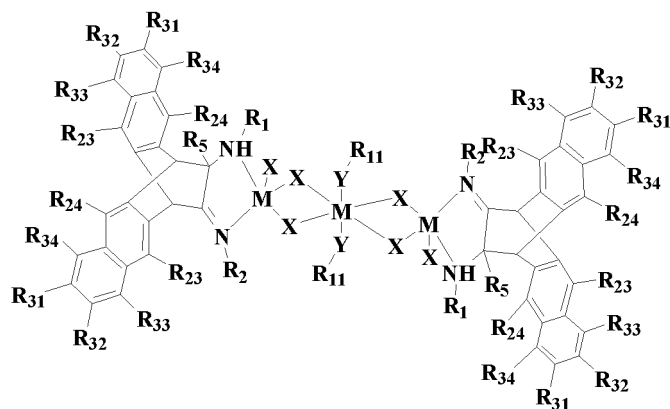
preferably, R₂₁-R₂₄ are each independently selected from the group consisting of hydrogen, halogen, hydroxy, C1-C10 alkyl with or without a substituent Q, C2-C10 alkenyl with or without a substituent Q, C2-C10 alkynyl with or without a substituent Q, C1-C10 alkoxy with or without a substituent Q, C2-C10 alkenoxy with or without a substituent Q, C2-C10 alkynoxy with or without a substituent Q, C6-C15 aryl with or without a substituent Q, C7-C15 aralkyl with or without a substituent Q, C7-C15 alkaryl with or without a substituent Q, C6-C15 aryloxy with or without a substituent Q, C7-C15 aralkoxy with or without a substituent Q and C7-C15 alkaryloxy with or without a substituent Q;

more preferably, R₂₁-R₂₄ are each independently selected from the group consisting of hydrogen, C1-C10 alkyl, halogenated C1-C10 alkyl, C1-C10 alkoxy, halogenated C1-C10 alkoxy and halogen, and more preferably from the group consisting of hydrogen, C1-C6 alkyl, halogenated C1-C6 alkyl, C1-C6 alkoxy, halogenated C1-C6 alkoxy and halogen.

8. The amino-imine metal complex as claimed in any one of claims 6 to 7, which has a structure represented by Formula IVa:

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Formula IVa

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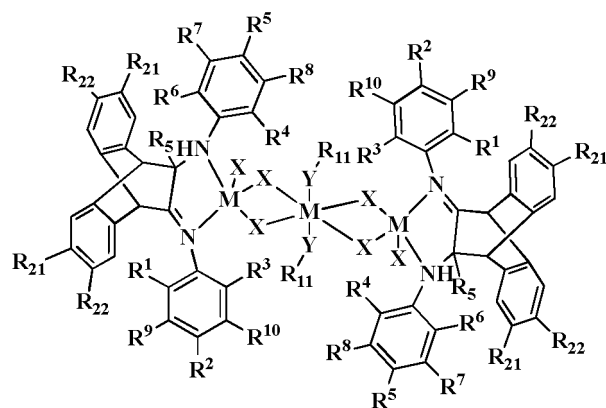
wherein R_{31} - R_{34} have the same meanings as R_{21} - R_{24} in Formula IV, preferably R_{33} and R_{34} are hydrogen, and R_1 , R_2 , R_5 , R_{11} , Y , M and X are as defined for Formula IV in claim 6.

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9. The amino-imine metal complex as claimed in any one of claims 6 to 8, which is represented by the following Formula V or V':

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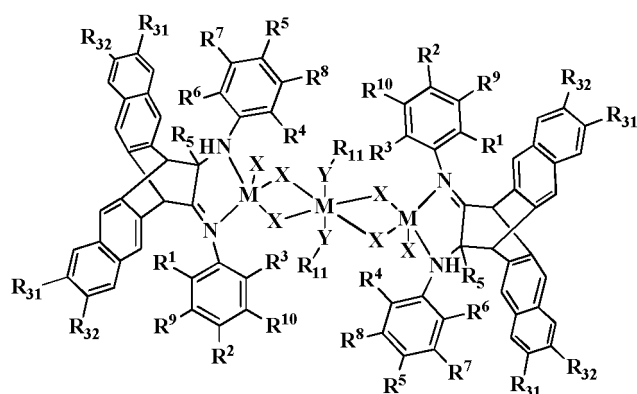


Formula V

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Formula V'

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wherein the individual symbols are as defined above,
preferably, the amino-imine metal complex is selected from the group consisting of:

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- 1) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 2) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$, $R_5=CH_3$, R_{11} =ethyl, $M=Ni$, $Y=O$, $X=Br$;
- 3) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{21}=R_{22}=H$,

R_{11} =isobutyl, M=Ni, Y=O, X=Br;

33) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

34) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

35) the complex represented by Formula V, wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{22}=H$, R_{21} =tert-butyl, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

36) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

37) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

38) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

39) the complex represented by Formula V', wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

40) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

41) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

42) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =ethyl, M=Ni, Y=O, X=Br;

43) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

44) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

45) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

46) the complex represented by Formula V', wherein R^1-R^6 =methyl, $R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

47) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

48) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

49) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=R_{31}=R_{32}=H$, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

50) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

51) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

52) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

53) the complex represented by Formula V', wherein R^1-R^6 =methyl, $R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

54) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

55) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

56) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

57) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =isopropyl, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}=R_{11}$ =ethyl, $R_5=CH_3$, M=Ni, Y=O, X=Br;

58) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =ethyl, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}$ =ethyl, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

59) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6$ =methyl, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}$ =ethyl, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

60) the complex represented by Formula V', wherein R^1-R^6 =methyl, $R^7-R^{10}=H$, $R_{31}=R_{32}$ =ethyl, $R_5=CH_3$, R_{11} =isobutyl, M=Ni, Y=O, X=Br;

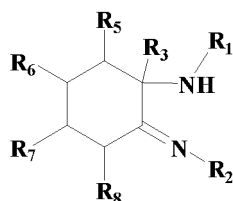
61) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Br$, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}$ =ethyl,

$R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

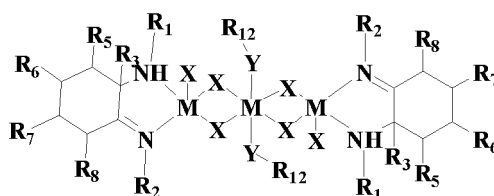
62) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=Cl$, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}$ =ethyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$;

63) the complex represented by Formula V', wherein $R^1=R^3=R^4=R^6=F$, $R^2=R^5=R^7-R^{10}=H$, $R_{31}=R_{32}$ =ethyl, $R_5=CH_3$, R_{11} =isobutyl, $M=Ni$, $Y=O$, $X=Br$.

10. A method for preparing the amino-imine metal complex according to claim 1, comprising step 1) reacting an amino-imine compound represented by Formula VI with MX_n and $R_{12}YH$ to generate the amino-imine metal complex represented by Formula I,



Formula VI



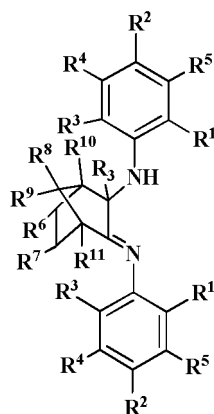
Formula I

wherein, R_1 , R_2 , R_3 , and R_5 - R_8 in Formula VI have the meanings as defined for Formula I in claim 1;

M and X in the MX_n have the meanings as defined for Formula I in claim 1, and n is the number of X satisfying the valence state of M ;

and Y and R_{12} in the $R_{12}YH$ have the meanings as defined for Formula I in claim 1;

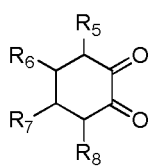
preferably, the amino-imine compound represented by Formula VI is as shown by the following Formula VIa:



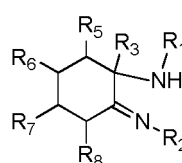
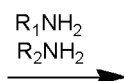
Formula VIa

wherein, R^1 - R^{11} and R_3 have the same meanings as defined for Formula III in claim 3.

11. The method as claimed in claim 10, wherein a preparation of the amino-imine compound represented by Formula VI comprises step 2) reacting a diketone compound represented by Formula VII with $A(R_3)_a$ and an amine compound, to generate the amino-imine compound represented by Formula VI, with the amine compound being R_1NH_2 and R_2NH_2 ;

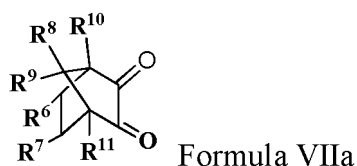


Formula VII



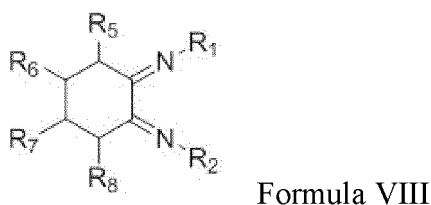
Formula VI

wherein, R_1, R_2, R_3, R_5-R_8 have the same meaning as defined for Formula I in claim 1, A is one or more of aluminum, zinc, lithium and magnesium, and preferably a molar ratio of the $A(R_3)_a$ to the amine compound is greater than or equal to 2.0, preferably from 2.0 to 6.0, and more preferably from 3.0 to 6.0; preferably, the diketone compound represented by Formula VII is represented by the following Formula VIIa:



wherein R^6-R^{11} have the same definitions as in Formula III.

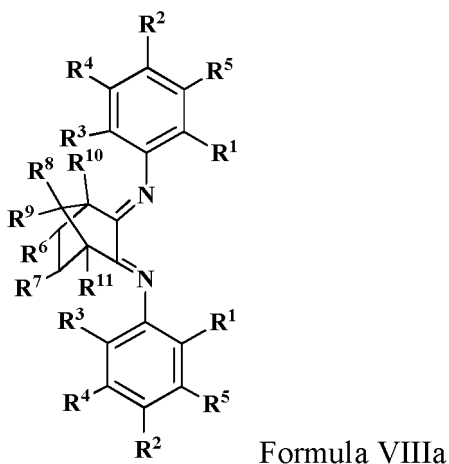
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12. The method as claimed in claim 11, wherein the reaction in step 1) is carried out in an organic solvent, and the organic solvent is preferably a halogenated alkane, more preferably the organic solvent is one or more of dichloromethane, trichloromethane and 1,2-dichloroethane; and the reaction in step 2) is carried out in an aprotic solvent, and the aprotic solvent is preferably one or more of toluene, benzene, and xylenes.
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13. The method as claimed in claim 10, wherein a preparation of the amino-imine compound represented by Formula VI comprises contacting and reacting a diimine compound represented by Formula VIII with $A(R_3)_a$ or a Grignard reagent to generate the amino-imine compound represented by Formula VI,



wherein $R_1, R_2,$ and R_5-R_8 have the same definitions as in Formula I;

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in the $A(R_3)_a$, A is one or more of aluminum, zinc, lithium and magnesium, R_3 has the same definitions as in Formula I, and a is the number of R_3 that satisfies the valence state of A; and the Grignard reagent has a general formula of R_3MgX , wherein R_3 has the same definitions as in Formula I, X is a halogen, preferably bromine and/or chlorine; preferably, the diimine compound represented by Formula VIII is represented the following Formula VIIIa:



wherein R^1-R^{11} have the same definition as in Formula III.

14. Use of the amino-imine metal complex as claimed in any one of claims 1 to 9 in olefin polymerization.

15. A catalyst for olefin polymerization, comprising the amino-imine metal complex as claimed in any one of claims 1 to 9, a cocatalyst and/or a chain transfer agent;

preferably, the cocatalyst is selected from organoaluminum compounds and organoboron compounds; the organoaluminum compounds are selected from alkylaluminoxanes, aluminum alkyls and alkyl aluminum halides; and the organoboron compounds are selected from aromatic hydrocarbyl borons and borates.

16. An olefin polymerization process, comprising carrying out an olefin polymerization reaction in the presence of the amino-imine metal complex according to any one of claims 1-9 or the catalyst according to claim 15, preferably the temperature for the polymerization reaction is from -78 °C to 200 °C, and preferably from -20 °C to 150 °C, and the polymerization pressure is from 0.01 to 10.0 MPa, and preferably from 0.01 to 2.0 MPa.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/125279

5	A. CLASSIFICATION OF SUBJECT MATTER	
	C07F 15/04(2006.01)i; C08F 4/70(2006.01)i; C08F 10/02(2006.01)i; C08F 210/16(2006.01)i	
	According to International Patent Classification (IPC) or to both national classification and IPC	
10	B. FIELDS SEARCHED	
	Minimum documentation searched (classification system followed by classification symbols) C07F; C08F	
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CNABS; CNTXT; CNKI; VEN; WEB OF SCIENCE; STN(REG, CAPLUS); 中国石油化工股份有限公司, 配合物, 络合物, 烯烃, 乙烯, 聚合, 催化, 镍, Ni, 二亚胺, 胺基亚胺, 三核, 醇, polyethylene, polymerization, complex+, cataly+, +diimine+, nikel, three, tri+, +alcohol+, structural formula search	
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT	
	Category*	Citation of document, with indication, where appropriate, of the relevant passages
		Relevant to claim No.
25	PX	Rong Gao et al. "One-step synthesis of hollow spherical polyethylene by dispersion polymerization" 《 <i>Journal of Catalysis</i> 》, Vol. 385, 31 March 2020 (2020-03-31), pp. 103-106
30	A	Xiaohui He et al. "Highly Symmetric Single Nickel Catalysts Bearing Bulky Bis(a-Diimine) Ligand: Synthesis, Characterization, and Electron-Effects on Copolymerization of Norbornene with 1-Alkene at Elevated Temperature" 《 <i>JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY</i> 》, Vol. 54, No. 21, 02 August 2016 (2016-08-02), pp. 3495-3505
35	A	CN 102250152 A (SUN YAT-SEN UNIVERSITY) 23 November 2011 (2011-11-23) entire document
	A	CN 106397264 A (CHINA PETROLEUM & CHEMICAL CORPORATION; BEIJING RESEARCH INSTITUTE OF CHEMICAL INDUSTRY, CHINA PETROLEUM & CHEMICAL CORPORATION) 15 February 2017 (2017-02-15) entire document
40	<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.	
45	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
50	Date of the actual completion of the international search 25 December 2020	Date of mailing of the international search report 11 January 2021
55	Name and mailing address of the ISA/CN China National Intellectual Property Administration (ISA/CN) No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088 China Facsimile No. (86-10)62019451	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/125279

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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	CN 105482000 A (CHINA PETROLEUM & CHEMICAL CORPORATION; BEIJING RESEARCH INSTITUTE OF CHEMICAL INDUSTRY, CHINA PETROLEUM & CHEMICAL CORPORATION) 13 April 2016 (2016-04-13) entire document	1-16
A	Mamdouh S. Masoud et al. "Structural and thermal studies on some morpholine complexes" <i>(Journal of Molecular Structure)</i> , Vol. 1175, 10 August 2018 (2018-08-10), pp. 648-662	1-16
A	Clara S. B. Gomes et al. "Reactivity of cationic α -diimine cyclopentadienyl nickel complexes towards AlEt ₂ Cl: synthesis, characterisation and ethylene polymerisation" <i>(Catal. Sci. Technol.)</i> , Vol. 7, No. 14, 05 June 2017 (2017-06-05), pp. 3128-3142	1-16

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/CN2020/125279

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