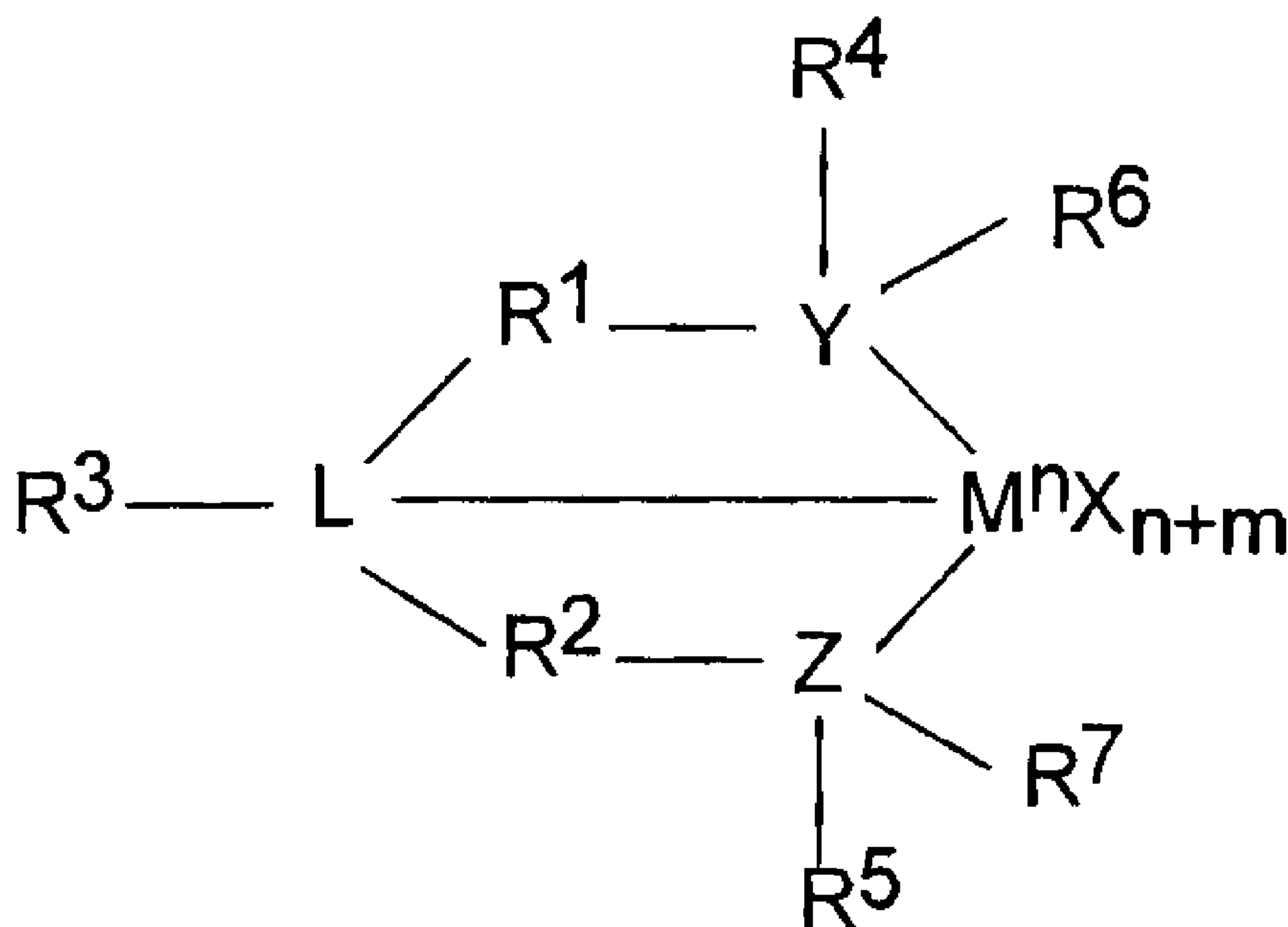




(86) Date de dépôt PCT/PCT Filing Date: 2000/05/15
 (87) Date publication PCT/PCT Publication Date: 2000/11/23
 (45) Date de délivrance/Issue Date: 2008/01/08
 (85) Entrée phase nationale/National Entry: 2001/11/14
 (86) N° demande PCT/PCT Application No.: US 2000/013312
 (87) N° publication PCT/PCT Publication No.: 2000/069922
 (30) Priorité/Priority: 1999/05/17 (US09/312,878)

(51) Cl.Int./Int.Cl. *C08F 210/16* (2006.01),
C08F 2/34 (2006.01), *C08F 4/02* (2006.01),
C08F 4/64 (2006.01), *C08J 5/18* (2006.01)
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(54) Titre : PROCÉDE DE POLYMERISATION
 (54) Title: METHOD OF POLYMERIZATION



(57) Abrégé/Abstract:

This invention relates to a composition of matter represented by formula (I), and to a polymerization process comprising combining an olefin in the gas or slurry phase with an activator, a support and a compound represented by formula (I): wherein M is a group 3 to 14 metal, each X is independently an anionic leaving group, n is the oxidation state of M, m is the formal charge of the YZL ligand, Y is a group 15 element, Z is a group 15 element, L is a group 15 or 16 element, R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, phosphorus, a halogen, R¹ and R² may also be interconnected to each other, R³ is absent, or is hydrogen, a group 14 atom containing group, a halogen, a heteroatom containing group, R⁴ and R⁵ are independently an aryl group, a substituted aryl group, a cyclic alkyl group, a substitutedcyclic alkyl group, or multiple ring system, R⁶ and R⁷ are independently absent or hydrogen, halogen, a heteroatom or a hydrocarbonyl group, or heteroatom containing group.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



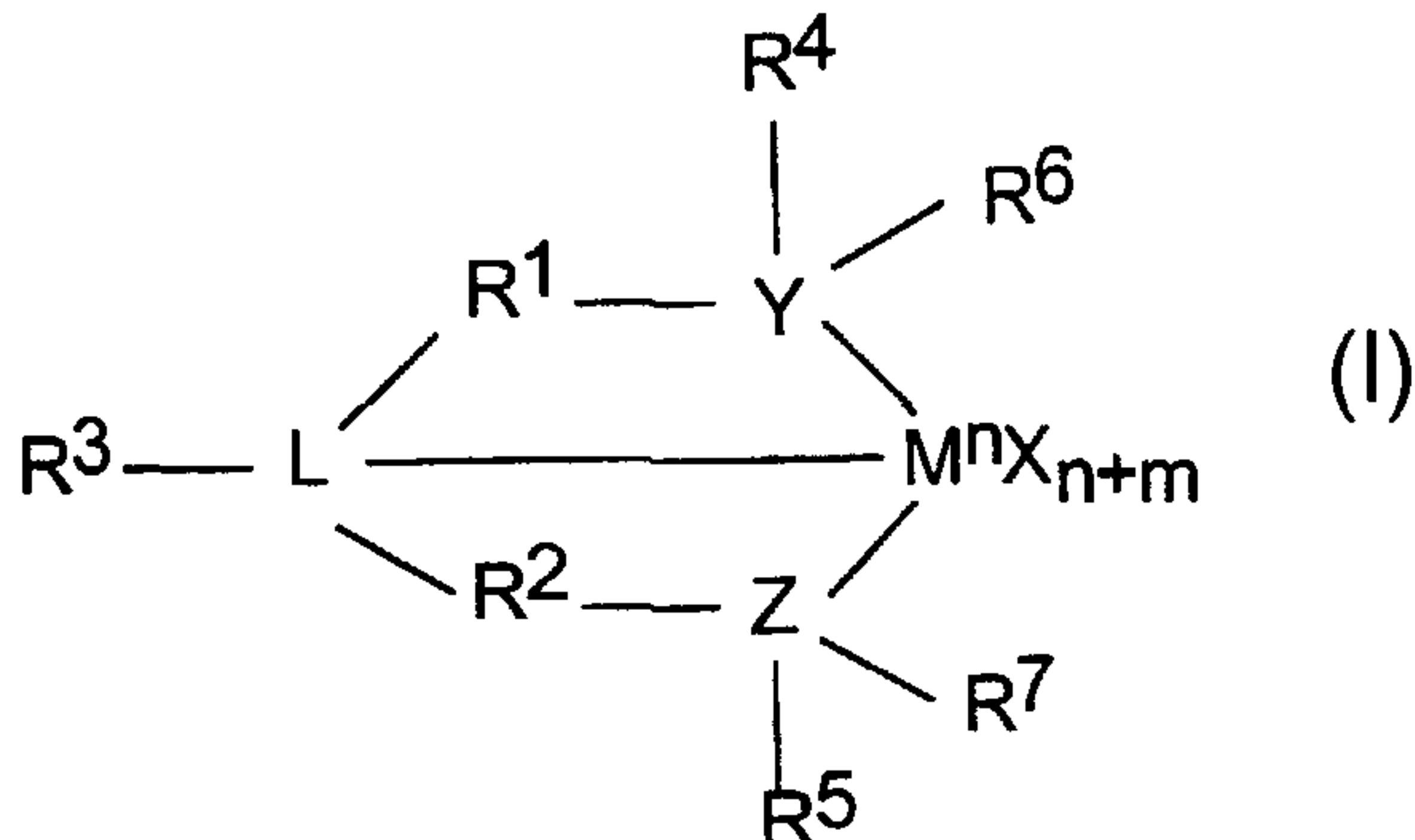
(43) International Publication Date
23 November 2000 (23.11.2000)

PCT

(10) International Publication Number
WO 00/69922 A3

- (51) International Patent Classification⁷: C08F 10/00, 210/16, 4/64
- (74) Agents: SHER, Jaimes et al.; Univation Technologies LLC, 5555 San Felipe, Suite 1950, Houston, TX 77056 (US).
- (21) International Application Number: PCT/US00/13312
- (81) Designated States (*national*): AU, BR, BY, CA, CN, CZ, ID, IL, IN, JP, KR, MX, NO, PL, RU, SG, SK, TR, ZA.
- (22) International Filing Date: 15 May 2000 (15.05.2000)
- (84) Designated States (*regional*): Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/312,878 17 May 1999 (17.05.1999) US
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- Published:**
— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- (88) Date of publication of the international search report: 8 February 2001
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: METHOD OF POLYMERIZATION



group, a substitutedcyclic alkyl group, or multiple ring system, R⁶ and R⁷ are independently absent or hydrogen, halogen, a heteroatom or a hydrocarbyl group, or heteroatom containing group.

WO 00/69922 A3

METHOD OF POLYMERIZATION

Field of the Invention:

5 This invention relates to olefin polymerization catalysts containing a metal atom bound to at least two group 15 atoms and their use in gas or slurry phase to produce polyolefins.

Background of the Invention:

10

 The intense commercialization of metallocene polyolefin catalysts (metallocene being cyclopentadienyl based transition metal catalyst compounds) has led to widespread interest in the design of non-metallocene, homogeneous catalysts, particularly for use in the economical gas and slurry phase processes. This field is more than an academic curiosity as new, non-metallocene catalysts in gas or slurry phase may provide an easier, more economical pathway to currently available products and may also provide product and process opportunities which are beyond the capability of metallocene catalysts in the gas or slurry phase.

20

 Anionic, multidentate heteroatom ligands have received the most attention in non-metallocene polyolefins catalysis. Notable classes of bidentate anionic ligands which form active polymerization catalysts include N-N⁻ and N-O⁻ ligand sets. Examples of these types of non-metallocene catalysts include amidopyridines (Kempe, R., "Aminopyridinato Ligands - New Directions and Limitations", 80th Canadian Society for Chemistry Meeting, Windsor, Ontario, Canada, June 1-4, 1997. Kempe, R. et al, *Inorg. Chem.* 1996 vol 35 6742.) Likewise, recent reports by Jordan *et al.* of polyolefin catalysts based on hydroxyquinolines (Bei, X.; Swenson, D. C.; Jordan, R. F., *Organometallics* 1997, 16, 3282) have been interesting even though the catalytic activities of Jordan's hydroxyquinoline catalysts are low.

30

 Schrock et al in US 5, 889,128 discloses a process for the living polymerization of olefins in solution using initiators having a metal atom and a ligand having two group 15 atoms and a group 16 atom or three group 15 atoms. In particular, the solution phase polymerization of ethylene using

-2-

{[NON]ZrMe}[MeB(C₆F₅)₃] or {[NON]ZrMe(PhNMe₂)}[B(C₆F₅)₄] is disclosed in examples 9 and 10.

EP 893 454 A1 discloses unsupported transition metal amide compounds used in combination with activators to polymerize olefins in the solution phase.

Ethylenebis(salicylideneiminato)zirconium dichloride combined with methyl alumoxane deposited on a support and unsupported versions were used to polymerize ethylene by Repo et al in Macromolecules 1997, 30, 171-175.

Thus there is a need in the art for gas or slurry phase processes to produce polyolefins using new and different supported catalyst systems.

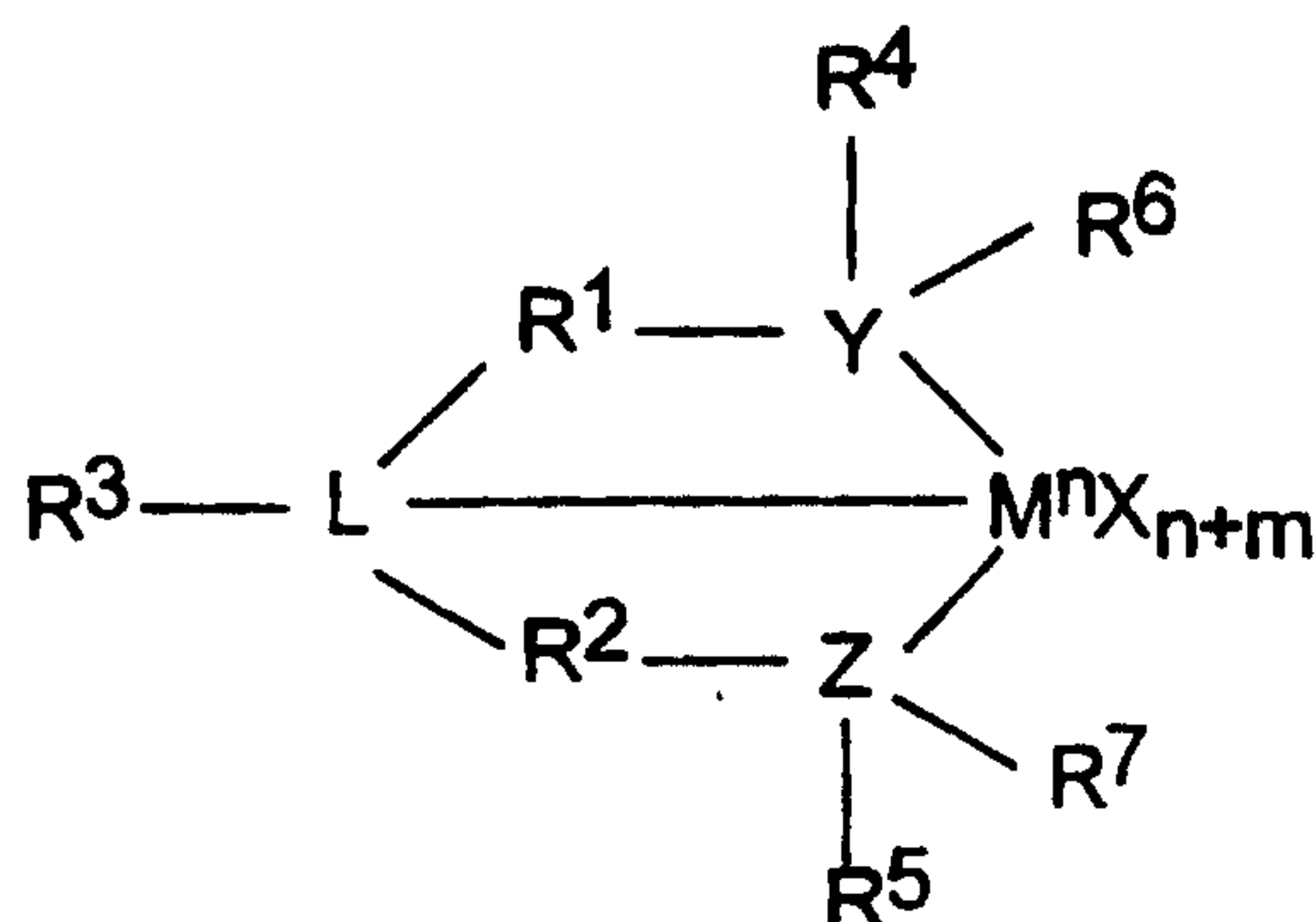
Summary of the Invention:

This invention relates to a catalytic molecule, and a catalyst system comprising a support, an activator, and a metal catalyst compound.

In one aspect, the invention relates to a catalyst system comprising a support, an activator and a metal catalyst compound comprising a group 3 to 14 metal atom bound to at least one anionic leaving group and also bound to at least two group 15 atoms, at least one of which is also bound to a group 15 or 16 atom through another group which may be a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead or phosphorus, or a halogen, wherein the group 15 or 16 atom may also be bound to nothing or a hydrogen, a group 14 atom containing group, a halogen, or a heteroatom containing group, and wherein each of the two group 15 atoms are also bound to a cyclic group and may optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.

This invention relates to the gas or slurry phase polymerization of olefins using an olefin polymerization catalyst system comprising an activator, a support and a transition metal compound represented by the formula:

-3-



wherein

M is a group 3 to 12 transition metal or a group 13 or 14 main group metal,
 each X is independently an anionic leaving group,

5 n is the oxidation state of M,

m is the formal charge of the YZL ligand,

Y is a group 15 element,

Z is a group 15 element,

L is a group 15 or 16 element,

10 R¹ and R² are independently silicon, germanium, tin, lead, phosphorus, a C₁ to C₂₀
 hydrocarbon group, or a heteroatom containing group,

R¹ and R² may also be interconnected to each other,

R³ is absent, or is hydrogen, a group 14 atom containing group, a halogen, a
 heteroatom containing group,

15 R⁴ and R⁵ are independently an aryl group, a substituted aryl group, a cyclic alkyl
 group, a substituted cyclic alkyl group, or multiple ring system, and

R⁶ and R⁷ are independently absent or hydrogen, halogen, heteroatom or a
 hydrocarbyl group, or a heteroatom containing group.

20 By "formal charge of the YZL ligand" is meant the charge of the entire ligand
 absent the metal and the leaving groups X.

By "R¹ and R² may also be interconnected to each other" is meant that R¹ and
 R² may be directly bound to each other or may be bound to each other through other
 25 groups.

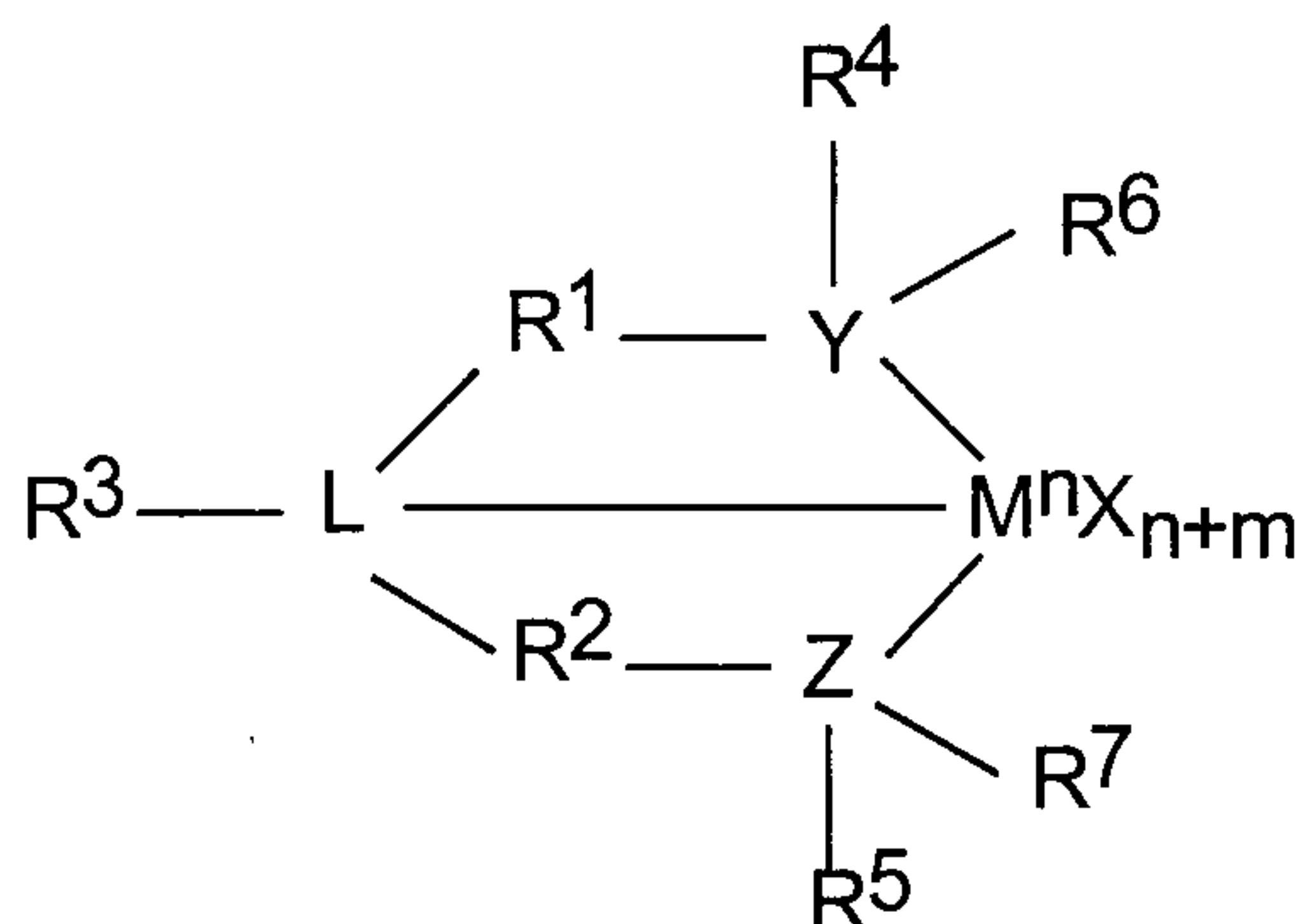
The activator is preferably an aluminum alkyl, an alumoxane, a modified alumoxane, a non-coordinating anion, a borane, a borate or a combination thereof.

In another aspect, the invention relates to a catalytic molecule comprising the transition metal compound represented by the formula set forth above.

Detailed Description of the Invention:

The present invention relates to a catalytic molecule (metal catalyst), and a catalyst system comprising a support, an activator, and the metal catalyst. The metal catalyst shows surprising ability to be immobilized on a support, activated by an activator, and surprising robustness and catalytic activity when supported and activated. The catalyst molecule itself is described, hereinafter, with reference to its combination with an activator.

In a preferred embodiment the activator is combined with a compound represented by the formula:



wherein

M is a group 3-12 transition metal or a group 13 or 14 main group metal, preferably a group 4, 5, or 6 metal, preferably zirconium or hafnium,
 each X is independently an anionic leaving group, preferably hydrogen, a hydrocarbyl group, a heteroatom or a halogen,
 n is the oxidation state of M, preferably +3, +4, or +5, preferably +4,
 m is the formal charge of the YZL ligand, preferably 0, -1, -2 or -3, preferably -2,
 L is a group 15 or 16 element, preferably nitrogen,
 Y is a group 15 element, preferably nitrogen or phosphorus,
 Z is a group 15 element, preferably nitrogen or phosphorus,

-5-

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms of silicon, germanium, tin, lead or phosphorus, a halogen, preferably a C₂ to C₆ hydrocarbon group, preferably a C₂ to C₂₀ alkyl, aryl or aralkyl group, preferably a linear, branched or cyclic C₂ to C₂₀ alkyl group, R¹ and R² may also be interconnected to each other,

R³ is absent or a hydrocarbon group, hydrogen, a halogen, a heteroatom containing group, preferably a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms, more preferably R³ is absent or hydrogen,

R⁴ and R⁵ are independently an aryl group, a substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic aralkyl group, a substituted cyclic aralkyl group or multiple ring system, preferably having up to 20 carbon atoms, preferably between 3 and 10 carbon atoms, preferably a C₁ to C₂₀ hydrocarbon group, a C₁ to C₂₀ aryl group or a C₁ to C₂₀ aralkyl group, and

R⁶ and R⁷ are independently absent, or hydrogen, halogen, heteroatom or a hydrocarbyl group, preferably a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms, more preferably absent.

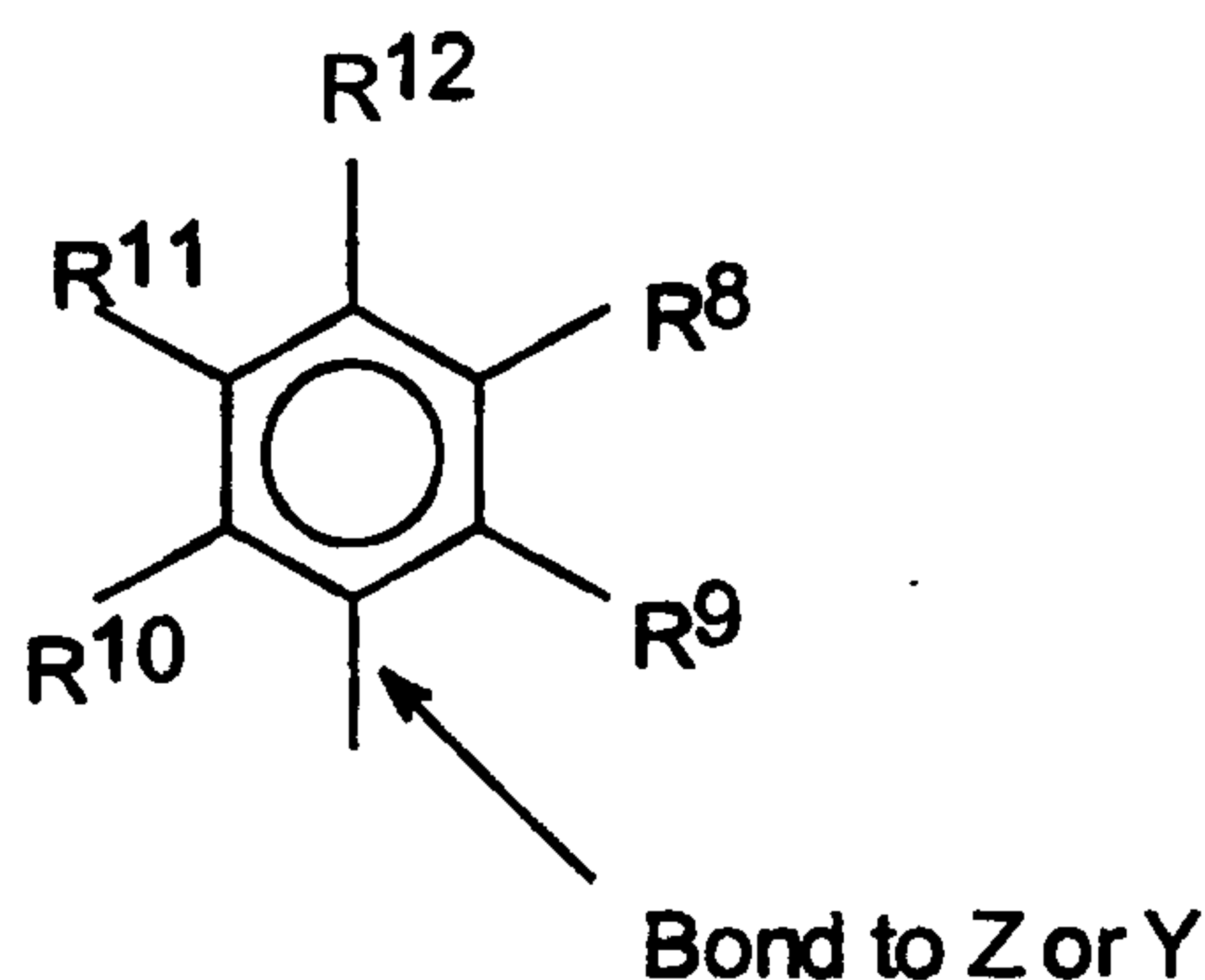
An aralkyl group is defined to be a substituted aryl group.

In a preferred embodiment, L is bound to one of Y or Z and one of R¹ or R² is bound to L and not to Y or Z.

In an alternate embodiment R³ and L do not form a heterocyclic ring.

In a preferred embodiment R⁴ and R⁵ are independently a group represented by the following formula:

-6-

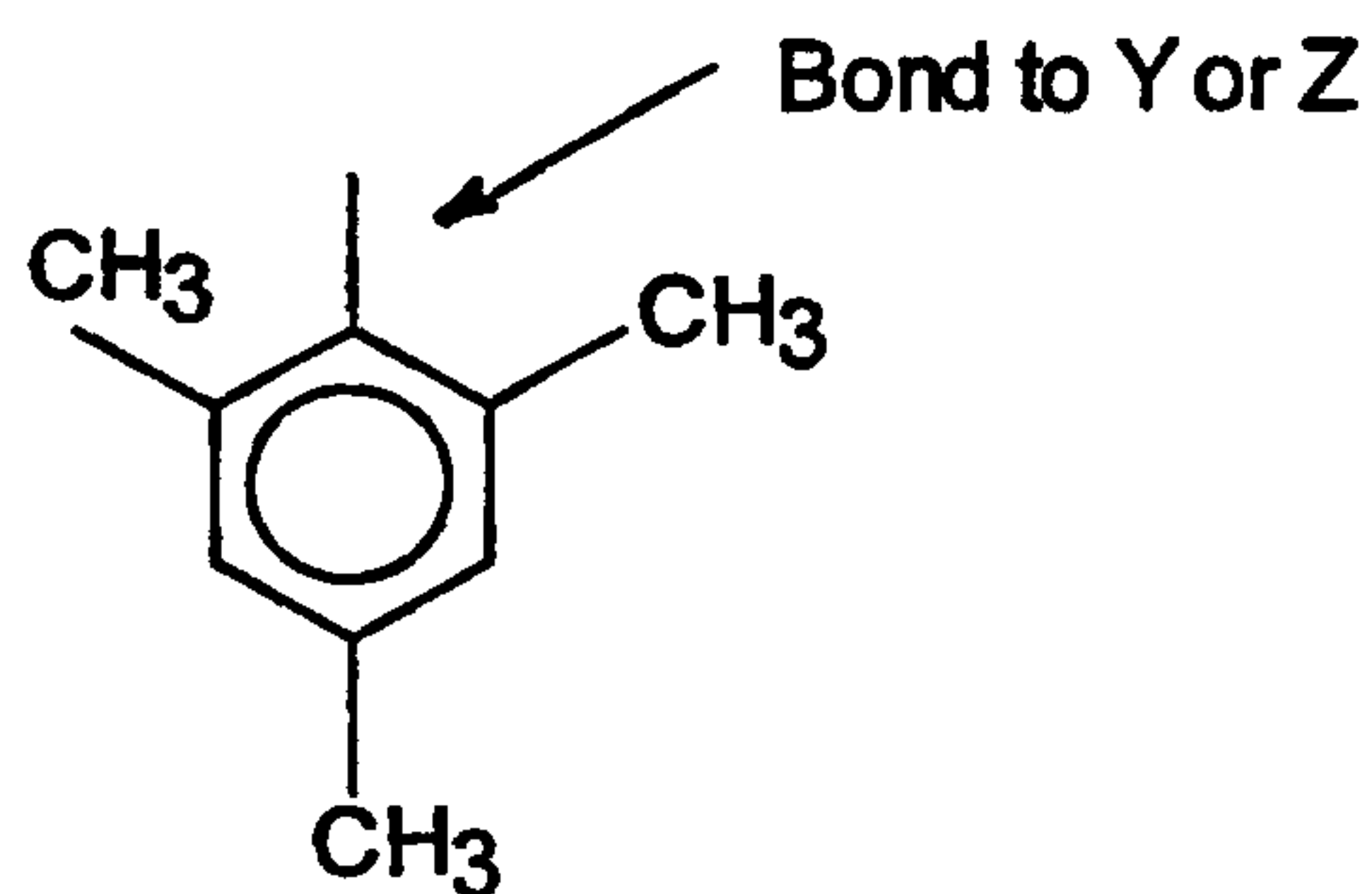


wherein

R⁸ to R¹² are each independently hydrogen, a C₁ to C₄₀ alkyl group, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, preferably a C₁ to C₂₀ linear or branched alkyl group, preferably a methyl, ethyl, propyl or butyl group, any two R groups may form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic. In a preferred embodiment R⁹, R¹⁰ and R¹² are independently a methyl, ethyl, propyl or butyl group, in a preferred embodiment R⁹, R¹⁰ and R¹² are methyl groups, and R⁸ and R¹¹ are hydrogen.

10

In a particularly preferred embodiment R⁴ and R⁵ are both a group represented by the following formula:



15

In this embodiment, M is preferably zirconium or hafnium, most preferably zirconium; each of L, Y, and Z is nitrogen; each of R¹ and R² is -CH₂-CH₂-; R³ is hydrogen; and R⁶ and R⁷ are absent.

20

These metal compounds are prepared by methods known in the art, such as those disclosed in US 5,889,128.

A preferred direct synthesis of these compounds comprises reacting the neutral ligand with M^nX_n (M is a group 3-14 metal, n is the oxidation state of M, X is an anionic group, such as halide, in a non-coordinating or weakly coordinating solvent, such as ether, toluene, xylene, benzene, methylene chloride, and/or hexane or other solvent having a boiling point above 60 °C, at about 5 20 to about 150 °C (preferably 20 to 100 °C), preferably for 24 hours or more, then treating the mixture with an excess (such as four equivalents) of an alkylating agent, such as methyl magnesium bromide in ether. The magnesium salts are removed by filtration, and the metal complex isolated by standard techniques.

10

In a preferred embodiment this invention relates to a method to prepare a metal compound comprising reacting a neutral ligand with a compound represented by the formula M^nX_n (where M is a group 3-14 metal, n is the oxidation state of M, X is an anionic leaving group) in a non-coordinating or weakly coordinating solvent, at 15 about 20 °C or above, preferably at about 20 to about 100 °C, then treating the mixture with an excess of an alkylating agent, then recovering the metal complex. In a preferred embodiment the solvent has a boiling point above 60 °C, such as ether, toluene, xylene, benzene, methylene chloride and/or hexane.

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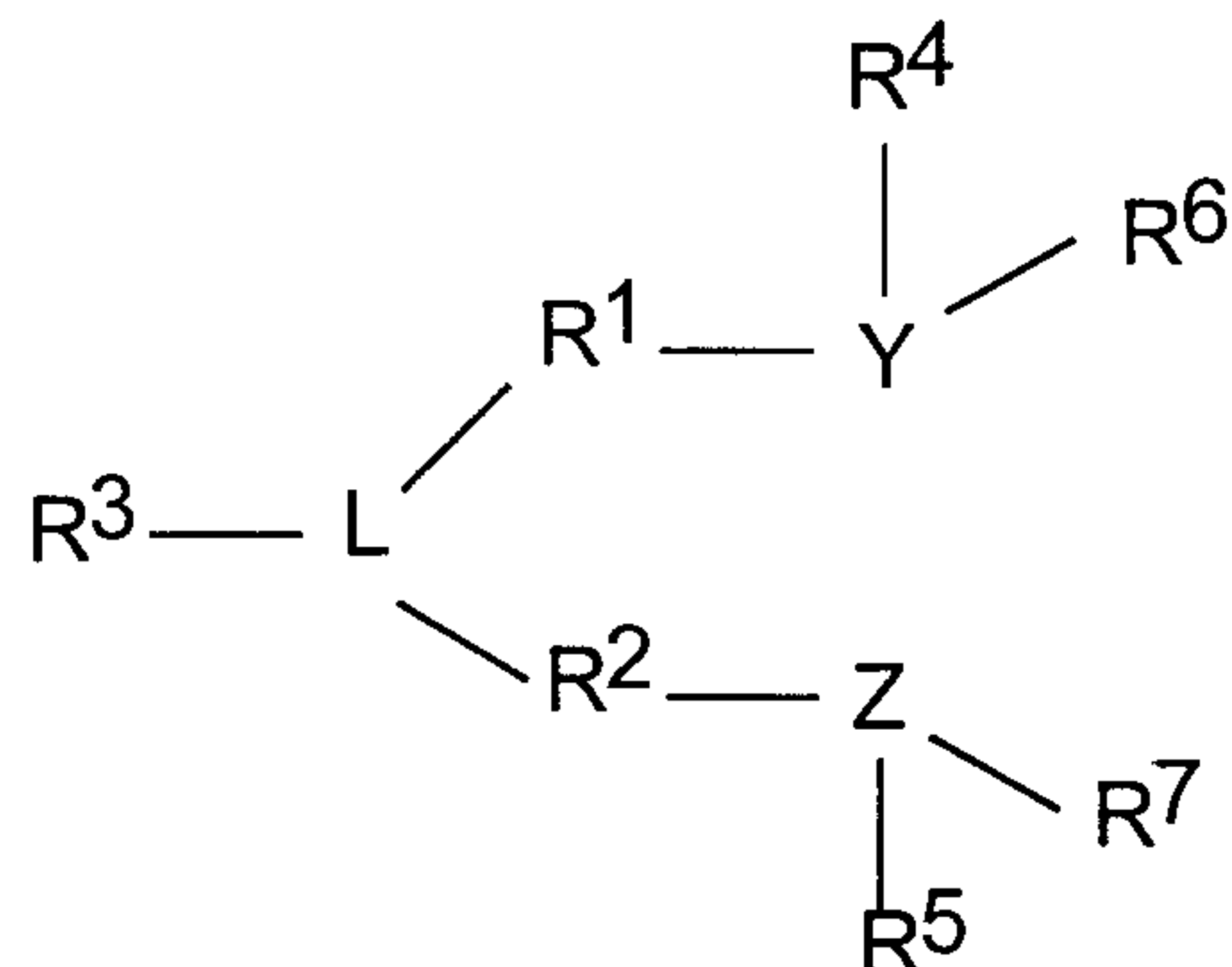
This invention further relates to a method to prepare a metal adduct comprising reacting a neutral ligand with a compound represented by the formula M^nX_n (where M is Zr or Hf, n is the oxidation state of M, X is a halogen) in a non-coordinating or weakly coordinating solvent, at 20°C or more, preferably at about 20 to about 100 °C then recovering the metal adduct.

25

This invention further relates to the reaction product of a neutral ligand reacted with a compound represented by the formula M^nX_n (where M is Zr or Hf, n is the oxidation state of M, X is an anionic leaving group), in a non-coordinating or weakly coordinating solvent at about 20 °C or above, preferably at about 20 to about 100 °C.

30

In a preferred embodiment the neutral ligand is represented by the formula:



Y is a group 15 element, preferably nitrogen or phosphorus,

5 Z is a group 15 element, preferably nitrogen or phosphorus,

L is a group 15 or 16 element, preferably nitrogen,

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, phosphorus, a halogen,

R¹ and R² may also be interconnected to each other,

10 R³ is absent, or is hydrogen, a group 14 atom containing group, a halogen, a heteroatom containing group,

R⁴ and R⁵ are independently an aryl group, a substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, or multiple ring system,

15 R⁶ and R⁷ are independently absent or hydrogen, halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.

The transition metal compounds described herein are preferably combined with one or more activators to form an olefin polymerization catalyst system.

Preferred activators include alkyl aluminum compounds (such as diethylaluminum chloride), alumoxanes, modified alumoxanes, non-coordinating anions, non-coordinating group 13 metal or metalliod anions, boranes, borates and the like. It is within the scope of this invention to use alumoxane or modified alumoxane as an activator, and/or to also use ionizing activators, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron or a trisperfluorophenyl boron
 25 metalloid precursor which ionize the neutral metallocene compound. Other useful compounds include triphenyl boron, triethyl boron, tri-n-butyl ammonium

-9-

tetraethylborate, triaryl borane and the like. Other useful compounds include aluminate salts as well.

There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253 and 5,731,451 and European publications EP-A-0 561 476, EP-B1-0 279 586 and EP-A-0 594-218, and PCT publication WO 94/10180.

Ionizing compounds may contain an active proton, or some other cation associated with but not coordinated to or only loosely coordinated to the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-A-0 426 637, EP-A-500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,387,568, 5,384,299 and 5,502,124 and U.S. Patent No. 5,643,847. Other activators include those described in PCT publication WO 98/07515 such as tris(2, 2', 2''-nonafluorobiphenyl) fluoroaluminate. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, PCT publications WO 94/07928 and WO 95/14044 and U.S. Patent Nos. 5,153,157 and 5,453,410. Also, methods of activation such as using radiation and the like are also contemplated as activators for the purposes of this invention.

25

In general the transition metal compound and the activator are combined in ratios of about 1000:1 to about 0.5:1. In a preferred embodiment the transition metal compound and the activator are combined in a ratio of about 300:1 to about 1:1, preferably about 10:1 to about 1:1, for boranes, borates, aluminates, etc. the ratio is preferably about 1:1 to about 10:1 and for alkyl aluminum compounds (such as

diethylaluminum chloride combined with water) the ratio is preferably about 0.5:1 to about 10:1.

Polymerization Process of the Invention:

5

The catalysts and catalyst systems described above are suitable for use in the polymerization process of the invention. The polymerization process of the invention includes a solution, gas or slurry process or a combination thereof, most preferably a gas or slurry phase process.

10

In an embodiment, this invention is directed toward the slurry or gas phase polymerization or copolymerization reactions involving the polymerization of one or more monomers having from 2 to 30 carbon atoms, preferably 2-12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the copolymerization reactions involving the polymerization of one or more olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, 3-methyl-pentene-1, 3,5,5-trimethyl-hexene-1 and cyclic olefins or a combination thereof. Other monomers can include vinyl monomers, diolefins such as dienes, polyenes, norbornene, norbornadiene monomers. Preferably a copolymer of ethylene is produced, where the comonomer is at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, more preferably from 4 to 8 carbon atoms and most preferably from 4 to 7 carbon atoms. In an alternate embodiment, the geminally disubstituted olefins disclosed in WO 98/37109 may be polymerized or copolymerized using the invention herein described.

25

In another embodiment ethylene or propylene is polymerized with at least two different comonomers to form a terpolymer. The preferred comonomers are a combination of alpha-olefin monomers having 4 to 10 carbon atoms, more preferably 4 to 8 carbon atoms, optionally with at least one diene monomer. The preferred terpolymers include the combinations such as ethylene/butene-1/hexene-1, ethylene/propylene/butene-1, propylene/ethylene/hexene-1, ethylene/propylene/norbornene and the like.

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-11-

In a particularly preferred embodiment the process of the invention relates to the polymerization of ethylene and at least one comonomer having from 4 to 8 carbon atoms, preferably 4 to 7 carbon atoms. Particularly, the comonomers are butene-1, 4-methyl-pentene-1, hexene-1 and octene-1, the most preferred being hexene-1 and/or
5 butene-1.

Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by
10 the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the
15 fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228.)

20

The reactor pressure in a gas phase process may vary from about 10 psig (69 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 100 psig (690 kPa) to about 400 psig (2759 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from
25 about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

The reactor temperature in the gas phase process may vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70°C to 110°C, and most preferably in the range of from about 70
30 °C to about 95°C.

-12-

The productivity of the catalyst or catalyst system is influenced by the main monomer partial pressure. The preferred mole percent of the main monomer, ethylene or propylene, preferably ethylene, is from about 25 to 90 mole percent and the monomer partial pressure is in the range of from about 75 psia (517 kPa) to about 5 300 psia (2069 kPa), which are typical conditions in a gas phase polymerization process.

In a preferred embodiment, the reactor utilized in the present invention and the process of the invention produce greater than 500 lbs of polymer per hour (227 Kg/hr) 10 to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 15 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

Other gas phase processes contemplated by the process of the invention include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200, EP-A- 0 802 202 and EP-B- 634 421. 20

A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres and even greater and temperatures in the range of 0° C to about 120°C. In a slurry polymerization, a suspension of solid, particulate 25 polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium 30 is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above

-13-

the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

In one embodiment, a preferred polymerization technique of the invention is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Patent No. 3,248,179. The preferred temperature in the particle form process is within the range of about 185°F (85°C) to about 230°F (110°C). Two preferred polymerization methods for the slurry process are those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484.

15

In another embodiment, the slurry process is carried out continuously in a loop reactor. The catalyst as a slurry in isobutane or as a dry free flowing powder is injected regularly to the reactor loop, which is itself filled with circulating slurry of growing polymer particles in a diluent of isobutane containing monomer and comonomer. Hydrogen, optionally, may be added as a molecular weight control. The reactor is maintained at pressure of about 525 psig to 625 psig (3620 kPa to 4309 kPa) and at a temperature in the range of about 140 °F to about 220 °F (about 60 °C to about 104 °C) depending on the desired polymer density. Reaction heat is removed through the loop wall since much of the reactor is in the form of a double-jacketed pipe. The slurry is allowed to exit the reactor at regular intervals or continuously to a heated low pressure flash vessel, rotary dryer and a nitrogen purge column in sequence for removal of the isobutane diluent and all unreacted monomer and comonomers. The resulting hydrocarbon free powder is then compounded for use in various applications.

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-14-

In an embodiment the reactor used in the slurry process of the invention is capable of and the process of the invention is producing greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment
5 the slurry reactor used in the process of the invention is producing greater than 15,000 lbs of polymer per hour (6804 Kg/hr), preferably greater than 25,000 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

In another embodiment in the slurry process of the invention the total reactor
10 pressure is in the range of from 400 psig (2758 kPa) to 800 psig (5516 kPa), preferably 450 psig (3103 kPa) to about 700 psig (4827 kPa), more preferably 500 psig (3448 kPa) to about 650 psig (4482 kPa), most preferably from about 525 psig (3620 kPa) to 625 psig (4309 kPa).

In yet another embodiment in the slurry process of the invention the
15 concentration of ethylene in the reactor liquid medium is in the range of from about 1 to 10 weight percent, preferably from about 2 to about 7 weight percent, more preferably from about 2.5 to about 6 weight percent, most preferably from about 3 to about 6 weight percent.

20

A preferred process of the invention is where the process, preferably a slurry or gas phase process is operated in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, tri-isobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This
25 preferred process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352,

In another preferred embodiment the one or all of the catalysts are combined with up to 10 weight % of a metal stearate, (preferably a aluminum stearate, more
30 preferably aluminum distearate) based upon the weight of the catalyst, any support and the stearate, preferably 2 to 3 weight %. In an alternate embodiment a solution of the metal stearate is fed into the reactor. In another embodiment the metal stearate is mixed with the catalyst and fed into the reactor separately. These agents may be

mixed with the catalyst or may be fed into the reactor in a solution with or without the catalyst system or its components.

The catalyst and/or the activator may be placed on, deposited on, contacted
5 with, incorporated within, adsorbed, or absorbed in a support. Typically the support can be of any of the solid, porous supports, including microporous supports. Typical support materials include talc; inorganic oxides such as silica, magnesium chloride, alumina, silica-alumina; polymeric supports such as polyethylene, polypropylene, polystyrene, cross-linked polystyrene; and the like. Preferably the support is used in
10 finely divided form. Prior to use the support is preferably partially or completely dehydrated. The dehydration may be done physically by calcining or by chemically converting all or part of the active hydroxyls. For more information on how to support catalysts please see US 4,808,561 which discloses how to support a
15 metalocene catalyst system. The techniques used therein are generally applicable for this invention.

In a preferred embodiment, the polyolefin recovered typically has a melt index as measured by ASTM D-1238, Condition E, at 190°C of 3000 g/10 min or less. In a preferred embodiment the polyolefin is ethylene homopolymer or copolymer. IN a
20 preferred embodiment for certain applications, such as films, molded article and the like a melt index of 100 g/10 min or less is preferred. For some films and molded article a melt index of 10 g/10 min is preferred. In a preferred embodiment the polymer produced has a molecular weight of 200,000 Daltons or more.

25 In a preferred embodiment the catalyst system described above is used to make a polyethylene having a density of between 0.88 and 0.970 g/cm³ (as measured by ASTM 2839), a melt index of 1.0 or less g/10min or less (as measured by ASTM D-1238, Condition E, at 190°C). Polyethylene having a melt index of between 0.01 to
10 dg/min is preferably produced. In some embodiments, a density of 0.915 to
30 0.940g/cm³ would be preferred, in other embodiments densities of 0.930 to 0.960g/cm³ are preferred.

The polyolefins then can be made into films, molded articles, sheets, wire and cable coating and the like. The films may be formed by any of the conventional technique known in the art including extrusion, co-extrusion, lamination, blowing and casting. The film may be obtained by the flat film or tubular process which may be followed by orientation in an uniaxial direction or in two mutually perpendicular directions in the plane of the film to the same or different extents. Orientation may be to the same extent in both directions or may be to different extents. Particularly preferred methods to form the polymers into films include extrusion or coextrusion on a blown or cast film line.

10

The films produced may further contain additives such as slip, antiblock, antioxidants, pigments, fillers, antifog, UV stabilizers, antistats, polymer processing aids, neutralizers, lubricants, surfactants, pigments, dyes and nucleating agents. Preferred additives include silicon dioxide, synthetic silica, titanium dioxide, polydimethylsiloxane, calcium carbonate, metal stearates, calcium stearate, zinc stearate, talc, BaSO₄, diatomaceous earth, wax, carbon black, flame retarding additives, low molecular weight resins, hydrocarbon resins, glass beads and the like. The additives may be present in the typically effective amounts well known in the art, such as 0.001 weight % to 10 weight %.

20

This invention further relates to a library of a plurality of metal compounds represented by the formula above. These libraries may then be used for the simultaneous parallel screening of catalysts by combining the library with one or more olefins, preferably in order to determine the relative capabilities of the different compounds.

25

Examples:

Mn and Mw were measured by gel permeation chromatography on a waters 150°C GPC instrument equipped with differential refraction index detectors. The GPC columns were calibrated by running a series of narrow polystyrene standards and the molecular weights were calculated using Mark Houwink coefficients for the polymer is question.

30

Density was measured according to ASTM D 1505.

Melt Index (MI) I_2 and I_{21} were measured according to ASTM D-1238, Condition E, at 190°C.

Melt Index Ratio (MIR) is the ratio of I_{21} over I_2 as determined by ASTM D-1238.

5 **Weight % comonomer** was measured by proton NMR.

MWD = M_w/M_n

Example 1: Catalyst A Preparation

10 **Preparation of [iPrNH(*o*-C₆H₄)]₂O**

A 250 mL one-neck flask was charged with [H₂N(*o*-C₆H₄)]₂O (10.0 g, 50 mmol), acetone (15 mL), activated Zn dust (25.0 g, 382 mmol) and glacial acetic acid (100 mL). The flask was capped with a rubber septum, connected to an oil-bubbler via a needle and then heated under rapid stirring to 60°C for 24 h. After cooling to
15 room temperature the reaction mixture was poured onto ice (200 mL), concentrated aqueous NH₃ (200 mL), and methylene chloride (150 mL). The layers were separated and the aqueous layer extracted with methylene chloride (2 x 100 mL). The combined methylene chloride layers were dried over MgSO₄. Removal of methylene chloride in vacuo afforded crude material as an orange oil. The oil was dissolved in
20 acetone (150 mL) and concentrated HCl (10 mL) was added. Within one minute colorless crystals began to form. The mixture was allowed to stand overnight and the colorless crystalline solid was isolated by filtration, washed with acetone, and dried overnight under vacuum. A mixture of aqueous NaOH (100 mL, 10%) and ether (100 mL) was added to this solid. The mixture was stirred until the solid dissolved. The
25 layers were separated and the aqueous layer extracted with ether (3 x 50 mL). The combined organic layers were dried over MgSO₄. Activated charcoal was added prior to filtering through a bed of Celite. Ether was removed in vacuo leaving a pale yellow oil (yield: 13.2 g, 93%). ¹H NMR (C₆D₆) δ 6.98(t, 2), 6.63 (d, 2), 6.55 (t, 2), 4.14 (br s, 2), 3.37 (br m, 2), 0.89 (d, 12). ¹³C NMR (C₆D₆) δ 144.8, 140.0, 125.1,
30 118.8, 117.1, 112.5, 44.4, 23.2.

Preparation of {[iPrN(*o*-C₆H₄)]₂O}ZrCl₂•C₇H₈

[iPrNH(*o*-C₆H₄)]₂O (3.02 g, 10.6 mmol) and Zr(NMe₂)₄ (2.84 g, 10.6 mmol) were dissolved in pentane (40 mL). The solution was stirred at room temperature for 3 h. All volatile components were removed in vacuo to give an oil. To this oil was added toluene (40 mL) and Me₃SiCl (2.9 g, 26.7 mmol). The solution quickly turned bright orange and was left to stand at room temperature for 14 h. Small amounts of solid were removed by filtration and pentane (40 mL) added. The solution was cooled to -25°C for 24 h. A solid was isolated by filtration (4.11 g, 72%). According to ¹H NMR spectroscopy one equivalent of toluene was present. ¹H NMR (CD₂Cl₂, resonances for toluene are not given) δ 7.67 (d, 2), 7.08 (t, 2), 6.83 (d, 2), 6.77 (t, 2), 4.66 (sept, 2), 1.52 (d, 12). ¹³C NMR (CD₂Cl₂, toluene resonances not given) δ 148.2, 143.4, 126.1, 117.7, 114.7, 113.8, 48.9, 20.0. Analysis calculated for C₂₅H₃₀Cl₂N₂OZr: C, 55.95; H, 5.63, N, 5.22. Found: C, 55.84; H, 5.61; N, 5.27.

To 1.239 g of MAO (4.131 g of a 30 weight percent solution in toluene, Albemarle) and 4.274 g of toluene in a 250 mL round bottom flask was added 0.037 g of {[iPrN(*o*-C₆H₃)]₂O}ZrCl₂•C₇H₈. The solution was stirred for 15 minutes. 3.098 g of silica (Davison 948, calcined at 800°C) was added followed by mixing. The mixture was dried overnight under vacuum yielding 4.114 g of finished catalyst with a loading of 0.14 weight percent zirconium and an Al/Zr ratio of 310:1.

Example 2: Slurry-Phase Ethylene-Hexene Polymerization

Polymerization was performed in the slurry-phase in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry nitrogen and ethylene. The reactor was dried and degassed at 160°C. Isobutane (400 mL) was added as a diluent, 35 mL of 1-hexene, and 0.4 mL of a 25 weight percent triisobutyl aluminum solution in hexane was added as a scavenger using a gas tight syringe. The reactor was heated to 60°C. 0.256 g of finished catalyst A was added with ethylene pressure and the reactor was pressurized with 79 psi (545 kPa) of ethylene. The polymerization was continued for 30 minutes while maintaining the reactor at 60°C and 79 psi (545 kPa) by constant ethylene flow. The reaction was stopped by rapid cooling and venting. No polymer was recovered.

Example 3: Catalyst B Preparation

To 1.902 g of MAO (6.340 g of a 30 weight percent solution in toluene, Albemarle) and 6.521 g of toluene in a 250 mL round bottom flask was added 0.126 g of $\{[(\text{CD}_3)_2\text{MeCN}(o\text{-C}_6\text{H}_3)]_2\text{O}\}\text{ZrCl}_2$. The solution was stirred for 15 minutes.

5 5.003 g of silica (Davison 948, calcined at 600°C) was added followed by mixing. The mixture was dried overnight under vacuum yielding 6.869 g of finished catalyst with a loading of 0.35 weight percent zirconium and an Al/Zr ratio of 123:1. The $\{[(\text{CD}_3)_2\text{MeCN}(o\text{-C}_6\text{H}_3)]_2\text{O}\}\text{ZrCl}_2$ was prepared according to the method in Baumann, Journal of the American Chemical Society, Vol 119, pg 3830, 1997.

10 Example 4: Slurry-Phase Ethylene-Hexene Polymerization

Polymerization was performed in the slurry-phase in a 2-liter autoclave reactor equipped with a mechanical stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry nitrogen and ethylene. The reactor is dried and degassed at 100°C. Hexane (800 mL) is added as a diluent, 90
15 mL of 1-hexene, and 0.2 mL of a 25 weight percent triethyl aluminum solution in heptane is added as a scavenger using a gas tight syringe. The reactor was heated to 60°C. 0.400 g of finished catalyst B was added with nitrogen pressure and the reactor was pressurized with 75 psi (545 kPa) of ethylene. The polymerization was continued for 30 minutes while maintaining the reactor at 60°C and 75 psi (517 kPa) by constant
20 ethylene flow. The reaction was stopped by rapid cooling and venting. 8.8 g of ethylene-hexene copolymer were recovered (MW = 281,700, MWD = 4.68, 5.6 weight percent hexene, activity = 229 g PE/mmol cat.·atm·h).

Example 5: Catalyst C Preparation

To 2.034 g of MAO (6.783 g of a 30 weight percent solution in toluene,
25 Albemarle) and 7.216 g of toluene in a 250 mL round bottom flask was added 0.130 g of $\{[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{CH}_2]_2\text{O}\}\text{ZrCl}_2$. The solution was stirred for 15 minutes. 5.024 g of silica (Davison 948, calcined at 800°C) was added followed by mixing. The mixture was dried overnight under vacuum yielding 7.131 g of finished catalyst with a loading of 0.35 weight percent zirconium and an Al/Zr ratio of 127:1. The

$\{[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{CH}_2]_2\text{O}\}\text{ZrCl}_2$ was synthesized according to the method of Aizenberg, Organometallics, vol. 17, pg 4795, 1998.

Example 6: Slurry-Phase Ethylene-Hexene Polymerization

The polymerization was conducted as per example 4. 0.200 g of finished
5 catalyst C yielded 37.4 g of ethylene-hexene copolymer (MW = 259,900, MWD = 6.63, 5.6 weight percent hexene, activity = 1950 g PE/mmol cat. • atm • h).

Example 7: Catalyst D Preparation

Preparation of $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NHCH}_2\text{CH}_2]_2\text{NH}$

10 A 2 L one-armed Schlenk flask was charged with a magnetic stir bar, diethylenetriamine (23.450 g, 0.227 mol), mesityl bromide (90.51 g, 0.455 mol), tris(dibenzylideneacetone)dipalladium (1.041 g, 1.14 mmol), racemic-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (2.123 g, 3.41 mmol), sodium tert-butoxide (65.535 g, 0.682 mol), and toluene (800 mL). The reaction mixture was heated to
15 95°C and stirred. After 4 days the reaction was complete, as judged by proton NMR spectroscopy. All solvent was removed under vacuum and the residues dissolved in diethyl ether (1 L). The ether was washed three times with water (1 L) and saturated aqueous NaCl (500 mL) and dried over magnesium sulfate. Removal of the ether in vacuo yielded a red oil which was dried at 70°C for 12 h under vacuum (yield: 71.10
20 g, 92%). ^1H NMR δ 6.83 (s, 4), 3.39 (br s, 2), 2.86 (t, 4), 2.49 (t, 4), 2.27 (s, 12), 2.21 (s, 6), 0.68 (br s, 1). ^{13}C NMR δ 143.74, 131.35, 129.83, 129.55, 50.17, 48.56, 20.70, 18.51.

Preparation of $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{ZrMe}_2$

25 10.798 g of $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NHCH}_2\text{CH}_2]_2\text{NH}$ (31.8 mmol) was dissolved in 250 mL of toluene in a 500 mL round bottom flask. 7.411 g of ZrCl_4 (31.8 mmol) was added as a solid and the mixture heated to 80°C with stirring for 24 hours. The mixture was cooled to room temperature (the insoluble product $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NHCH}_2\text{CH}_2]_2\text{NH}\}\text{ZrCl}_4$ can be isolated by filtration and stored for future
30 use).and 43.5 mL of MeMgBr (3.0 M in ether, 130.3 mmol) added dropwise with

stirring over 30 minutes. The mixture was stirred for 60 minutes followed by filtration to remove MgClBr. The toluene and ether were removed under vacuum and the solids extracted with toluene (200 mL). The volume of toluene was reduced to 10 mL and 250 mL of pentane added causing the precipitation of a pale brown solid. The solid product was isolated by filtration, washed with 50 mL of cold pentane, and dried under vacuum (15.201 g, 86% yield). ^1H NMR (C_6D_6 , δ) 6.98 (s, 2), 6.96 (s, 2), 3.32 (m, 2), 3.12 (m, 2), 2.54 (s, 6), 2.42 (s, 6), 2.36 (m, 4), 2.21 (s, 6), 1.16 (s, 1), 0.24 (s, 3), 0.07 (s, 3). ^{13}C NMR (C_6D_6 , δ) 146.56, 136.07, 135.55, 134.23, 130.29, 129.98, 57.46, 51.27, 42.45, 39.63, 21.44, 19.39, 19.28. Analysis calculated for $\text{C}_{24}\text{H}_{37}\text{N}_3\text{Zr}$: C, 62.83; H, 8.13; N, 9.16. Found: C, 62.91; H, 8.02; N, 9.04.

To 0.617 g of MAO (2.058 g of a 30 weight percent solution in toluene, Albemarle) and 3.009 g of toluene in a 250 mL round bottom flask was added 0.080 g of $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{ZrMe}_2$. The solution was stirred for 15 minutes. 3.000 g of silica (Davison 948, calcined at 800°C) was added followed by mixing. The mixture was dried overnight under vacuum yielding 3.528 g of finished catalyst with a loading of 0.43 weight percent zirconium and an Al/Zr ratio of 61:1.

Example 8: Slurry-Phase Ethylene-Hexene Polymerization

Polymerization was performed in the slurry-phase in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry nitrogen and ethylene. The reactor was dried and degassed at 160°C . Isobutane (400 mL) was added as a diluent, 35 mL of 1-hexene, and 0.7 mL of a 25 weight percent trioctyl aluminum solution in hexane was added as a scavenger using a gas tight syringe. The reactor was heated to 60°C . 0.078 g of finished catalyst D was added with ethylene pressure and the reactor was pressurized with 74 psi (510 kPa) of ethylene. The polymerization was continued for 30 minutes while maintaining the reactor at 60°C and 74 psi (510 kPa) by constant ethylene flow. The reaction was stopped by rapid cooling and venting. 59.2 g of ethylene-hexene copolymer were recovered (MW = 578,900, MWD = 5.40, 11.8 weight percent hexene, activity = 6530 g PE/mmol cat. \cdot atm \cdot h).

Example 9: Catalyst E Preparation

To 11.230 g of MAO (37.434 g of a 30 weight percent solution in toluene, Albemarle) and 43.002 g of toluene in a 500 mL round bottom flask was added 0.742 g of $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{ZrMe}_2$. (Synthesized according to the procedure in Example 7.) The solution was stirred for 15 minutes. 30.002 g of silica (Davison 948, calcined at 600°C) was added followed by mixing. The mixture was dried overnight under vacuum yielding 41.002 g of finished catalyst with a loading of 0.35 weight percent zirconium and an Al/Zr ratio of 120:1.

Example 10: Gas-Phase Ethylene-Hexene Polymerization

Catalyst E described above was used for ethylene-hexene copolymerization studies described below. A continuous fluid bed gas-phase reactor operated at 300 psi (2.07 MPa) total pressure and 1.64 ft/s (0.5 m/s) cycle gas velocity was used for determining catalyst efficiency, ability to incorporate comonomer (1-hexene) and molecular weight capability. The polymer properties were as follows: 8.4 weight percent hexene, $\text{MI}_2 = 0.31$, $\text{MI}_{21} = 13.53$, $\text{MIR} = 43.65$, density 0.9243 g/cm³. A summary of the process data is included in Table 1.

TABLE 1

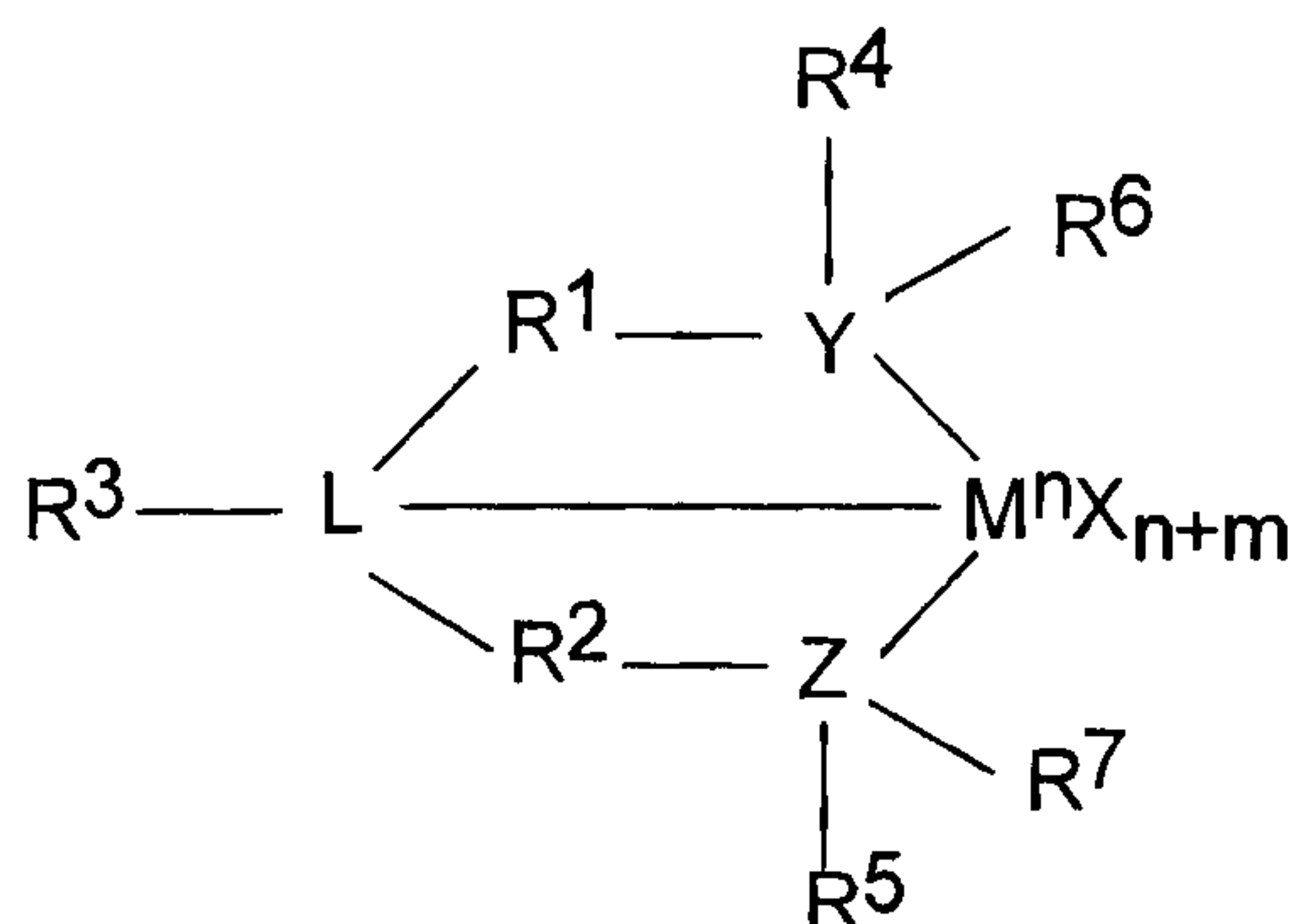
H ₂ conc. (ppm)	6451
C ₂ conc. (mol %)	35.0
Hexene conc. (mol %)	0.40
H ₂ /C ₂ Ratio	184.5
C ₆ /C ₂ Ratio	0.087
Reactor Temp (F/ C)	145/62.8
Avg. Bed weight (g)	1891
Production (g/h)	315
Residence Time (h)	6.0
Productivity (g/g) – MB ¹	696
Productivity (g/g) – XRF ²	1171
Total Bed Turnovers	3.0

¹MB = Material Balance²XRF = X-ray Fluorescence

As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made
5 without departing from the spirit and scope of the invention. Accordingly it is not intended that the invention be limited thereby.

CLAIMS:

1. A polymerization process comprising combining, in the gas phase at a reactor temperature of from 60° to 115°C or slurry phase as particle form polymerization at a temperature of 85°C to 110°C, ethylene and 1-hexene or 1-butene with an activator, a support and a compound represented by the following formula:



wherein

M is zirconium,

each X is independently an anionic leaving group,

n is the oxidation state of M,

m is the formal charge of the YZL ligand,

Y is a group 15 element,

Z is a group 15 element,

L is a group 15 or 16 element,

R¹ and R² are independently silicon, germanium, tin, lead, phosphorus, a C₁ to C₂₀ hydrocarbon group, or a heteroatom containing group,

R¹ and R² may also be interconnected to each other,

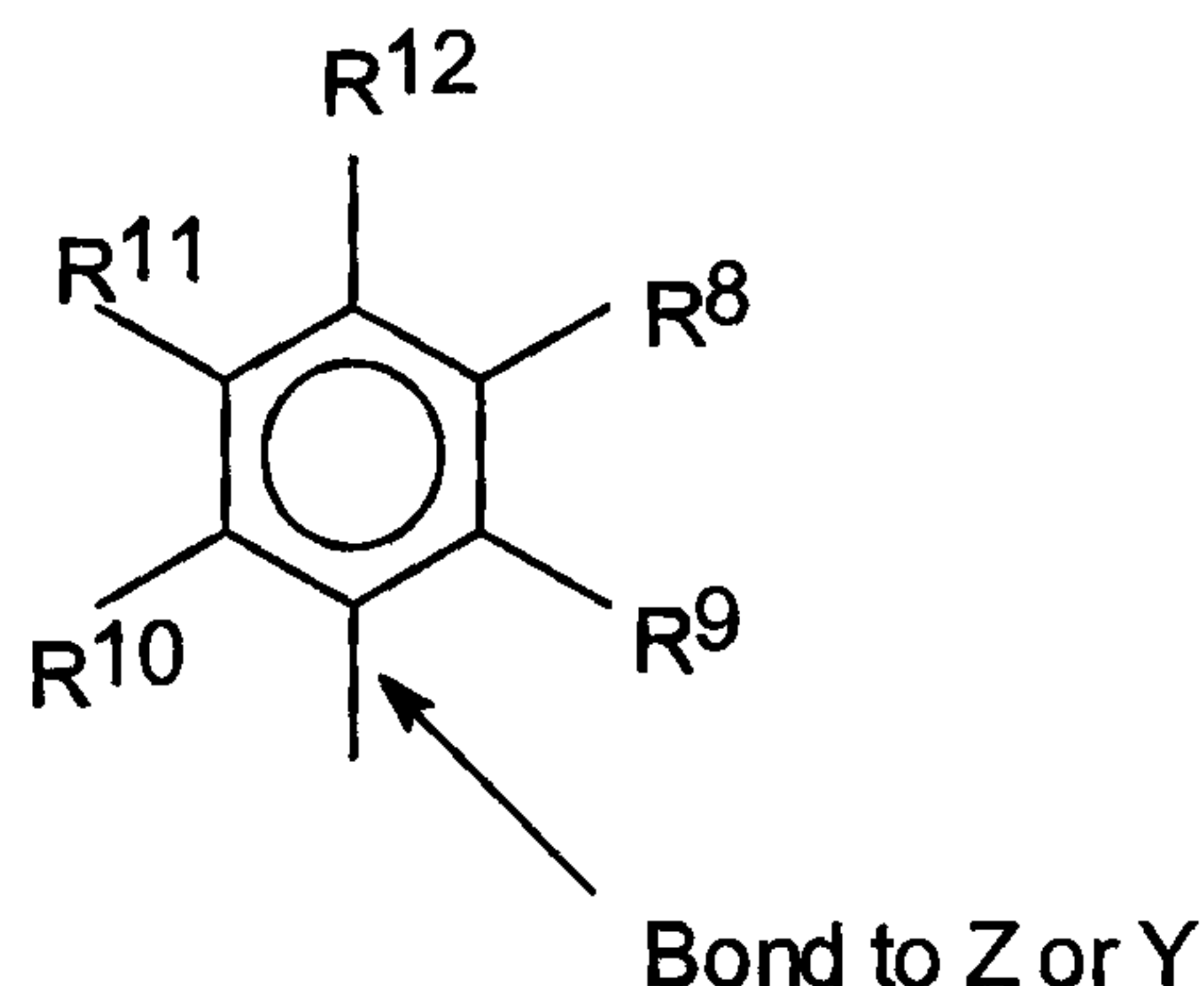
R³ is absent, or is hydrogen, a group 14 atom containing group, a halogen, or a heteroatom containing group,

R⁴ and R⁵ are independently an aryl group, a substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, or a multiple ring system,

R⁶ and R⁷ are independently absent, hydrogen, halogen, a heteroatom, a hydrocarbyl group, or a heteroatom containing group; and

wherein the reactor utilized produces greater than 227 kg polymer/hr.

2. The process of claim 1 wherein each X is independently hydrogen, halogen or a hydrocarbyl group.
3. The process of claim 1 wherein R^1 and R^2 are independently a C_1 to C_6 hydrocarbon group.
4. The process of claim 1 wherein R^1 and R^2 are a C_1 to C_{20} alkyl, aryl or arylalkyl group.
5. The process of claim 1 wherein m is 0, -1, -2, or -3 and n is +3, +4 or +5.
6. The process of claim 1 wherein R^3 is absent, hydrogen or methyl.
7. The process of claim 1 wherein R^4 and R^5 are independently a hydrocarbon group having up to 20 carbon atoms.
8. The process of claim 1 wherein R^4 and R^5 are independently an aryl group or an arylalkyl group.
9. The process of claim 1 wherein R^4 and R^5 are independently an arylalkyl group.
10. The process of claim 1 wherein R^4 and R^5 are independently a group represented by the following formula:



wherein

each R⁸ to R¹² are independently hydrogen, or a C₁ to C₂₀ alkyl group, a heteroatom, or a heteroatom containing group having up to 40 carbon atoms, and any two R groups can combine to form a cyclic group or a heterocyclic group.

11. The process of claim 10 wherein
R⁸ is methyl, ethyl, propyl or butyl,
R⁹ is methyl, ethyl, propyl or butyl,
R¹⁰ is methyl, ethyl, propyl or butyl,
R¹¹ is methyl, ethyl, propyl or butyl,
R¹² is methyl, ethyl, propyl or butyl, or any combination thereof.
12. The process of claim 11 wherein R⁹, R¹⁰ and R¹² are methyl and R⁸ and R¹¹ are hydrogen.
13. The process of claim 1 wherein the activator comprises alumoxanes or modified alumoxanes.
14. The process of claim 1 wherein the polymer produced has a molecular weight of 200,000 Daltons or more.
15. The process of claim 1 wherein the transition metal compound, the activator, or both are placed on a support before being placed in the gas or slurry phase.

16. The process of claim 15 wherein the support is a finely divided polyolefin, talc, or an oxide of silica, magnesia, titania, alumina, or silica-alumina.
17. The process of claim 1 wherein the transition metal compound and the activator are combined, then placed on a support, then placed in the gas or slurry phase.
18. The process of claim 1 wherein a metal stearate is combined with the transition metal compound, or the activator, or a support, or any combination.
19. The process of claim 18 wherein the metal stearate is an aluminum stearate.
20. The process of claim 18 wherein the aluminum stearate is aluminum distearate.
21. The process of claim 1 wherein the gas phase reactor temperature is 70° to 110°C.
22. A film formed from a polymer formed from the process of any one of claims 1 to 21.

