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(54) Title: LIGANDS FOR CATALYSTS

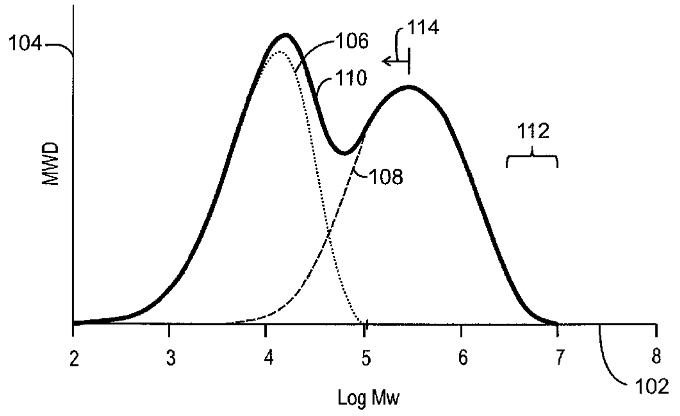

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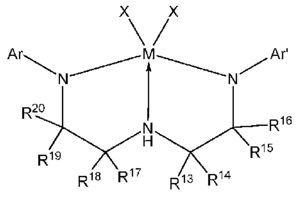
FIG. 1



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WO 2014/149361 A1

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(57) Abstract: Catalyst systems and methods for making and using the same. A catalyst system can include a non-metallocene catalyst having the structure: wherein M is a group 4 element, each of R^{13} -R^{20} are independently a hydrogen or a methyl group, wherein at least one of R^{13}-R^{20} is a methyl group, Ar is an aryl group or a substituted aryl group, Ar' is an aryl group or a substituted aryl group, and each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

LIGANDS FOR CATALYSTS

BACKGROUND

[0001] Ethylene alpha-olefin (polyethylene) copolymers are typically produced in a low pressure reactor, utilizing, for example, solution, slurry, or gas phase polymerization processes. Polymerization takes place in the presence of catalyst systems such as those employing, for example, a Ziegler-Natta catalyst, a chromium based catalyst, a metallocene catalyst, or combinations thereof.

[0002] A number of catalyst compositions containing single site, *e.g.*, metallocene, catalysts have been used to prepare polyethylene copolymers, producing relatively homogeneous copolymers at good polymerization rates. In contrast to traditional Ziegler-Natta catalyst compositions, single site catalyst compositions, such as metallocene catalysts, are catalytic compounds in which each catalyst molecule contains one or only a few polymerization sites. Single site catalysts often produce polyethylene copolymers that have a narrow molecular weight distribution. Although there are single site catalysts that can produce broader molecular weight distributions, these catalysts often show a narrowing of the molecular weight distribution (MWD) as the reaction temperature is increased, for example, to increase production rates. Further, a single site catalyst will often incorporate comonomer among the molecules of the polyethylene copolymer at a relatively uniform rate.

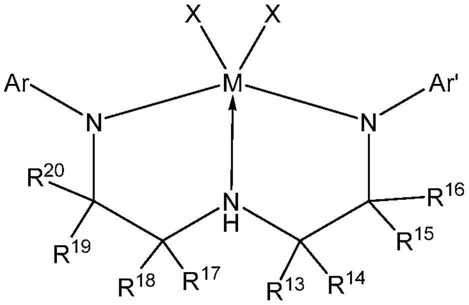
[0003] It is generally known in the art that a polyolefin's MWD will affect certain product attributes. For example, polymers having a broad molecular weight distribution may have improved physical properties, such as stiffness, toughness, processibility, and environmental stress crack resistance (ESCR), among others.

[0004] To achieve these properties, bimodal polymers have become increasingly important in the polyolefins industry, with a variety of manufacturers offering products of this type. Whereas older technology relied on two-reactor systems to generate such material, advances in catalyst design and supporting technology have allowed for the development of single-reactor bimetallic catalyst systems capable of producing bimodal high density polyethylene (HDPE). These systems are attractive both from a cost perspective and ease of use.

[0005] Control of these properties is obtained for the most part by the choice of the catalyst system. Thus, the catalyst design is important for producing polymers that are attractive from a commercial standpoint. Because of the improved physical properties of polymers with the broad molecular distributions needed for commercially desirable products, there exists a need for controlled techniques for forming polyethylene copolymers having a broad molecular weight distribution.

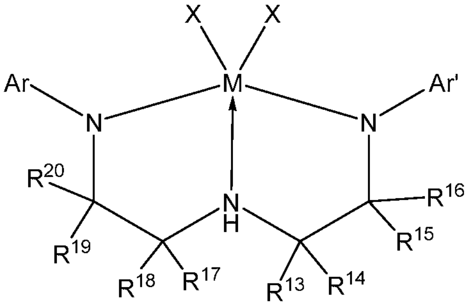
SUMMARY

[0006] An exemplary embodiment described herein provides a catalyst system that includes a non-metallocene catalyst having the structure:



wherein M is a group 4 element, each of R^{13}-R^{20} are independently a hydrogen or a methyl group, wherein at least one of R^{13}-R^{20} is a methyl group, Ar is an aryl group or a substituted aryl group, Ar' is an aryl group or a substituted aryl group, and each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

[0007] Another embodiment provides a method for generating a polymer. The method includes reacting at least ethylene with a catalyst system comprising:



wherein M is a group 4 element, each of R^{13}-R^{20} are independently a hydrogen or a methyl group, wherein at least one of R^{13}-R^{20} is a methyl group, Ar is an aryl group or a substituted aryl group, Ar' is an aryl group or a substituted aryl group, and each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

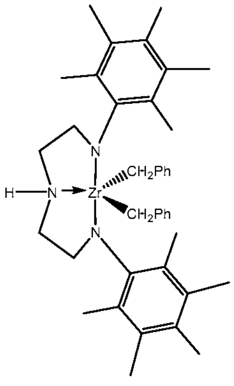
BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Fig. 1 is a plot of molecular weight distributions for a three catalyst system that includes a metallocene and a non-metallocene catalyst, in accordance with embodiments described herein.

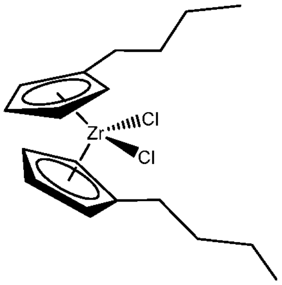
DETAILED DESCRIPTION

[0009] A catalyst support impregnated with multiple catalysts may be used to form polymeric materials with improved balance of properties, such as stiffness, toughness, processibility, and environmental stress crack resistance, can be achieved, for example, by controlling the amounts and types of catalysts present on the support. Appropriate selection of the catalysts and ratios may be used to adjust the combined molecular weight distribution (MWD) of the polymer produced. The MWD can be controlled by combining catalysts with the appropriate weight average molecular weight (Mw) and individual molecular weight distributions. For example, the typical MWD for linear metallocene polymers is 2.5 - 3.5. Blend studies indicate it would be desirable to broaden this distribution by employing mixtures of catalysts that each provide different average molecular weights. The ratio of the Mw for a low molecular weight component and a high molecular weight component would be between 1:1 and 1:10, or about 1:2 and 1:5.

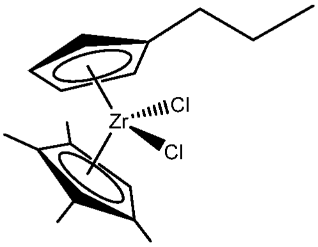
[0010] Fig. 1 is a plot 100 of molecular weight distributions for a two catalyst system that includes a metallocene and a non-metallocene catalyst, in accordance with embodiments described herein. In the plot 100, the x-axis 102 represents the log of the molecular weight, and the y-axis 104 represents the molecular weight distribution, i.e., the amount of each molecular weight that is present. Each of the catalysts can be selected to contribute a certain molecular weight component. For example, a metallocene may then be selected to produce a low molecular weight component 106, wherein, for example, a first metallocene catalyst, shown in structure (II), may be selected for resins to be used for film and blow-molding applications, while another metallocene catalyst, shown in structure (III), for pipe applications. Other metallocenes, as described herein, may be selected for other types of applications. A non-metallocene, such as the catalyst shown in structure (I) may be selected to produce a higher molecular weight component 108. The individual molecular weight components form a single molecular weight distribution (MWD) 110 for the polymer.



(I)



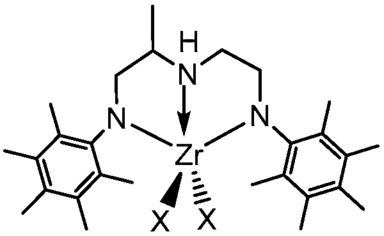
(II)



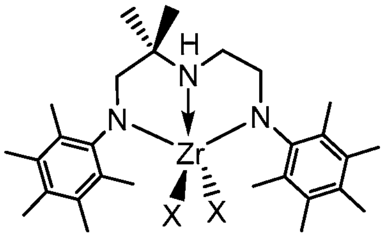
(III)

[0011] Although two catalyst combinations, such as (I) and (II) or (I) and (III), provide attractive properties, some problematic issues still remain. For example, while a high molecular weight portion or tail 112 in the MWD 110, for example, having polymer chains with log molecular weights 102 higher than about 6.5, is thought to impart strength that is important in products such as extruded pipe and blown film, a substantial difference in molecular weight of the two fractions may cause them to phase separate, leading to problems such as melt fracture and bubble instability.

[0012] Thus, it is desirable to maintain the molecular weight separation of higher molecular weight components 108 and low molecular weight components 106 while filling the gap between the high and low molecular weights. In an embodiment described herein, substituents can be introduced along the backbone of the catalyst shown as structure (I), for example, as shown in structures (IV) and (V) in which X is defined below. The substituents may shift the higher molecular weight components 108 to slightly lower molecular weights, as indicated by an arrow 114, filling in the gap between the higher molecular weight components 108, and the lower molecular weight components 106. The substituted non-metallocene catalysts, termed HN5-N catalysts herein, may have productivities equal to, or greater than, previously tested non-metallocene catalysts, a molecular weight distribution 114 that is greater than previously tested non-metallocene catalysts, and a high molecular weight tail 112. The HN5-N catalysts may also retain the high molecular weight tail 112, maintaining the polymer strength associated with the high molecular weight tail 112. Further, this may also allow the polymerization to be run at a lower temperature, which can further increase productivity. The substituted non-metallocenes, HN5-N structures, are not limited to the formulas shown in structures (IV) and (V), but may include any number of other catalyst structures, as discussed herein.



(IV)



(V)

[0013] Generally, the two component mixed catalyst system, comprising the metallocene and the HN5-N provides a polymer with a mix of beneficial properties as a result of the broad molecular weight distribution and the density of each of the low and high molecular weight components 106 and 108. The ability to control the molecular weight distribution and the short-chain branching of each component of the system is vital in determining the processibility and strength of the resultant polymer.

[0014] Employing multiple pre-catalysts that are co-supported on a single support mixed with an activator, such as a silica methylaluminoxane (SMAO), can provide a cost advantage by making the product in one reactor instead of multiple reactors. Further, using a single support also ensures intimate mixing of the polymers and offers improved operability relative to preparing a mixture of polymers of different molecular weight and density independently from multiple catalysts in a single reactor. As used herein, a pre-catalyst is a catalyst compound prior to exposure to monomer and the initiation of the catalyst reaction. The catalysts can be co-supported during a single operation, or may be used in a trim operation, in which additional catalysts are added to catalysts that are supported.

[0015] These factors can be adjusted by controlling the MWD, which, in turn, can be adjusted by changing the relative amount of the combination of pre-catalysts on the support. This may be adjusted during the formation of the pre-catalysts, for example, by supporting the three, or more, catalysts on a single support. In some embodiments, the relative amounts of the pre-catalysts can be adjusted by adding one of the components to a catalyst mixture en-route to the reactor in a process termed “trim.” Trim is discussed in U.S. Patent Nos.: 6,605,675; 6,608,149; 6,689,847; and 6,825,287, herein included by reference. Feedback of polymer property data can be used to control the amount of catalyst addition. Metallocenes (MCNs) are known to trim well with other catalysts.

[0016] Various catalyst systems and components may be used to generate the polymers and molecular weight compositions disclosed. These are discussed in the sections to follow. The first section discusses catalyst compounds that can be used in embodiments, including metallocene and non-metallocene catalysts, among others. The second section discusses generating catalyst slurries that may be used for implementing the techniques described. The third section discusses supports that may be used. The fourth section discusses catalyst activators that may be used. The fifth section discusses the catalyst component solutions that may be used to add additional catalysts in trim systems. Gas phase polymerizations may use static control or continuity agents, which are discussed in the fifth section. A gas-phase polymerization reactor with a trim feed system is discussed in the sixth section. The use of the catalyst composition to control product properties is discussed in a sixth section and an exemplary polymerization process is discussed in the seventh section. Examples of the implementation of the procedures discussed in incorporated into an eighth section.

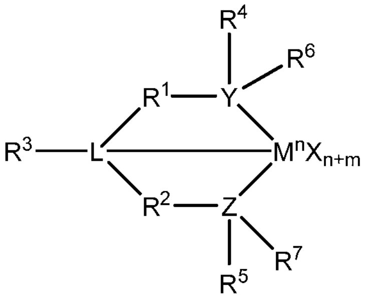
Catalyst Compounds

Group 15 Atom and Non-metallocene Catalyst Compounds

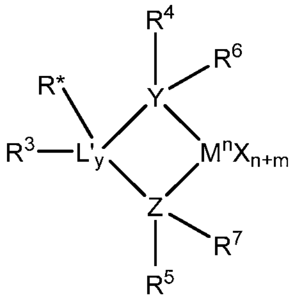
[0017] The catalyst system can include one or more Group 15 metal-containing catalyst compounds, such as shown in structure (I), above. As used herein, these are termed non-metallocene catalyst compounds. The Group 15 metal-containing compound generally includes a Group 3 to 14 metal atom, a Group 3 to 7, or a Group 4 to 6 metal atom. In many embodiments, the Group 15 metal-containing compound includes a Group 4 metal atom bound to at least one 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.

[0018] In one or more embodiments, at least one of the Group 15 atoms is also bound to a Group 15 or 16 atom through another group which may be a C_1 to C_{20} hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, or phosphorus, 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 can optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.

[0019] The Group 15-containing metal compounds can be described more particularly with respect to structures (IV) or (V).



(IV)



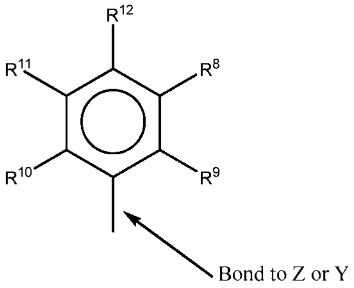
(V)

In structures (IV) and (V), M is a Group 3 to 12 transition metal or a Group 13 or 14 main group metal, a Group 4, 5, or 6 metal. In many embodiments, M is a Group 4 metal, such as zirconium, titanium, or hafnium. Each X is independently a leaving group, such as an anionic leaving group. The leaving group may include a hydrogen, a hydrocarbyl group, an amide, a benzyl, a heteroatom, a halogen, or an alkyl; y is 0 or 1 (when y is 0 group L' is absent). The term 'n' is the oxidation state of M. In various embodiments, n is +3, +4, or +5. In many embodiments, n is +4. The term 'm' represents the formal charge of the YZL or the YZL' ligand, and is 0, -1, -2 or -3 in various embodiments. In many embodiments, m is -2. L is a Group 15 or 16 element, such as nitrogen or oxygen; L' is a Group 15 or 16 element or Group 14 containing group, such as carbon, silicon or germanium. Y is a Group 15 element, such as nitrogen or phosphorus. In many embodiments, Y is nitrogen. Z is a Group 15 element, such as nitrogen or phosphorus. In many embodiments, Z is nitrogen. R^1 and R^2 are, independently, a C_1 to C_{20} hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus. In many embodiments, R^1 and R^2 are a C_2 to C_{20} alkyl, aryl or aralkyl group, such as a linear, branched or cyclic C_2 to C_{20} alkyl group, or a C_2 to C_6 hydrocarbon group, such as the X described with respect to structures (VI) and (VII) above. R^1 and R^2 may also be interconnected to each other. In some embodiments, R^1 and R^2 may be further substituted, for example, if either R^1 or R^2 is an ethyl group, an aryl group, an alkyl group, or other substituents, may be located along the chain. For example, an aryl group may be located on the carbon atom nearest L. R^3 may be absent or may be a hydrocarbon group, a hydrogen, a halogen, a heteroatom containing group.

[0020] In many embodiments, R^3 is absent, for example, if L is an oxygen, or a hydrogen, or a linear, cyclic, or branched alkyl group having 1 to 20 carbon atoms. R^4 and R^5 are independently an alkyl group, an aryl group, 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, often having up to 20 carbon atoms. In many embodiments, R^4 and R^5 have between 3 and 10 carbon atoms, or are a C_1 to C_{20} hydrocarbon group, a C_1 to C_{20} aryl group or a C_1 to C_{20} aralkyl group, or a heteroatom containing group. R^4 and R^5 may be interconnected to each other. R^6 and R^7 are independently absent, hydrogen, an alkyl group, halogen, heteroatom, or a hydrocarbyl group, such as a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms. In many embodiments, R^6 and R^7 are absent. R^* may be absent, or may be a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group.

[0021] By "formal charge of the YZL or YZL' ligand," it is meant the charge of the entire ligand absent the metal and the leaving groups X. By "R^1 and R^2 may also be interconnected" it is meant that R^1 and R^2 may be directly bound to each other or may be bound to each other through other groups. By "R^4 and R^5 may also be interconnected" it is meant that R^4 and R^5 may be directly bound to each other or may be bound to each other through other groups. An alkyl group may be linear, branched alkyl radicals, alkenyl radicals, alkynyl radicals, cycloalkyl radicals, aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbamoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. An aralkyl group is defined to be a substituted aryl group.

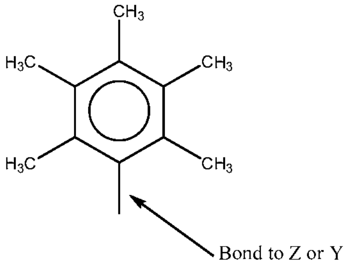
[0022] In one or more embodiments, R^4 and R^5 are independently a group represented by the structure (VI).



(VI)

When R^4 and R^5 are as in structure (VI), R^8 to R^{12} are each independently hydrogen, a C_1 to C_{40} alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms. In many embodiments, R^8 to R^{12} are a C_1 to C_{20} linear or branched alkyl group, such as a methyl, ethyl, propyl, or butyl group. Any two of the R groups may form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic. In one embodiment R^9, R^{10} and R^{12} are independently a methyl, ethyl, propyl, or butyl group (including all isomers). In another embodiment, R^9, R^{10} and R^{12} are methyl groups, and R^8 and R^{11} are hydrogen.

[0023] In one or more embodiments, R^4 and R^5 are both a group represented by structure (VII).

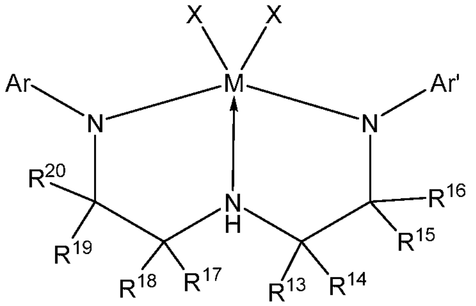


(VII)

When R^4 and R^5 follow structure (VII), M is a Group 4 metal, such as zirconium, titanium, or hafnium. In many embodiments, M is zirconium. Each of L, Y, and Z may be a nitrogen. Each of R^1 and R^2 may be $-CH_2-CH_2-$. R^3 may be hydrogen, and R^6 and R^7 may be absent.

[0024] Representative Group 15-containing metal compounds and preparation thereof can be as discussed and described in U.S. Patent Nos. 5,318,935; 5,889,128; 6,333,389; 6,271,325; and 6,689,847; WO Publications WO 99/01460; WO 98/46651; WO 2009/064404; WO 2009/064452; and WO 2009/064482; and EP 0 893 454; and EP 0 894 005.

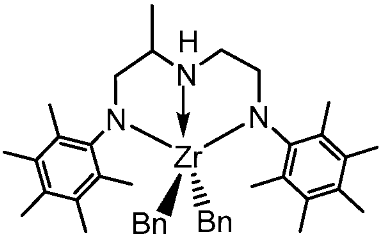
[0025] In some embodiments, the Group 15 metal-containing catalyst compound may have structure (VIII).



(VIII)

In structure (VIII), M may be a group 4 element, such as Ti, Zr, or Hf. Each of R^{13}-R^{20} may independently be a hydrogen or a methyl group. At least one of R^{13}-R^{20} is a methyl group. Ar may be an aryl group or a substituted aryl group, and Ar’ may be an aryl group or a substituted aryl group. Each X may individually be a hydride, a methyl group, an alkyl group, a benzyl group, an amide group, or a halo group, such as a chloro group, a bromo group, a fluoro group, or an iodo group.

[0026] An example of a group 15 metal containing catalyst compound that may be formed in embodiments described herein is shown in structure (IX).



(IX)

In structure (IX), and others, Bn represents a benzyl leaving group, i.e., $-CH_2-C_6H_6$. However, the leaving groups are not limited to benzyl groups, and may be any of the groups defined as 'X' herein.

Metallocene Catalyst Compounds

[0027] Metallocene catalyst compounds are generally described 1 & 2 METALLOCENE-BASED POLYOLEFINS (John Scheirs & W. Kaminsky eds., John Wiley & Sons, Ltd. 2000); G. G. Hlatky in 181 COORDINATION CHEM. REV. 243-296 (1999); and, in particular, for use in the synthesis of polyethylene in 1 METALLOCENE-BASED POLYOLEFINS 261-377 (2000). The metallocene catalyst compounds can include "half sandwich" and/or "full sandwich" compounds having one or more Cp ligands (cyclopentadienyl and ligands isolobal to cyclopentadienyl) bound to at least one Group 3 to Group 12 metal atom, and one or more leaving group(s) bound to the at least one metal atom. As used herein, all reference to the Periodic Table of the Elements and groups thereof is to the NEW NOTATION published in HAWLEY'S CONDENSED CHEMICAL DICTIONARY, Thirteenth Edition, John Wiley & Sons, Inc., (1997) (reproduced there with permission from IUPAC), unless reference is made to the Previous IUPAC form noted with Roman numerals (also appearing in the same), or unless otherwise noted.

[0028] The Cp ligands are one or more rings or ring system(s), at least a portion of which includes π-bonded systems, such as cycloalkadienyl ligands and heterocyclic analogues. The ring(s) or ring system(s) typically include atoms selected from the group consisting of Groups 13 to 16 atoms, and, in a particular exemplary embodiment, the atoms that make up the Cp ligands are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron, aluminum, and combinations thereof, where carbon makes up at least 50 % of the ring members. In a more particular exemplary embodiment, the Cp ligand(s) are selected from the group consisting of substituted and unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, non-limiting examples of which include cyclopentadienyl, indenyl, fluorenyl and other structures. Further non-limiting examples of such ligands include cyclopentadienyl, cyclopentaphenanthreneyl, indenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7-H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated versions thereof (*e.g.*, 4,5,6,7-tetrahydroindenyl, or "H_4 Ind"), substituted versions thereof (as discussed and described in more detail below), and heterocyclic versions thereof.

[0029] The metal atom "M" of the metallocene catalyst compound can be selected from the group consisting of Groups 3 through 12 atoms and lanthanide Group atoms in one exemplary embodiment; and selected from the group consisting of Groups 3 through 10 atoms in a more particular exemplary embodiment; and selected from the group consisting of Sc, Ti, Zr, Hf, V, Nb, Ta, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni in yet a more particular exemplary embodiment; and selected from the group consisting of Groups 4, 5, and 6 atoms in yet a more particular exemplary embodiment; and Ti, Zr, Hf atoms in yet a more particular exemplary embodiment; and Zr in yet a more particular exemplary embodiment. The oxidation state of the metal atom "M" can range from 0 to +7 in one exemplary embodiment; and in a more particular exemplary embodiment, can be +1, +2, +3, +4, or +5; and in yet a more particular exemplary embodiment can be +2, +3, or +4. The groups bound to the metal atom "M" are such that the compounds described below in the formulas and structures are electrically neutral, unless otherwise indicated. The Cp ligand forms at least one chemical bond with the metal atom M to form the "metallocene catalyst compound." The Cp ligands are distinct from the leaving groups bound to the catalyst compound in that they are not highly susceptible to substitution/abstraction reactions.

[0030] The one or more metallocene catalyst compounds can be represented by structure (X).

$$Cp^ACp^BMX_n \qquad (X)$$

In structure (X), M is as described above; each X is chemically bonded to M; each Cp group is chemically bonded to M; and n is 0 or an integer from 1 to 4, and either 1 or 2 in a particular exemplary embodiment.

[0031] The ligands represented by Cp^A and Cp^B in structure (X) can be the same or different cyclopentadienyl ligands or ligands isolobal to cyclopentadienyl, either or both of which can contain heteroatoms and either or both of which can be substituted by a group R. In at least one specific embodiment, Cp^A and Cp^B are independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, and substituted derivatives of each.

[0032] Independently, each Cp^A and Cp^B of structure (X) can be unsubstituted or substituted with any one or combination of substituent groups R. Non-limiting examples of substituent groups R as used in structure (X) as well as ring substituents in structures discussed and described below, include groups selected from the group consisting of hydrogen radicals, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbamoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, and combinations thereof. More particular non-limiting examples of alkyl substituents R associated with structures (X) through (XV) include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl, phenyl, methylphenyl, and tert-butylphenyl groups and the like, including all their isomers, for example, tertiary-butyl, isopropyl, and the like. Other possible radicals include substituted alkyls and aryls such as, for example, fluoromethyl, fluroethyl, difluroethyl, iodopropyl, bromohexyl, chlorobenzyl, hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl, and the like, and halocarbyl-substituted organometalloid radicals, including tris(trifluoromethyl)silyl, methylbis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron, for example; and disubstituted Group 15 radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, as well as Group 16 radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Other substituent groups R include, but are not limited to, olefins such as olefinically unsaturated substituents including vinyl-terminated ligands such as, for example, 3-butenyl, 2-propenyl, 5-hexenyl, and the like. In one exemplary embodiment, at least two R groups (two adjacent R groups in a particular exemplary embodiment) are joined to form a ring structure having from 3 to 30 atoms selected from the group consisting of carbon, nitrogen, oxygen, phosphorous, silicon, germanium, aluminum, boron, and combinations thereof. Also, a substituent group R such as 1-butanyl can form a bonding association to the element M.

[0033] Each leaving group, or X, in the structure (X) above and for the structures in (XI) through (XIII) below is independently selected from the group consisting of: halogen ions, hydrides, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12}

alkoxys, C_6 to C_{16} aryloxys, C_7 to C_8 alkylaryloxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, and C_1 to C_{12} heteroatom-containing hydrocarbons and substituted derivatives thereof, in a more particular exemplary embodiment; hydride, halogen ions, C_1 to C_6 alkyls, C_2 to C_6 alkenyls, C_7 to C_{18} alkylaryls, C_1 to C_6 alkoxys, C_6 to C_{14} aryloxys, C_7 to C_{16} alkylaryloxys, C_1 to C_6 alkylcarboxylates, C_1 to C_6 fluorinated alkylcarboxylates, C_6 to C_{12} arylcarboxylates, C_7 to C_{18} alkylarylcarboxylates, C_1 to C_6 fluoroalkyls, C_2 to C_6 fluoroalkenyls, and C_7 to C_{18} fluoroalkylaryls in yet a more particular exemplary embodiment; hydride, chloride, fluoride, methyl, phenyl, phenoxy, benzoxy, tosyl, fluoromethyls and fluorophenyls, in yet a more particular exemplary embodiment; C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, substituted C_1 to C_{12} alkyls, substituted C_6 to C_{12} aryls, substituted C_7 to C_{20} alkylaryls and C_1 to C_{12} heteroatom-containing alkyls, C_1 to C_{12} heteroatom-containing aryls, and C_1 to C_{12} heteroatom-containing alkylaryls, in yet a more particular exemplary embodiment; chloride, fluoride, C_1 to C_6 alkyls, C_2 to C_6 alkenyls, C_7 to C_{18} alkylaryls, halogenated C_1 to C_6 alkyls, halogenated C_2 to C_6 alkenyls, and halogenated C_7 to C_{18} alkylaryls, in yet a more particular exemplary embodiment; chloride, methyl, ethyl, propyl, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, fluoromethyls (mono-, di- and trifluoromethyls) and fluorophenyls (mono-, di-, tri-, tetra- and pentafluorophenyls), in yet a more particular exemplary embodiment.

[0034] Other non-limiting examples of X groups include amines, phosphines, ethers, carboxylates, dienes, hydrocarbon radicals having from 1 to 20 carbon atoms, fluorinated hydrocarbon radicals (*e.g.*, $-C_6F_5$ (pentafluorophenyl)), fluorinated alkylcarboxylates (*e.g.*, $CF_3C(O)O^-$), hydrides, halogen ions and combinations thereof. Other examples of X ligands include alkyl groups such as cyclobutyl, cyclohexyl, methyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methylidene, methyoxy, ethyoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like. In one exemplary embodiment, two or more X's form a part of a fused ring or ring system. In at least one specific embodiment, X can be a leaving group selected from the group consisting of chloride ions, bromide ions, C_1 to C_{10} alkyls, and C_2 to C_{12} alkenyls, carboxylates, acetylacetonates, and alkoxides.

[0035] The metallocene catalyst compound includes those of structure (X) where Cp^A and Cp^B are bridged to each other by at least one bridging group, (A), such that the structure is represented by structure (XI).

$$Cp^A(A)Cp^BMX_n \qquad \text{(XI)}$$

[0036] The bridged compounds represented by structure (XI) are known as "bridged metallocenes." The elements Cp^A, Cp^B, M, X and n in structure (XI) are as defined above for structure (X); where each Cp ligand is chemically bonded to M, and (A) is chemically bonded to each Cp. The bridging group (A) can include divalent hydrocarbon groups containing at least one Group 13 to 16 atom, such as, but not limited to, at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium, tin atom, and combinations thereof; where the heteroatom can also be C_1 to C_{12} alkyl or aryl substituted to satisfy neutral valency. In at least one specific embodiment, the bridging group (A) can also include substituent groups R as defined above (for structure (X)) including halogen radicals and iron. In at least one specific embodiment, the bridging group (A) can be represented by C_1 to C_6 alkylenes, substituted C_1 to C_6 alkylenes, oxygen, sulfur, $R'_2C=$, $R'_2Si=$, $=Si(R')_2Si(R'_2)=$, $R'_2Ge=$, and $R'P=$, where "=" represents two chemical bonds, R′ is independently selected from the group consisting of hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 atoms, substituted Group 16 atoms, and halogen radical; and where two or more R′ can be joined to form a ring or ring system. In at least one specific embodiment, the bridged metallocene catalyst compound of structure (XI) includes two or more bridging groups (A). In one or more embodiments, (A) can be a divalent bridging group bound to both Cp^A and Cp^B selected from the group consisting of divalent C_1 to C_{20} hydrocarbyls and C_1 to C_{20} heteroatom containing hydrocarbonyls, where the heteroatom containing hydrocarbonyls include from one to three heteroatoms.

[0037] The bridging group (A) can include methylene, ethylene, ethylidene, propylidene, isopropylidene, diphenylmethylene, 1,2-dimethylethylene, 1,2-diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylsilyl, diethylsilyl, methyl-ethylsilyl, trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di(n-butyl)silyl, di(n-propyl)silyl, di(i-propyl)silyl, di(n-hexyl)silyl, dicyclohexylsilyl, diphenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di(t-butylphenyl)silyl, di(p-tolyl)silyl and the corresponding moieties where the Si atom is replaced by a Ge or a C atom; as well as dimethylsilyl, diethylsilyl, dimethylgermyl and diethylgermyl.

[0038] The bridging group (A) can also be cyclic, having, for example, 4 to 10 ring members; in a more particular exemplary embodiment, bridging group (A) can have 5 to 7 ring members. The ring members can be selected from the elements mentioned above, and, in a particular embodiment, can be selected from one or more of B, C, Si, Ge, N, and O.

Non-limiting examples of ring structures which can be present as, or as part of, the bridging moiety are cyclobutylidene, cyclopentylidene, cyclohexylidene, cycloheptylidene, cyclooctylidene and the corresponding rings where one or two carbon atoms are replaced by at least one of Si, Ge, N and O. In one or more embodiments, one or two carbon atoms can be replaced by at least one of Si and Ge. The bonding arrangement between the ring and the Cp groups can be cis-, trans-, or a combination thereof.

[0039] The cyclic bridging groups (A) can be saturated or unsaturated and/or can carry one or more substituents and/or can be fused to one or more other ring structures. If present, the one or more substituents can be, in at least one specific embodiment, selected from the group consisting of hydrocarbyl (*e.g.*, alkyl, such as methyl) and halogen (*e.g.*, F, Cl). The one or more Cp groups to which the above cyclic bridging moieties can optionally be fused can be saturated or unsaturated, and are selected from the group consisting of those having 4 to 10, more particularly 5, 6, or 7 ring members (selected from the group consisting of C, N, O, and S in a particular exemplary embodiment) such as, for example, cyclopentyl, cyclohexyl and phenyl. Moreover, these ring structures can themselves be fused such as, for example, in the case of a naphthyl group. Moreover, these (optionally fused) ring structures can carry one or more substituents. Illustrative, non-limiting examples of these substituents are hydrocarbyl (particularly alkyl) groups and halogen atoms. The ligands Cp^A and Cp^B of structures (X) and (XI) can be different from each other. The ligands Cp^A and Cp^B of structures (X) and (XI) can be the same.

[0040] The metallocene catalyst compound can include bridged mono-ligand metallocene compounds (*e.g.*, mono-cyclopentadienyl catalyst components). Exemplary metallocene catalyst compounds are further described in U.S. Patent No. 6,943,134.

[0041] It is contemplated that the metallocene catalyst components discussed and described above include their structural or optical or enantiomeric isomers (racemic mixture), and, in one exemplary embodiment, can be a pure enantiomer. As used herein, a single, bridged, asymmetrically substituted metallocene catalyst compound having a racemic and/or meso isomer does not, itself, constitute at least two different bridged, metallocene catalyst components.

[0042] The amount of the transition metal component of the one or more metallocene catalyst compounds in the catalyst system can range from a low of about 0.2 wt. %, about 3 wt. %, about 0.5 wt. %, or about 0.7 wt. % to a high of about 1 wt. %, about 2 wt. %, about 2.5 wt. %, about 3 wt. %, about 3.5 wt. %, or about 4 wt. %, based on the total weight of the catalyst system.

[0043] The metallocene catalyst compounds can include any combination of any embodiment discussed and described herein. For example, the metallocene catalyst compound can include, but is not limited to, bis(n-butylcyclopentadienyl)$Zr(CH_3)_2$, bis(n-butylcyclopentadienyl)$ZrCl_2$, bis(n-butylcyclopentadienyl)$ZrCl_2$, (n-propylcyclopentadienyl, tetramethylcyclopentadienyl)$ZrCl_2$, [(pentamethylbenzyl$N(CH_2CH(CH_2))$(pentamethylbenzyl$N(CH_2CH_2)NH]ZrBn_2$, [(pentamethylbenzyl$N(CH_2C(CH_2)_2)$(pentamethylbenzyl$N(CH_2CH_2)NH]ZrBn_2$, or any combinations thereof.

[0044] In addition to the metallocene catalyst compounds discussed and described above, other suitable metallocene catalyst compounds can include, but are not limited to, metallocenes discussed and described in U.S. Patent Nos.: 7,741,417; 7,179,876; 7,169,864; 7,157,531; 7,129,302; 6,995,109; 6,958,306; 6,884,748; 6,689,847; and WO Publications: WO 1997/022635; WO 1998/046651; WO 2000/069922; WO 2001/030860; WO 2001/030861; WO 2002/046246; WO 2002/050088; WO 2004/026921; and WO 06/019494.

[0045] Although the catalyst compounds may be written or shown with methyl-, chloro-, or phenyl- leaving groups attached to the central metal, it can be understood that these groups may be different without changing the catalyst involved. For example, each of these ligands may independently be a phenyl group (Ph), a methyl group (Me), a chloro group (Cl), a fluoro group (F), or any number of other groups, including organic groups, or heteroatom groups. Further, these ligands will change during the reaction, as a pre-catalyst is converted to the active catalyst for the reaction.

Catalyst forms

[0046] Any number of combinations of catalyst components may be used in embodiments. For example, the catalyst mentioned above may be used alone or in combinations with other catalysts, such as metallocenes. The catalysts can be formed together to make a dry catalyst powder that is directly added to the reactor, or may be used in a slurry formed from the catalyst, an activator, and a support.

[0047] A catalyst slurry may be used in a catalyst trim system wherein a second catalyst is added to the slurry to broaden the molecular weight distribution of the resulting polymer. The slurry may include one or more activators and supports, and one more catalyst compounds. For example, the slurry may include two or more activators (such as alumoxane and a modified alumoxane) and a catalyst compound, or the slurry may include a supported activator and more than one catalyst compounds. In one embodiment, the slurry includes a support, an activator, and two catalyst compounds. In another embodiment the slurry includes a support, an activator and two different catalyst compounds, which may be added to the slurry separately or in combination. The slurry, containing silica and alumoxane, may be contacted with a catalyst compound, allowed to react, and thereafter the slurry is contacted with another catalyst compound, for example, in a trim system.

[0048] The molar ratio of metal in the activator to metal in the catalyst compound in the slurry may be 1000:1 to 0.5:1, 300:1 to 1:1, or 150:1 to 1:1. The slurry can include a support material which may be any inert particulate carrier material known in the art, including, but not limited to, silica, fumed silica, alumina, clay, talc or other support materials such as disclosed above. In one embodiment, the slurry contains silica and an activator, such as methyl aluminoxane ("MAO"), modified methyl aluminoxane ("MMAO"), as discussed further below.

[0049] One or more diluents or carriers can be used to facilitate the combination of any two or more components of the catalyst system in the slurry or in the trim catalyst solution. For example, the single site catalyst compound and the activator can be combined together in the presence of toluene or another non-reactive hydrocarbon or hydrocarbon mixture to provide the catalyst mixture. In addition to toluene, other suitable diluents can include, but are not limited to, ethylbenzene, xylene, pentane, hexane, heptane, octane, other hydrocarbons, or any combination thereof. The support, either dry or mixed with toluene can then be added to the catalyst mixture or the catalyst/activator mixture can be added to the support.

[0050] The catalyst is not limited to a slurry arrangement, as a mixed catalyst system may be made on a support and dried. The dried catalyst system can then be fed to the reactor through a dry feed system.

Support

[0051] As used herein, the terms "support" and "carrier" are used interchangeably and refer to any support material, including a porous support material, such as talc, inorganic oxides, and inorganic chlorides. The one or more catalyst compounds can be supported on the same or separate supports together with the activator, or the activator can be used in an unsupported form, or can be deposited on a support different from the single site catalyst compounds, or any combination thereof. This may be accomplished by any technique commonly used in the art. There are various other methods in the art for supporting a catalyst compound. For example, the catalyst compound can contain a polymer bound ligand as described in, for example, U.S. Patent Nos. 5,473,202, and 5,770,755. The catalyst compounds of the slurry can be spray dried as described in, for example, U.S. Patent No. 5,648,310. The support used with the catalyst compound can be functionalized, as described in EP 0 802 203, or at least one substituent or leaving group is selected as described in U.S. Patent No. 5,688,880.

[0052] The support can be or include one or more inorganic oxides, for example, of Group 2, 3, 4, 5, 13, or 14 elements. The inorganic oxide can include, but is not limited to silica, alumina, titania, zirconia, boria, zinc oxide, magnesia, or any combination thereof. Illustrative combinations of inorganic oxides can include, but are not limited to, alumina-silica, silica-titania, alumina-silica-titania, alumina-zirconia, alumina-titania, and the like. The support can be or include silica, alumina, or a combination thereof. In one embodiment described herein, the support is silica.

[0053] Suitable commercially available silica supports can include, but are not limited to, ES757, ES70, and ES70W available from PQ Corporation. Suitable commercially available silica-alumina supports can include, but are not limited to, SIRAL® 1, SIRAL® 5, SIRAL® 10, SIRAL® 20, SIRAL® 28M, SIRAL® 30, and SIRAL® 40, available from SASOL®. Catalyst supports comprising silica gels with activators, such as methylaluminoxanes (MAOs), can be used in trim systems, since these supports may function better for cosupporting solution carried catalysts.

[0054] Suitable catalyst supports are discussed and described in Hlatky, Chem. Rev. (2000), 100, 1347 1376 and Fink et al., Chem. Rev. (2000), 100, 1377 1390, U.S. Patent Nos.: 4,701,432, 4,808,561, 4,912,075, 4,925,821, 4,937,217, 5,008,228, 5,238,892, 5,240,894, 5,332,706, 5,346,925, 5,422,325, 5,466,649, 5,466,766, 5,468,702, 5,529,965, 5,554,704, 5,629,253, 5,639,835, 5,625,015, 5,643,847, 5,665,665, 5,698,487, 5,714,424, 5,723,400, 5,723,402, 5,731,261, 5,759,940, 5,767,032 and 5,770,664, and WO 95/32995, WO 95/14044, WO 96/06187, and WO 97/02297.

Activator

[0055] As used herein, the term “activator” may refer to any compound or combination of compounds, supported, or unsupported, which can activate a catalyst compound or component, such as by creating a cationic species of the catalyst component. For example, this can include the abstraction of at least one leaving group (the “X” group in the single site catalyst compounds described herein) from the metal center of the single site catalyst compound/component. The activator may also be referred to as a “co-catalyst.”

[0056] For example, the activator can include a Lewis acid or a non-coordinating ionic activator or ionizing activator, or any other compound including Lewis bases, aluminum alkyls, and/or conventional-type co-catalysts. Illustrative activators can include, but are not limited to, methylaluminoxane ("MAO") and modified methylaluminoxane ("MMAO"), and/or ionizing compounds, neutral or ionic, such as tri (n-butyl)ammonium tetrakis(pentafluorophenyl)boron, dimethylanilinium tetrakis(pentafluorophenyl) boron a trisperfluorophenyl boron metalloid precursor, a trisperfluoronaphthyl boron metalloid precursor, or any combinations thereof. Further, activators may include titanium halides, titanium alkoxides, and organo-titanium compounds, such as titanium (IV) chloride, titanium (IV) tetra(isopropoxide), tetraethyl titanate, or any number of other suitable titanium compounds.

[0057] Aluminoxanes can be described as oligomeric aluminum compounds having -Al(R)-O- subunits, where R is an alkyl group. Examples of aluminoxanes include, but are not limited to, methylaluminoxane ("MAO"), modified methylaluminoxane ("MMAO"), ethylaluminoxane, isobutylaluminoxane, or a combination thereof. Aluminoxanes can be produced by the hydrolysis of the respective trialkylaluminum compound. MMAO can be produced by the hydrolysis of trimethylaluminum and a higher trialkylaluminum, such as triisobutylaluminum. MMAOs are generally more soluble in aliphatic solvents and more stable during storage. There are a variety of methods for preparing aluminoxane and modified aluminoxanes, non-limiting examples can be as discussed and described in U.S. Patent Nos. 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; 5,731,451; 5,744,656; 5,847,177; 5,854,166; 5,856,256; and 5,939,346; and EP 0 561 476; EP 0 279 586; EP 0 594-218; and EP 0 586 665; and WO Publications WO 94/10180 and WO 99/15534.

[0058] As noted above, one or more organo-aluminum compounds such as one or more alkylaluminum compounds can be used in conjunction with the aluminoxanes. For example, alkylaluminum species that may be used are diethylaluminum ethoxide, diethylaluminum chloride, and/or diisobutylaluminum hydride. Examples of trialkylaluminum compounds include, but are not limited to, trimethylaluminum, triethylaluminum ("TEAL"), triisobutylaluminum ("TiBAl"), tri-n-hexylaluminum, tri-n-octylaluminum, tripropylaluminum, tributylaluminum, and the like.

Continuity Additive/Static Control Agent

[0059] In gas-phase polyethylene production processes, it may be desirable to use one or more static control agents to aid in regulating static levels in the reactor. As used herein, a static control agent is a chemical composition which, when introduced into a fluidized bed reactor, may influence or drive the static charge (negatively, positively, or to zero) in the fluidized bed. The specific static control agent used may depend upon the nature of the static charge, and the choice of static control agent may vary dependent upon the polymer being produced and the single site catalyst compounds being used. For example, the use of static control agents is disclosed in European Patent No. 0229368 and U.S. Patent Nos. 4,803,251; 4,555,370; and 5,283,278, and references cited therein.

[0060] Control agents such as aluminum stearate may be employed. The static control agent used may be selected for its ability to receive the static charge in the fluidized bed without adversely affecting productivity. Other suitable static control agents may also include aluminum distearate, ethoxlated amines, and anti-static compositions such as those provided by Innospec Inc. under the trade name OCTASTAT. For example, OCTASTAT 2000 is a mixture of a polysulfone copolymer, a polymeric polyamine, and oil-soluble sulfonic acid.

[0061] Any of the aforementioned control agents, as well as those described in, for example, WO 2001/044322, listed under the heading Carboxylate Metal Salt and including those chemicals and compositions listed as antistatic agents may be employed either alone or in combination as a control agent. For example, the carboxylate metal salt may be combined with an amine containing control agent (*e.g.*, a carboxylate metal salt with any family member belonging to the KEMAMINE® (available from Crompton Corporation) or ATMER® (available from ICI Americas Inc.) family of products).

[0062] Other useful continuity additives include ethyleneimine additives useful in embodiments disclosed herein may include polyethyleneimines having the following general formula:

$$-(CH_2-CH_2-NH)_n-,$$

in which n may be from about 10 to about 10,000. The polyethyleneimines may be linear, branched, or hyperbranched (*e.g.*, forming dendritic or arborescent polymer structures). They can be a homopolymer or copolymer of ethyleneimine or mixtures thereof (referred to as polyethyleneimine(s) hereafter). Although linear polymers represented by the chemical formula --[CH_2-CH_2-NH]-- may be used as the polyethyleneimine, materials having primary, secondary, and tertiary branches can also be used. Commercial polyethyleneimine can be a compound having branches of the ethyleneimine polymer.

[0063] Suitable polyethyleneimines are commercially available from BASF Corporation under the trade name Lupasol. These compounds can be prepared as a wide range of molecular weights and product activities. Examples of commercial polyethyleneimines sold by BASF suitable for use in the present invention include, but are not limited to, Lupasol FG and Lupasol WF.

[0064] Another useful continuity additive can include a mixture of aluminum distearate and an ethoxylated amine-type compound, *e.g.*, IRGASTAT AS-990, available from Huntsman (formerly Ciba Specialty Chemicals). The mixture of aluminum distearate and ethoxylated amine type compound can be slurried in mineral oil *e.g.*, Hydrobrite 380. For example, the mixture of aluminum distearate and an ethoxylated amine type compound can be slurried in mineral oil to have total slurry concentration of ranging from about 5 wt. % to about 50 wt. % or about 10 wt. % to about 40 wt. %, or about 15 wt. % to about 30 wt. %. Other useful static control agents and additives are disclosed in U.S. Patent Application Publication No. 2008/0045663.

[0065] The continuity additive(s) or static control agent(s) may be added to the reactor in an amount ranging from 0.05 to 200 ppm, based on the weight of all feeds to the reactor, excluding recycle. In some embodiments, the continuity additive may be added in an amount ranging from 2 to 100 ppm, or in an amount ranging from 4 to 50 ppm.

Polymerization Process

[0066] The catalyst system can be used to polymerize one or more olefins, such as ethylene, to provide one or more polymer products therefrom. Any suitable polymerization process can be used, including, but not limited to, high pressure, solution, slurry, and/or gas phase polymerization processes.

[0067] As used herein, the terms “polyethylene” and “polyethylene copolymer” refer to a polymer having at least 50 wt. % ethylene-derived units. In various embodiments, the polyethylene can have at least 70 wt. % ethylene-derived units, at least 80 wt. % ethylene-derived units, at least 90 wt. % ethylene-derived units, or at least 95 wt. % ethylene-derived units. The polyethylene polymers described herein are generally copolymer, but may also include terpolymers, having one or more other monomeric units. As described herein, a polyethylene can include, for example, at least one or more other olefins or comonomers. Suitable comonomers can contain 3 to 16 carbon atoms, from 3 to 12 carbon atoms, from 4 to 10 carbon atoms, and from 4 to 8 carbon atoms. Examples of comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methylpent-1-ene, 1-decene, 1-dodecene, 1-hexadecene, and the like.

[0068] A gas phase polymerization may be conducted in a fluidized bed reactor which can include a reaction zone and a velocity reduction zone. The reaction zone can include a bed that includes growing polymer particles, formed polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of the gaseous monomer and diluent to remove heat of polymerization through the reaction zone. Optionally, some of the re-circulated gases can be cooled and compressed to form liquids that increase the heat removal capacity of the circulating gas stream when readmitted to the reaction zone. A suitable rate of gas flow can be readily determined by experimentation. Make-up of gaseous monomer to the circulating gas stream can be at a rate equal to the rate at which particulate polymer product and monomer associated therewith is withdrawn from the reactor and the composition of the gas passing through the reactor can be adjusted to maintain an essentially steady state gaseous composition within the reaction zone. The gas leaving the reaction zone can be passed to the velocity reduction zone where entrained particles are removed, for example, by slowing and falling back to the reaction zone. If desired, finer entrained particles and dust can be removed in a separation system, such as a cyclone and/or fines filter. The gas can be passed through a heat exchanger where at least a portion of the heat of polymerization can be removed. The gas can then be compressed in a compressor and returned to the reaction zone. Additional reactor details and means for operating the reactor are described in, for example, U.S. Patent Nos. 3,709,853; 4,003,712; 4,011,382; 4,302,566; 4,543,399; 4,882,400; 5,352,749; and 5,541,270; EP 0802202; and Belgian Patent No. 839,380.

[0069] The reactor temperature of the fluid bed process can be greater than about 30°C, about 40°C, about 50°C, about 90°C, about 100°C, about 110°C, about 120°C, about 150°C, or higher. In general, the reactor temperature is operated at the highest feasible temperature taking into account the sintering temperature of the polymer product within the reactor. Thus, the upper temperature limit in one embodiment is the melting temperature of the polyethylene copolymer produced in the reactor. However, higher temperatures may result in narrower MWDs, which can be improved by the addition of structure (IV), or other co-catalysts, as described herein.

[0070] Hydrogen gas can be used in olefin polymerization to control the final properties of the polyolefin, such as described in the “Polypropylene Handbook,” at pages 76-78 (Hanser Publishers, 1996). Using certain catalyst systems, increasing concentrations (partial pressures) of hydrogen can increase the flow index (FI), or melt index (MI) of the polyethylene copolymer generated. The flow index can thus be influenced by the hydrogen concentration. The amount of hydrogen in the polymerization can be expressed as a mole ratio relative to the total polymerizable monomer, for example, ethylene, or a blend of ethylene and hexene or propylene.

[0071] The amount of hydrogen used in the polymerization process can be an amount necessary to achieve the desired flow index of the final polyolefin polymer. For example, the mole ratio of hydrogen to total monomer (H_2:monomer) can be greater than about 0.0001, greater than about 0.0005, or greater than about 0.001. Further, the mole ratio of hydrogen to total monomer (H_2:monomer) can be less than about 10, less than about 5, less than about 3, and less than about 0.10. A desirable range for the mole ratio of hydrogen to monomer can include any combination of any upper mole ratio limit with any lower mole ratio limit described herein. Expressed another way, the amount of hydrogen in the reactor at any time can range to up to about 5,000 ppm, up to about 4,000 ppm in another embodiment, up to about 3,000 ppm, or between about 50 ppm and 5,000 ppm, or between about 50 ppm and 2,000 ppm in another embodiment. The amount of hydrogen in the reactor can range from a low of about 1 ppm, about 50 ppm, or about 100 ppm to a high of about 400 ppm, about 800 ppm, about 1,000 ppm, about 1,500 ppm, or about 2,000 ppm, based on weight. Further, the ratio of hydrogen to total monomer (H_2:monomer) can be about 0.00001:1 to about 2:1, about 0.005:1 to about 1.5:1, or about 0.0001:1 to about 1:1. The one or more reactor pressures in a gas phase process (either single stage or two or more stages) can vary from 690 kPa (100 psig) to 3,448 kPa (500 psig), in the range from 1,379 kPa (200 psig) to 2,759 kPa (400 psig), or in the range from 1,724 kPa (250 psig) to 2,414 kPa (350 psig).

[0072] The gas phase reactor can be capable of producing from about 10 kg of polymer per hour (25 lbs/hr) to about 90,900 kg/hr (200,000 lbs/hr), or greater, and greater than about 455 kg/hr (1,000 lbs/hr), greater than about 4,540 kg/hr (10,000 lbs/hr), greater than about 11,300 kg/hr (25,000 lbs/hr), greater than about 15,900 kg/hr (35,000 lbs/hr), and greater than about 22,700 kg/hr (50,000 lbs/hr), and from about 29,000 kg/hr (65,000 lbs/hr) to about 45,500 kg/hr (100,000 lbs/hr).

[0073] A slurry polymerization process may be used to prepare polymer in embodiments. A slurry polymerization process generally uses pressures in the range of from about 101 kPa (1 atmosphere) to about 5,070 kPa (50 atmospheres) or greater, and temperatures in the range of from about 0°C to about 120°C, and more particularly from about 30°C to about

100°C. In a slurry polymerization, a suspension of solid, particulate polymer can be formed in a liquid polymerization diluent medium to which ethylene, comonomers, and hydrogen along with catalyst can be added. The suspension including diluent can be 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 can be an alkane having from 3 to 7 carbon atoms, such as, for example, 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 should be operated above the reaction diluent critical temperature and pressure. A hexane, isopentane, or isobutane medium can be employed. The slurry can be circulated in a continuous loop system.

[0074] The product polyethylene can have a melt index ratio (MIR or I_{21}/I_2) ranging from about 10 to less than about 300, or, in many embodiments, from about 15 to about 150. Flow index (FI, HLMI, or I_{21} can be measured in accordance with ASTM D1238 (190°C, 21.6 kg). The melt index (MI, I_2) can be measured in accordance with ASTM D1238 (at 190°C, 2.16 kg weight).

[0075] Density can be determined in accordance with ASTM D-792. Density is expressed as grams per cubic centimeter (g/cm^3) unless otherwise noted. The polyethylene can have a density ranging from a low of about 0.89 g/cm^3, about 0.90 g/cm^3, or about 0.91 g/cm^3 to a high of about 0.95 g/cm^3, about 0.96 g/cm^3, or about 0.97 g/cm^3. The polyethylene can have a bulk density, measured in accordance with ASTM D1895 method B, of from about 0.25 g/cm^3 to about 0.5 g/cm^3. For example, the bulk density of the polyethylene can range from a low of about 0.30 g/cm^3, about 0.32 g/cm^3, or about 0.33 g/cm^3 to a high of about 0.40 g/cm^3, about 0.44 g/cm^3, or about 0.48 g/cm^3.

[0076] The polyethylene can be suitable for such articles as films, fibers, nonwoven and/or woven fabrics, extruded articles, and/or molded articles. Examples of films include blown or cast films formed in single layer extrusion, coextrusion, or lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications, agricultural films and sheets. Examples of fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, hygiene products, medical garments, geotextiles, etc. Examples of extruded articles include tubing, medical tubing, wire and cable coatings, pipe, geomembranes, and pond liners. Examples of molded articles include single and multi-layered constructions by injection molding or rotation molding or blow molding processes in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

Examples

General

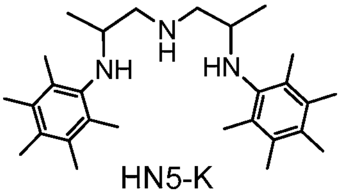
[0077] All reactions were carried out under a purified nitrogen atmosphere using standard glovebox, high vacuum or Schlenk techniques, unless otherwise noted. All solvents used were anhydrous, sparged with nitrogen and stored over 4Å molecular sieves. All starting materials were either purchased from Aldrich and purified prior to use or prepared according to procedures known to those skilled in the art. ^1H NMR spectroscopy on ligand and catalyst samples was performed at 250 MHz on a Bruker Avance DPX 250 instrument. In the procedures described herein, a label is included after each compound's name. Corresponding labels identify each structure shown below and in the synthetic sequences. In various reaction sequences shown herein, wavy lines are used to indicate a substituent that may be a methyl group.

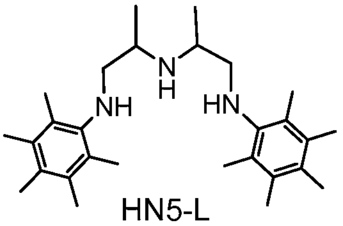
Syntheses

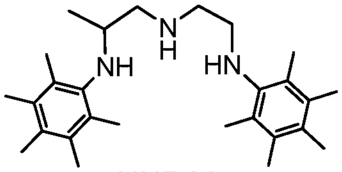
Ligands

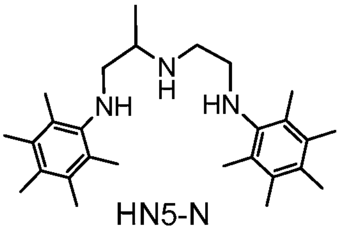
[0078] The ligands that are made in embodiments are shown in Table 1. Table 1 also illustrates the abbreviations that are used for these ligands, herein. It can be noted that the abbreviation, in this table and those that follow, is merely an identifier of the structure, and does not indicate the structure of the ligand itself.

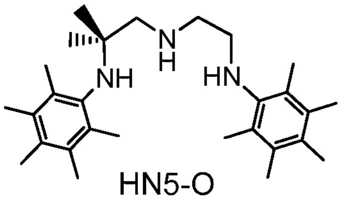
Table 1: Ligands described in this invention and abbreviations

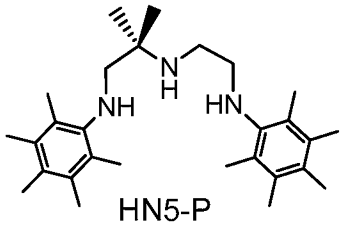

HN5-K


HN5-L


HN5-M

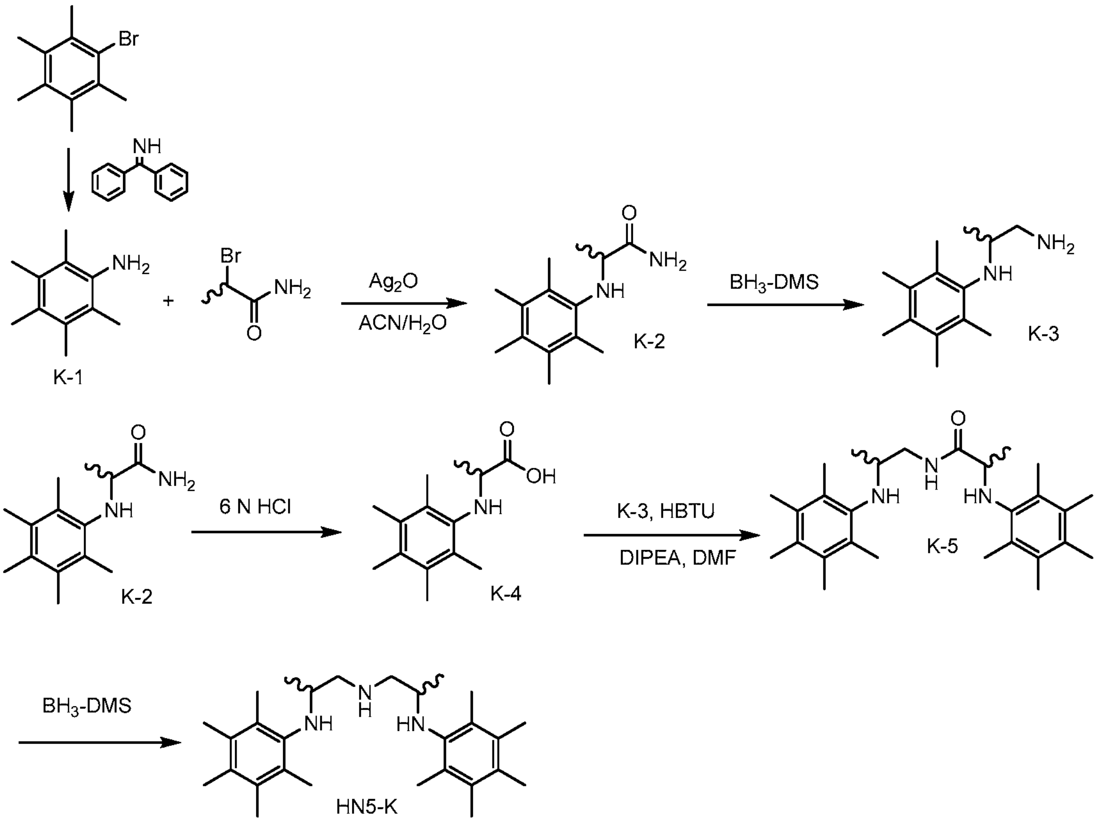

HN5-N


HN5-O


HN5-P

[0079] 2,3,4,5,6-Pentamethylaniline (K-1): Toluene (800 mL) was heated to reflux for three hours with a Dean-Stark trap to remove residual water. The toluene was purged with a stream of nitrogen for five minutes. 1-Bromo-2,3,4,5,6-pentamethylbenzene (40 g, 176.1 mmol, 1 equiv.), benzophenone imine (38.3 g, 211.3 mmol, 1.2 equiv.), tris(dibenzylideneacetone)dipalladium(0) (1.93 g, 2.1 mmol, 0.012 equiv.), *rac*-BINAP (4.38 g, 7.03 mmol, 0.04 equiv.), and potassium *tert*-butoxide (23.7 g, 211.3 mmol, 1.2 equiv.) were added to the toluene and the mixture was refluxed for 48 hours. The reaction was cooled and poured into water (1 L). The layers were separated and the organic layer washed with aqueous1N HCl (2 x 500 mL). The organic layer was concentrated under reduced pressure to yield a brown solid that was dissolved in tetrahydrofuran (1.5 L). An aqueous 6N HCl (500 mL) solution was added to the dissolved material and the mixture was allowed to stir overnight. Ethyl acetate (1.5 L) was added and the layers were separated. The organic layer was washed with aqueous 1N HCl (2 x 1L) and the aqueous layers were combined. The combined aqueous layer was basified to pH ~9 with aqueous sodium hydroxide (24% w/v). The basified aqueous layer was extracted with ethyl acetate (3 x 500 mL) and the organic layer dried over sodium sulfate, filtered, and concentrated under reduced pressure to yield 2,3,4,5,6-pentamethylaniline as a pale yellow solid (20.4 g, 71% yield).

[0080] The synthetic scheme for **HN5-K** is shown in sequence (1). Each of the components in sequence (1) are labeled to identify the corresponding synthesis procedure.



(1)

Similar sequences can be used to generate a number of other ligands, each with a unique substituent pattern.

[0081] **2-((2,3,4,5,6-Pentamethylphenyl)amino)propanamide (K-2)**: To a solution of **K-1** (1 g, 6.13 mmol, 1 equiv) and 2-bromo propionamide (1.12 g, 7.36 mmol, 1.2 equiv) in acetonitrile (25 mL) was added silver oxide (2.84 g, 12.26 mmol, 2 equiv), followed by the addition of water (1 mL). The resulting suspension was heated to 60 °C for 4 hours and monitored by LC-MS. Upon completion, the reaction was diluted with ethyl acetate (25 mL) and filtered through a thin pad of Celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography to give 2-((2,3,4,5,6-pentamethylphenyl)amino)propanamide as a light yellow solid (0.9 g, 63% yield).

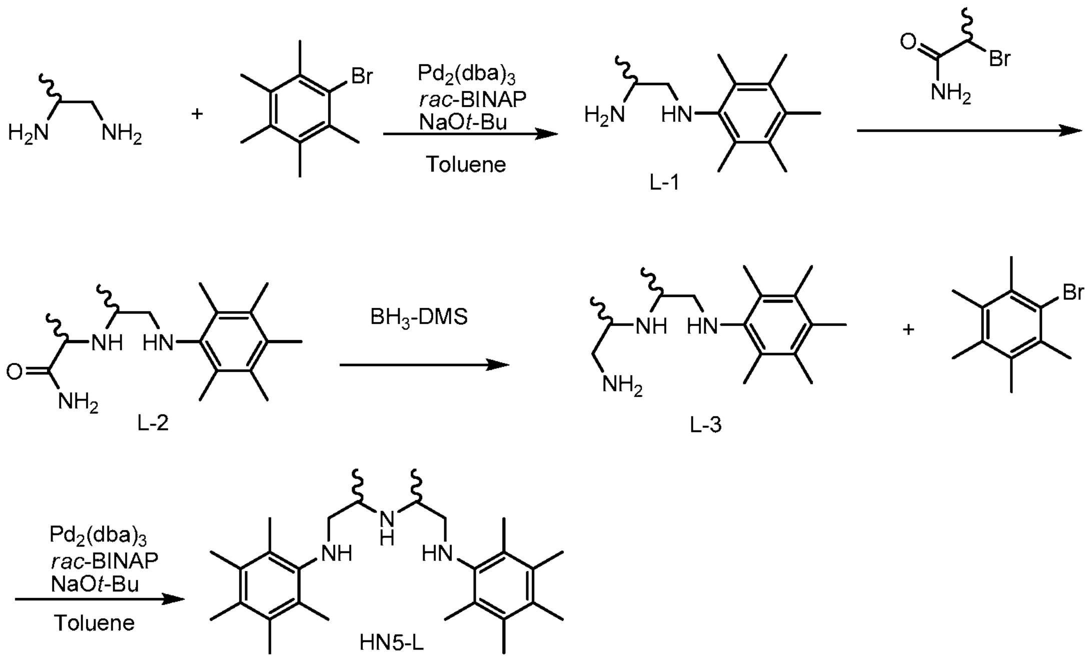
[0082] **N2-(2,3,4,5,6-Pentamethylphenyl)propane-1,2-diamine (K-3)**: To a solution of compound **K-2** (2 g, 8.5 mmol, 1 equiv) in THF (40 mL) was added borane-dimethyl sulfide (1.94 g, 25.5 mmol, 3 equiv). The resulting mixture was heated to reflux overnight and monitored by LC-MS. Upon completion, the reaction was cooled to room temperature and quenched with methanol. The solution was concentrated under reduced pressure and co-stripped with methanol several times to break up the borane complex. The crude product (~1.8 g) was used for the next step without further purification.

[0083] 2-(2,3,4,5,6-pentamethylphenylamino)propanoic acid (K-4): Compound **K-2** (1.5 g, 6.4 mmol) was suspended in aqueous 6 N HCl (50 mL) and the resulting mixture was heated to reflux for 4 hours. Upon completion, the reaction mixture was concentrated under reduced pressure to give crude **K-4** (~1.5 g) which was used for the next step without further purification.

[0084] 2-(2,3,4,5,6-Pentamethylphenylamino)-N-(2-(2,3,4,5,6-pentamethylphenylamino)propyl)-propanamide (K-5): To a solution of **K-3** (1.4 g, 5.9 mmol, 1 equiv) and **K-4** (1.4 g, 5.9 mmol, 1 equiv) in DMF (40 mL) was added HBTU (2.47 g, 6.5 mmol, 1.1 equiv), followed by the addition of diisopropyl ethylamine (2.3 mL, 13.2 mmol, 2.2 equiv). The resulting mixture was stirred at room temperature overnight. The reaction was diluted with ethyl acetate (100 mL) and water (100 mL). The layers were separated and the organic layer was concentrated under reduced pressure. The crude product was purified by flash chromatography eluting with a gradient of 20 to 100% ethyl acetate in heptanes to give **K-5** as an off-white solid (1 g, 40% yield).

[0085] N2-(2,3,4,5,6-Pentamethylphenyl)-N1-(2-(2,3,4,5,6-pentamethylphenylamino)propyl)-propane-1,2-diamine (HN5-K): To a solution of compound **K-5** (1 g, 2.3 mmol, 1 equiv) in THF (20 mL) was added borane-dimethyl sulfide (0.59 g, 6.9 mmol, 3 equiv). The resulting mixture was heated to reflux overnight and monitored by LC-MS. Upon completion, the reaction was cooled to room temperature and quenched with methanol/ammonia. The solution was concentrated under reduced pressure and co-stripped with methanol/ammonia several times to break up the borane complex. The crude product was purified by flash chromatography eluting with a gradient of 0 to 7% methanol in dichloromethane to give compound **HN5-K** (460 mg, 48% yield) as a light yellow solid.

[0086] The synthetic scheme for **HN5-L** is shown in sequence (2). Each of the components in sequence (2) are labeled to identify the corresponding synthesis procedure.



(2)

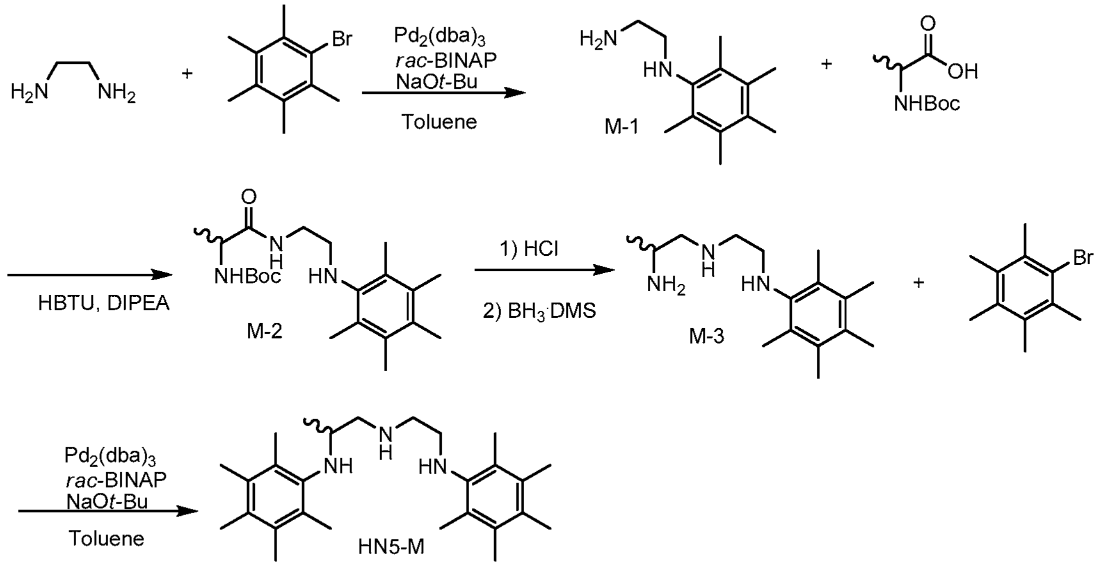
[0087] N1-(2,3,4,5,6-Pentamethylphenyl)propane-1,2-diamine (L-1): To a flask containing 1,2-diaminopropane (6.8 g, 92 mmol, 1 equiv.) was added 1-bromo-2,3,4,5,6-pentamethylbenzene (25 g, 110 mmol, 1.2 equiv.) in toluene (350 mL). Tris(dibenzylideneacetone)dipalladium(0) (0.42 g, 0.46 mmol, 0.005 equiv.), *rac*-BINAP (0.86 g, 1.38 mmol, 0.015 equiv.), and sodium *tert*-butoxide (26.4 g, 275 mmol, 3 equiv.) were added to the toluene and the reaction allowed to heat at 100°C for 24 hours. The reaction was cooled and poured into water (1L) and diluted with toluene (1L). The layers were separated and the organic layer concentrated under reduced pressure to yield a dark brown oil. The oil was purified on silica gel eluting with a gradient of 0 to 7% methanol in dichloromethane. The cleanest fractions were concentrated under reduced pressure and the resulting solid dried at 40°C in a vacuum oven overnight to yield N1-(2,3,4,5,6-pentamethylphenyl)propane-1,2-diamine as a light brown solid (12 g, 59% yield).

[0088] 2-(1-(2,3,4,5,6-Pentamethylphenylamino)propan-2-ylamino)propanamide (L-2): To a solution of **L-1** (5 g, 22.7 mmol, 1 equiv) in acetonitrile (170 mL) was added 2-bromopropionamide (3.42 g, 22.7 mmol, 1 equiv) and potassium hydrogen carbonate (4.54 g, 45.4 mmol, 2 equiv). The resulting mixture was heated to reflux with vigorous stirring overnight. Upon completion, the reaction was diluted with ethyl acetate (170 mL) and filtered. The filtrate was concentrated under reduced pressure and used in the next step without further purification (6.58 g).

[0089] N2-(1-Aminopropan-2-yl)-N1-(2,3,4,5,6-pentamethylphenyl)propane-1,2-diamine (L-3): To a solution of compound **L-2** (6.58 g, 22.7 mmol, 1 equiv) in THF (200 mL) was added borane-dimethyl sulfide (5.17 g, 68.1 mmol, 3 equiv). The resulting mixture was heated to reflux overnight and monitored by LC-MS. Upon completion, the reaction was cooled to room temperature and quenched with methanol. The solution was concentrated under reduced pressure and co-stripped with methanol several times to break up the borane complex. The crude product was purified by flash chromatography eluting with 5% methanol in dichloromethane with 0.5% ammonia to give **L-3** as a light yellow solid (3.2 g, 51% yield over two steps).

[0090] N1-(2,3,4,5,6-Pentamethylphenyl)-N2-(1-(2,3,4,5,6-pentamethylphenylamino)propan-2-yl)propane-1,2-diamine (HN5-L): To a solution of **L-3** (3.2 g, 11.5 mmol, 1 equiv) and pentamethylphenyl bromide (3.14 g, 13.8 mmol, 1.2 equiv) in toluene (100 mL) was added sodium *tert*-butoxide (3.31 g, 34.5 mmol, 3 equiv). The resulting mixture was degassed with a stream of nitrogen for 5 minutes. Tris(dibenzylideneacetone)dipalladium(0) (52 mg, 0.057 mmol, 0.5 mol%) and *rac*-BINAP (107 mg, 0.172 mmol, 1.5 mol%) were added and the reaction mixture was heated to reflux overnight. Upon completion, the reaction was diluted with toluene (200 mL) and water (300 mL). The layers were separated and the organic layer was concentrated under reduced pressure. The crude product was purified by flash chromatography eluting with 5% methanol in dichloromethane with 0.5% ammonia to give **HN5-L** as a light yellow solid (3.3 g, 68% yield), which is a mixture of diastereomers. The mixture was triturated with heptane three times to give one pure diastereomer (1 g) as a solid. The filtrate was concentrated to afford a mixture of diastereomers (2.3 g).

[0091] The synthetic scheme for **HN5-M** is shown in sequence (3). Each of the components in sequence (3) are labeled to identify the corresponding synthesis procedure.



(3)

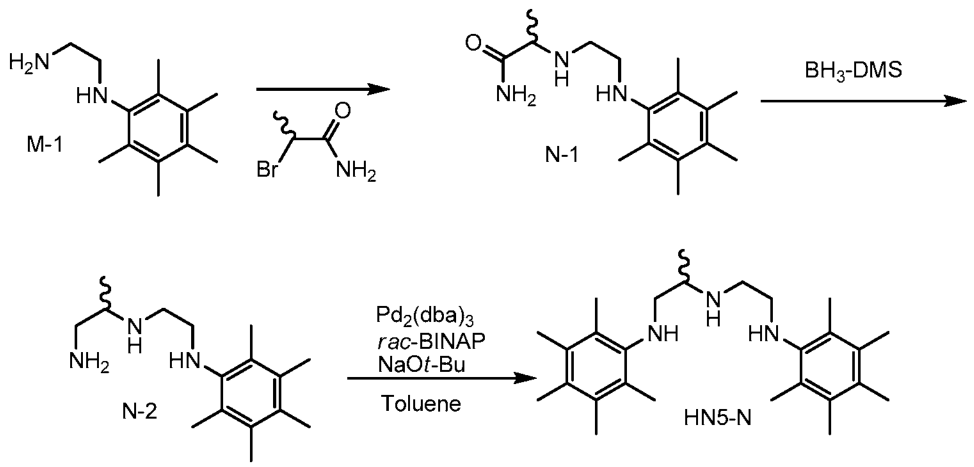
[0092] N^1-(2,3,4,5,6-Pentamethylphenyl)ethane-1,2-diamine (M-1): To a flask containing ethylenediamine (11 g, 183 mmol, 1 equiv.) was added 1-bromo-2,3,4,5,6-pentamethylbenzene (49.9 g, 220 mmol, 1.2 equiv.) in toluene (700 mL). Tris(dibenzylideneacetone)dipalladium(0) (0.84 g, 0.92 mmol, 0.005 equiv.), *rac*-BINAP (1.71 g, 2.75 mmol, 0.015 equiv.), and sodium *tert*-butoxide (52.8 g, 549 mmol, 3 equiv.) were added to the toluene and the reaction allowed to heat at 100 °C for 24 hours. The reaction was cooled and poured into water (1L) and diluted with toluene (1L). The layers were separated and the organic layer concentrated under reduced pressure to give a reddish brown oil. The oil was purified on silica gel eluting with 0-10% methanol in methylene chloride followed by 10% methanol in methylene chloride with 2% ammonium hydroxide. The cleanest fractions were concentrated under reduced pressure and the resulting solid dried at 40 °C in a vacuum oven overnight to yield N1-(2,3,4,5,6-pentamethylphenyl)ethane-1,2-diamine as a beige solid (13.2 g, 35% yield).

[0093] *tert*-Butyl 1-oxo-1-(2-(2,3,4,5,6-pentamethylphenylamino)ethylamino)propan-2-ylcarba-mate (M-2): To a solution of **M-1** (4.12 g, 20 mmol, 1 equiv) and 2-(*tert*-butoxycarbonylamino)propanoic acid (3.78 g, 20 mmol, 1 equiv) in dichloromethane (100 mL) was added HBTU (8.34 g, 22 mmol, 1.1 equiv), followed by the addition of diisopropyl ethylamine (7.7 mL, 44 mmol, 2.2 equiv). The resulting mixture was stirred at room temperature overnight. The reaction was diluted with dichloromethane (100 mL) and water (200 mL). The layers were separated and the organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give **M-2** as a white solid (7 g, 93% yield).

[0094] N1-(2-(2,3,4,5,6-Pentamethylphenylamino)ethyl)propane-1,2-diamine (M-3): To a solution of **M-2** (7 g, 18.5 mmol) in methanol (150 mL) was added aqueous 6 N HCl (80 mL). The resulting mixture was stirred at room temperature overnight. Upon completion, the solvent was removed under reduced pressure and the residue was dissolved in water (200 mL). Solid potassium carbonate was added until the solution became basic (pH ~9). The solution was extracted with dichloromethane (2 x 150 mL). The solvent was removed under reduced pressure. The crude product (3.8 g, 13.7 mmol) was dissolved in THF (100 mL) and borane-dimethyl sulfide (3.12 g, 41 mmol, 3 equiv) was added. The resulting mixture was heated to reflux overnight and monitored by LC-MS. Upon completion, the reaction was cooled to room temperature and quenched with methanol. The solution was concentrated under reduced pressure and co-stripped with methanol several times to break up the borane complex. The crude product was purified by flash chromatography eluting with 5% methanol in dichloromethane with 0.5% ammonia to give **M-3** as a light yellow solid (2.2 g, 45% yield over two steps).

[0095] N2-(2,3,4,5,6-Pentamethylphenyl)-N1-(2-(2,3,4,5,6-pentamethylphenylamino)ethyl)propane-1,2-diamine (HN5-M): To a solution of **M-3** (2.2 g, 8.3 mmol, 1 equiv) and pentamethylphenyl bromide (2.27 g, 10 mmol, 1.2 equiv) in toluene (80 mL) was added sodium *tert*-butoxide (2.4 g, 25 mmol, 3 equiv). The resulting mixture was degassed with a stream of nitrogen for 5 minutes. Tris(dibenzylideneacetone)dipalladium(0) (38 mg, 0.04 mmol, 0.5 mol%) and *rac*-BINAP (77 mg, 0.12 mmol, 1.5 mol%) were added and the reaction mixture was heated to reflux overnight. Upon completion, the reaction was diluted with toluene (200 mL) and water (300 mL). The layers were separated and the organic layer was concentrated under reduced pressure. The crude product was purified by flash chromatography eluting with 5% methanol in dichloromethane with 0.5% ammonia to give **HN5-M** as a light tan solid (1.9 g).

[0096] The synthetic scheme for **HN5-N** is shown in sequence (4). Each of the components in sequence (4) are labeled to identify the corresponding synthesis procedure.



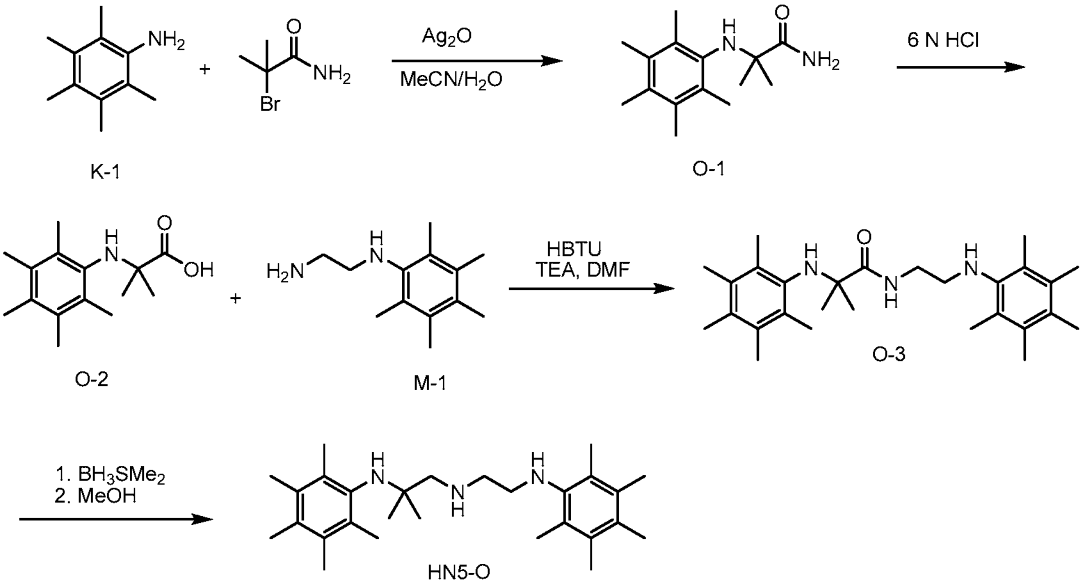
(4)

[0097] 2-(2-(2,3,4,5,6-Pentamethylphenylamino)ethylamino)propanamide (N-1): To a solution of **M-1** (4.12 g, 20 mmol, 1 equiv) in acetonitrile (150 mL) was added 2-bromopropionamide (3.02 g, 20 mmol, 1 equiv) and potassium hydrogen carbonate (4 g, 40 mmol, 2 equiv). The resulting mixture was heated to reflux with vigorous stirring overnight. Upon completion, the reaction was diluted with ethyl acetate (150 mL) and filtered. The filtrate was concentrated under reduced pressure and used in the next step without further purification (5.56 g).

[0098] N2-(2-(2,3,4,5,6-Pentamethylphenylamino)ethyl)propane-1,2-diamine (N-2): To a solution of compound **N-1** (5.56 g, 20 mmol, 1 equiv) in THF (100 mL) was added borane-dimethyl sulfide (4.56 g, 60 mmol, 3 equiv). The resulting mixture was heated to reflux overnight and monitored by LC-MS. Upon completion, the reaction was cooled to room temperature and quenched with methanol. The solution was concentrated under reduced pressure and co-stripped with methanol several times to break up the borane complex. The crude product was purified by flash chromatography eluting with 5% methanol in dichloromethane with 0.5% ammonia to give **N-2** as a light yellow solid (3.2 g, 60% yield over two steps).

[0099] N1-(2,3,4,5,6-pentamethylphenyl)-N2-(2-(2,3,4,5,6-pentamethylphenylamino)ethyl)propane-1,2-diamine (HN5-N): To a solution of **N-2** (3.2 g, 12.1 mmol, 1 equiv) and pentamethylphenyl bromide (3.3 g, 14.5 mmol, 1.2 equiv) in toluene (100 mL) was added sodium *tert*-butoxide (3.48 g, 36.3 mmol, 3 equiv). The resulting mixture was degassed with a stream of nitrogen for 5 minutes. Tris(dibenzylideneacetone)dipalladium(0) (55 mg, 0.06 mmol, 0.5 mol%) and *rac*-BINAP (113 mg, 0.18 mmol, 1.5 mol%) were added and the reaction mixture was heated to reflux overnight. Upon completion, the reaction was diluted with toluene (200 mL) and water (300 mL). The layers were separated and the organic layer was concentrated under vacuum. The crude product was purified by flash chromatography eluting with 5% methanol in dichloromethane with 0.5% ammonia to afford **HN5-N** as a white solid (2.1 g).

[00100] The synthetic scheme for **HN5-O** is shown in sequence (5). Each of the components in sequence (5) are labeled to identify the corresponding synthesis procedure.



(5)

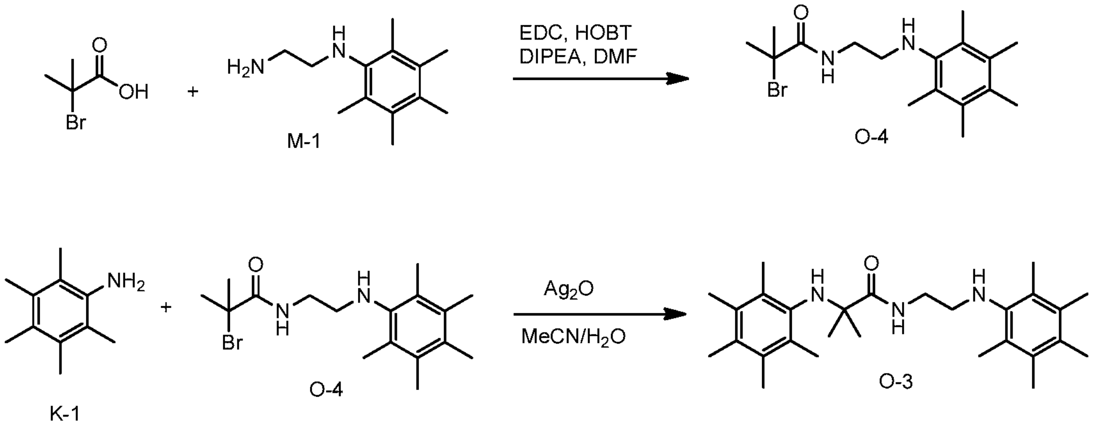
[00101] 2-Methyl-2-((2,3,4,5,6-pentamethylphenyl)amino)propanamide (O-1): K-1 (2.0 g, 12.3 mmol, 1 equiv) and 2-bromo-2-methylproprionamide (3.1 g, 18.7 mmol, 1.5 equiv) were dissolved in acetonitrile (50 mL) and water (2 mL). Silver (I) oxide (5.7 g, 24.6 mmol, 2 equiv) was added and the resulting suspension was heated to 60 °C for 2 hr. The reaction was cooled to room temperature and the solids removed via vacuum filtration washing with acetonitrile. The filtrate was evaporated under reduced pressure leaving an orange/brown foam. The crude product was purified using an AnaLogix automated chromatography system eluting with 20-80 % ethyl acetate in heptanes over 30 minutes. Fractions containing product were evaporated under reduced pressure to give **O-1** (860 mg, 28% yield) as an off-white solid.

[00102] 2-Methyl-2-((2,3,4,5,6-pentamethylphenyl)amino)propanoic acid (O-2): O-1 (860 mg, 3.5 mmol) was suspended in aqueous 6 N HCl (25 mL) and heated to reflux for 4 hours. Upon reflux, a clear solution was obtained. The reaction was cooled to room temperature, saturated with NaCl, and extracted with dichloromethane (4 x 200 mL). The combined organics were dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give **O-2** (810 mg) as a white solid which was used without further purification.

[00103] **2-Methyl-2-((2,3,4,5,6-pentamethylphenyl)amino)-N-(2-((2,3,4,5,6-pentamethylphenyl)amino)ethyl)propanamide (O-3):** **O-2** (810 mg, 3.2 mmol, 1 equiv), HBTU (1.2 g, 3.2 mmol, 1 equiv), and TEA (0.5 mL, 3.2 mmol, 1 equiv) were dissolved in dichloromethane (25 mL). To this solution was added compound **M-1** (660 mg, 3.2 mmol, 1 equiv). The reaction was stirred at room temperature overnight. The solvent was then evaporated and the crude material purified by silica gel chromatography eluting with 40 % ethyl acetate in heptanes to give **O-3** (350 mg, 25% yield) as a white solid.

[00104] **2-Methyl-N2-(2,3,4,5,6-pentamethylphenyl)-N1-(2-((2,3,4,5,6-pentamethylphenyl)amino)ethyl)propane-1,2-diamine (HN5-O):** Compound **O-3** (800 mg, 1.8 mmol, 1 equiv) was dissolved in THF (20 mL) and borane-dimethyl sulfide (0.5 mL, 5.5 mmol, 3 equiv) was added. The reaction was stirred at room temperature for 10 minutes and then heated to reflux overnight. The reaction was cooled to room temperature and quenched with MeOH (15 mL). The solvent was evaporated under reduced pressure and the residue dissolved in MeOH (10 mL). A 2 N NH_3 in MeOH (10 mL) was added and mixture was stirred for 1 hour. The solvent was evaporated and the crude material purified by silica gel chromatography eluting with 1-4 % 2 N NH_3 in MeOH in dichloromethane to give **HN5-O** (600 mg) as an oil which solidified upon standing. This material was dissolved in a minimal amount of dichloromethane and diluted with hexane. Slow evaporation of this solution gave compound **HN5-O** (510 mg, 67% yield) as a white solid.

[00105] An alternate synthetic scheme for **O-3** is shown in sequence (6). Each of the components in sequence (6) are labeled to identify the corresponding synthesis procedure.



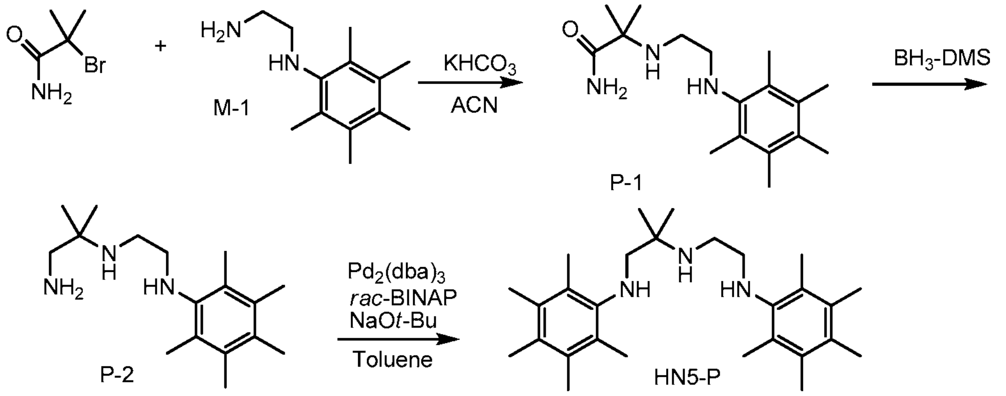
(6)

[00106] **2-Bromo-2-methyl-N-(2-((2,3,4,5,6-pentamethylphenyl)amino)ethyl) propanamide (O-4):** To a solution of 2-bromo-2-methylproprionic acid (2.4 g, 14.6 mmol, 1 equiv), EDCI•HCl (3.1 g, 16.1 mmol, 1.1 equiv), HOBT (2.2 g, 16.1 mmol, 1.1 equiv), and diisopropylethylamine amine (2.8 mL, 16.1 mmol, 1.1 equiv) in DMF (100 mL) was

added **M-1** (3.0 g, 14.6 mmol, 1 equiv). The reaction was stirred at room temperature overnight. Water (100 mL) was added resulting in yellow precipitate. This mixture was extracted with MTBE (5 x 500 mL). The combined organics were washed with saturated aqueous $NaHCO_3$ (500 mL), water (500 mL), and saturated brine (500 mL). The MTBE layer was dried over sodium sulfate, filtered, and evaporated under reduced pressure leaving 8.1 g of a brown oil. The crude material was adsorbed onto silica gel and purified using an AnaLogix automated chromatography system eluting with 20-80 % ethyl acetate in heptanes over 40 minutes to give compound **O-4** (2.3 g, 44% yield) as a white solid.

[00107] 2-Methyl-2-((2,3,4,5,6-pentamethylphenyl)amino)-N-(2-((2,3,4,5,6-pentamethylphenyl)-amino)ethyl)propanamide(O-3): O-4 (2.3 g, 6.5 mmol, 1.1 equiv) and compound **K-1** (960 mg, 5.9 mmol, 1 equiv) were dissolved in acetonitrile (25 mL) and water (1 mL). Silver (I) oxide (3.0 g, 13.0 mmol, 2 equiv) was added and the reaction heated to 50 °C overnight. TLC (30 % ethyl acetate in heptane) revealed both starting materials were still present along with the desired product and several side products so an additional portion of Ag_2O (1.0 g) was added and heating continued for an additional 5 hours. The reaction was cooled to room temperature and the solids removed by filtration, washing with acetonitrile. The filtrate was evaporated under reduced pressure and the crude product was adsorbed onto silica gel. Purification was achieved using an AnaLogix automated chromatography system eluting with 50-100% dichloromethane in heptanes over 20 minutes followed by 0-30% ethyl acetate in dichloromethane over 30 minutes to give **O-3** (450 mg, 17% yield) as a white solid.

[00108] The synthetic scheme for **HN5-P** is shown in sequence (7). Each of the components in sequence (7) are labeled to identify the corresponding synthesis procedure.



(7)

[00109] 2-Methyl-2-(2-(2,3,4,5,6-pentamethylphenylamino)ethylamino)propanamide (P-1): A mixture of 2-bromo-2-methylpropanamide (5.55 g, 33.44 mmol, 1.5 equiv.), **M-1**

(4.6 g, 22.33 mmol, 1 equiv.), potassium bicarbonate (8.93 g, 89.18 mmol, 4 equiv.) and acetonitrile (350 mL) was stirred under nitrogen at reflux for 32 hrs. After cooling the reaction mixture was filtered, the solvent was removed under reduced pressure and the residue was partitioned between water (200 mL) and ethyl acetate (400 mL). The organic phase was washed with water (200 mL) and saturated brine (300 mL), dried over sodium sulfate, concentrated to 60 mL and allowed to cool overnight. The crystals were collected by filtration, washed with 2:1 heptanes/ethyl acetate (20 mL) and dried in a vacuum oven (50 °C) to give **P-1** (3.92 g, 59%).

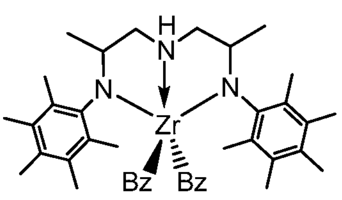
[00110] 2-Methyl-N2-(2-(2,3,4,5,6-pentamethylphenylamino)ethyl)propane-1,2-diamine (P-2): A solution of **P-1** (3.82 g, 1.1 mmol) in THF (100 mL) was stirred under nitrogen at room temperature and borane-dimethylsulfide complex (2.99 g, 3.73 mmol, 3 equiv.) was slowly added. The reaction mixture was stirred at room temperature for 1 hr and kept at reflux overnight. After cooling methanol (20 mL) was carefully added (foaming) over 1 hr. The solvents were removed under reduced pressure. Methanol (30 mL) was added and removed 3 times. The crude product was purified by chromatography on silica (80 g) with 2% 2N ammonia in methanol in dichloromethane (2 L) and 3% 2N ammonia in methanol in dichloromethane (2 L) to give **P-2** (1.43 g, 39%). An additional slightly impure batch (0.62 g) was also isolated.

[00111] 2-Methyl-N1-(2,3,4,5,6-pentamethylphenyl)-N2-(2-(2,3,4,5,6-pentamethylphenylamino)-ethyl)propane-1,2-diamine (HN5-P): A solution of **P-2** (1.43 g, 5.154 mmol), 1-bromo-2,3,4,5,6-pentamethylbenzene (1.41 g, 6.2 mmol) and potassium *tert*-butoxide (1.49 g, 15.5 mmol, 3 equiv.) in toluene (60 mL) was degassed for 10 min with a stream of nitrogen. *rac*-BINAP (48 mg) and Tris(dibenzylideneacetone)dipalladium(0) (24 mg) were added and the reaction mixture was stirred under nitrogen at reflux for 24 hrs. After cooling the reaction mixture was diluted with toluene (100 mL), washed with water (50 mL) and saturated brine (100 mL), dried over sodium sulfate and filtered. The solvent was removed under reduced pressure and the crude product was purified by chromatography on silica (40 g) with 1% 2N ammonia in methanol in dichloromethane (500 ml) and 2% 2N ammonia in methanol in dichloromethane (800 ml). The fractions containing the pure product were combined and the solvent was removed under reduced pressure. The residue was dissolved in 2:1 heptanes/ethyl acetate (30 mL), treated with charcoal and filtered. The solvent was removed under reduced pressure to give **HN5-P** (1.36 g, 62% yield).

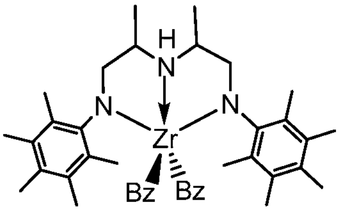
Catalysts

[00112] The HN5 zirconium dibenzyl compounds that are made in embodiments are shown in Table 2. Table 2 also illustrates the abbreviations that are used for these catalysts, herein. It can be noted that the abbreviation, in this table and those that follow, is merely an identifier of the structure, and does not indicate the structure of the ligand itself.

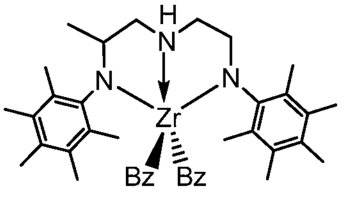
Table 2: HN5 zirconium dibenzyl compounds and abbreviations.



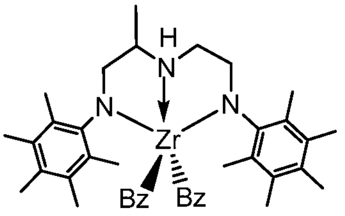
(HN5-K)ZrBn$_2$



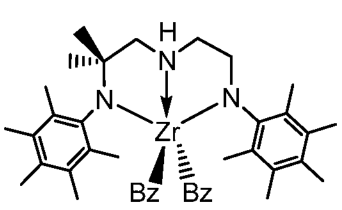
(HN5-L)ZrBn$_2$



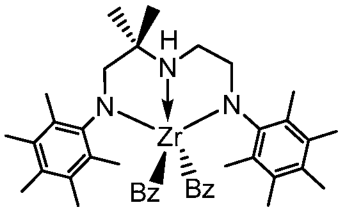
(HN5-M)ZrBn$_2$



(HN5-N)ZrBn$_2$



(HN5-O)ZrBn$_2$



(HN5-P)ZrBn$_2$

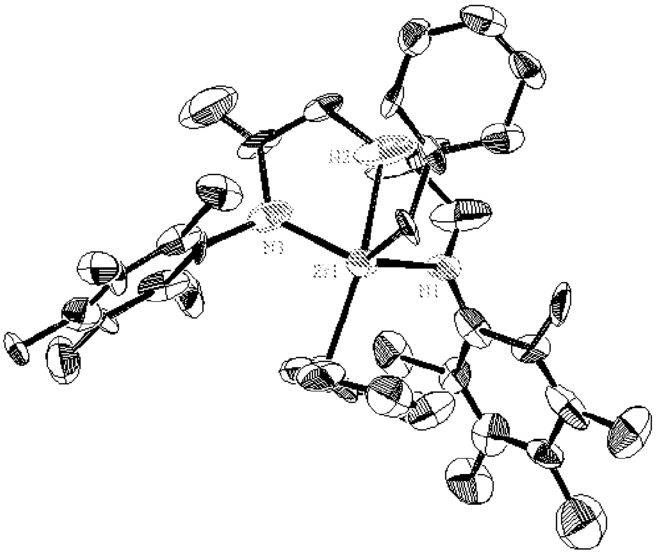
[00113] **Representative synthesis of (HN5-K)ZrBn$_2$:** A toluene solution of **HN5-K** (0.22 g, 0.52 mmol) was added to a toluene solution of ZrBn$_4$ (0.22 g, 0.48 mmol) and the mixture was stirred at room temperature overnight. The solvent was then removed under vacuum and the yellow solid was washed with pentane. The solid was dried on a frit to yield 0.28 g of **(HN5-K)ZrBn$_2$** (83% yield). Compounds **(HN5-L)ZrBn$_2$**, **(HN5-M)ZrBn$_2$**, **(HN5-N)ZrBn$_2$**, **(HN5-O)ZrBn$_2$** and **(HN5-P)ZrBn$_2$** were synthesized in a similar fashion.

[00114] **^{1}H NMR data for (HN5-K)ZrBn$_2$:** δ (C_6D_6): 7.29 – 6.84 (m, 8H, benzyl o,p,m-Ar), 5.71 (d, 2H, benzyl o-Ar), 4.36 - 2.75 (m, 7H, -CH$_2$, -C*H*Me), 2.55 – 2.05 (s, 30H, -Ar*Me*), 1.20, 0.78, 0.66, 0.54 (d, 4H, -C*H*$_2$Ph), 0.88 (d, 6H, CH*Me*); 78% yield.

[00115] **^{1}H NMR data for (HN5-L)ZrBn$_2$:** δ (C_6D_6): 7.13 – 6.88 (m, 8H, benzyl o,p,m-Ar), 5.78 (d, 2H, benzyl o-Ar), 4.00 - 2.90 (m, 7H, -CH$_2$, -C*H*Me), 2.61, 2.47, 2.43, 2.32, 2.24 (s, 30H, -Ar*Me*), 1.84, 1.75, 1.23, 0.78 (d, 4H, -C*H*$_2$Ph), 0.85 (d, 6H, CH*Me*); 54% yield.

[00116] **^{1}H NMR data for (HN5-M)ZrBn$_2$:** δ (C_6D_6): 7.24 (t, 4H, benzyl m-Ar), 6.90 (t, 2H, benzyl p-Ar), 5.74 (d, 4H, benzyl o-Ar), 3.95 - 2.65 (m, 7H, -CH$_2$, -C*H*Me), 2.60 – 2.05 (s, 30H, -Ar*Me*), 1.76, 1.55, 1.22, 0.66 (d, 4H, -C*H*$_2$Ph), 0.77 (d, 3H, CH*Me*); 90% yield.

[00117] The X-ray crystal structure of (HN5-M)ZrBn$_2$, made in an embodiment, is shown in structure (XII).



(XII)

[00118] **^{1}H NMR data for (HN5-N)ZrBn$_2$:** δ (d^8-THF): 7.25 – 7.00 (m, 6H, benzyl p,m-Ar), 5.47 (d, 4H, benzyl o-Ar), 3.50 - 2.80 (m, 7H, -CH$_2$, -C*H*Me), 2.39, 2.34, 2.25, 2.23, 2.20 (s, 30H, -Ar*Me*), 1.27, 1.23, 0.94, 0.43 (d, 4H, -C*H*$_2$Ph), 1.14 (d, 3H, CH*Me*); 76% yield.

[00119] **^{1}H NMR data for (HN5-O)ZrBn$_2$:** δ (C_6D_6): 7.23 (t, 4H, benzyl m-Ar), 7.05 (t, 2H, benzyl p-Ar), 5.76 (d, 4H, benzyl o-Ar), 4.07 – 2.85 (m, 6H, -CH$_2$), 2.58, 2.54, 2.48, 2.43, 2.41, 2.35, 2.26, 2.22, 2.18, 2.16 (s, 30H, -Ar*Me*), 1.79, 1.52, 1.18, 0.88 (d, 4H, -C*H*$_2$Ph), 1.03, 0.84 (s, 6H, C*Me*$_2$); 35% yield.

[00120] **^{1}H NMR data for (HN5-P)ZrBn$_2$:** δ (C_6D_6): 7.21 (t, 4H, benzyl m-Ar), 6.84 (t, 2H, benzyl p-Ar), 5.63 (d, 4H, benzyl o-Ar), 3.89, 3.71, 2.80 (m, 6H, -CH$_2$), 2.56, 2.55, 2.47, 2.44, 2.38, 2.24, 2.20, 2.17, 2.15, 2.10 (s, 30H, -Ar*Me*), 1.88, 1.85, 1.26, 0.77 (d, 4H, -C*H*$_2$Ph), 1.54, 0.85 (s, 6H, C*Me*$_2$); 72% yield.

[00121] Catalyst Testing - High Throughput Experimentation

[00122] Ethylene/1-octene copolymerizations were carried out in a parallel pressure reactor, which is described in U.S. Patent Nos. 6,306,658, 6,455,316 and 6,489,1681; WO

00/09255; and Murphy *et al., J. Am. Chem. Soc.*, **2003**, *125*, 4306-4317. A pre-weighed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor, which contains 48 individual reaction vessels. The reactor was then closed and each vessel was individually heated to a set temperature (usually 85 and/or 100 °C) and pressurized to a pre-determined pressure of ethylene (generally 135 psi). 100 uL of 1-octene (637 umol) was injected into each reaction vessel. 500 equivalents of MAO were then introduced to each cell to act as a co-catalyst/scavenger. The contents of the vessel were then stirred at 800 rpm. A toluene solution of catalyst (20 nmol) was then added and the volume of the cell made up to 5 mL with isohexane. All runs were performed in triplicate. The reaction was then allowed to proceed until a set time limit (usually 30 min) or until a set amount of ethylene had been taken up by the reaction (ethylene pressure was maintained in each reaction vessel at the pre-set level by computer control). At this point, the reaction was quenched by exposure to air. After the polymerization reaction, the glass vial insert containing the polymer product and solvent was removed from the pressure cell and the inert atmosphere glovebox and the volatile components were removed using a Genevac HT-12 centrifuge and Genevac VC3000D vacuum evaporator operating at elevated temperature and reduced pressure. The vial was then weighed to determine the yield of the polymer product. The resultant polymer was analyzed by Rapid GPC (see below) to determine the molecular weight, by FT-IR (see below) to determine comonomer incorporation, and by DSC (see below) to determine melting point.

[00123] High temperature, size exclusion chromatography was performed using an automated "Rapid GPC" system as described in U.S. Pat. Nos. 6,491,816, 6,491,823, 6,475,391, 6,461,515, 6,436,292, 6,406,632, 6,175,409, 6,454,947, 6,260,407 and 6,294,388. This apparatus has a series of three 30 cm x 7.5 mm linear columns, each containing PLgel 10 um, Mix B. The GPC system was calibrated using polystyrene standards ranging from 580 - 3,390,000 g/mol. The system was operated at an eluent flow rate of 2.0 mL/min and an oven temperature of 165 °C. 1,2,4-trichlorobenzene was used as the eluent. The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 0.1 - 0.9 mg/mL. 250 uL of a polymer solution were injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. The molecular weights obtained are relative to linear polystyrene standards.

[00124] Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220 °C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220 °C at a rate of 100 °C/min and then cooled at a rate of 50 °C/min. Melting points were collected during the heating period.

[00125] The ratio of 1-octene to ethylene incorporated in the polymers (weight %) was determined by rapid FT-IR spectroscopy on a Bruker Equinox 55+ IR in reflection mode. Samples were prepared in a thin film format by evaporative deposition techniques. Weight % 1-octene was obtained from the ratio of peak heights at 1378 and 4322 cm^{-1}. This method was calibrated using a set of ethylene/1-octene copolymers with a range of known wt. % 1-octene content.

Table 3. Activity, Molecular Weight, PDI and Comonomer Incorporation Results from High Throughput Catalyst Testing

Catalyst	Activity (g/mmol/h/bar)	MW (kDa)	PDI (Mw/Mn)	Comonomer Incorp. (wt %)
(HN5-K)ZrBn$_2$	36,900	222	1.5	9.0
(HN5-L)ZrBn$_2$	42,000	212	1.5	6.6
(HN5-M)ZrBn$_2$	37,000	265	1.6	9.6
(HN5-N)ZrBn$_2$	50,600	236	1.5	8.2
(HN5-O)ZrBn$_2$	10,100	634	1.7	7.9
(HN5-P)ZrBn$_2$	48,700	189	1.5	5.5

Preparation of Silica Supported Catalysts

[00126] 40 g of Ineous ES-757 silica gel (calcined at 600 °C) was slurried in 125 mL toluene and reacted with 47 g MAO (Albemarle, 30 wt%) at room temperature for 2 hrs. The SMAO was then filtered through a glass frit and washed with hexane. Drying under vacuum for 1 to 2 hrs yielded 54 g of dry free-flowing SMAO. Supported versions of HN5 catalysts were made by adding toluene solutions of the catalyst to toluene slurries of SMAO for one hour. The solid was collected on a frit and dried under vacuum resulting in an off-white solid. Catalyst loadings were kept constant at 37 umol/g, corresponding to a Al:Zr ratio of 130.

Catalyst Testing - Gas Phase Lab Reactor

[00127] The gas phase reactor employed is a 2 liter, stainless steel autoclave equipped with a variable speed mechanical agitator. In a standard HDPE run, the reactor was first dried for 1 hour, charged with 200g of NaCl and dried by heating at 100 °C under stream of nitrogen for 30 minutes. After baking out the reactor, 3g of SMAO (silica supported methylalumoxane) was introduced as a scavenger with help of nitrogen pressure. After adding SMAO, the reactor was sealed and components were gently stirred. This was then charged with hydrogen (~1600 ppm) and 1-hexene (~C6/C2 = 0.006). The reactor is then pressurized with ethylene (total pressure = 220 psi). Once the system reaches a steady state, catalyst is charged into the reactor to start polymerization. The reactor temperature is then brought up to 85 °C and maintained at this temperature through the run. The polymerization is typically carried for 60 minutes and during this time hydrogen, C6/C2 ratio and ethylene pressure remained constant. At the end of 60 minutes, the reactor is cooled down, vented and opened. The resulting mixture is then washed with water, methanol and dried.

[00128] Molecular weight distribution was characterized using a High Temperature Size Exclusion Chromatograph (Waters-Alliance GPCV 2000) equipped with a differential refractive index detector (DRI). Three Polymer Laboratories PLgel 10mm Mixed-B columns were used. The nominal flow rate was 1.0 mL/min, and the nominal injection volume was 300 uL. The various transfer lines, columns and differential refractometer (the DRI detector) were contained in an oven maintained at 145 °C. Polymer solutions were prepared by dissolving the desired amount of dry polymer in the appropriate volume of 1,2,4-trichlorobenzene to yield concentrations ranging from 0.25 to 1.5 mg/mL. The sample mixtures were heated at 160 °C with continuous agitation for ~2 hours. The solution was filtered through a 2 micron stainless steel filter (Polymer Labs) into scintillation vials using a Polymer Labs SP260 Sample Prep Station. The separation efficiency of the column set was calibrated using a series of narrow MWD polystyrene standards (Polymer Laboratories), which reflects the expected MW range for samples and the exclusion limits of the column set. Seventeen individual polystyrene standards, ranging from Mp ~580 to 10,000,000, were used to generate the calibration curve. Some GPC's were also obtained on a Polymer Labs PL220 Gel Permeation Chromatograph operating at 160 °C to accommodate higher molecular weight samples.

Table 4. Activity, Molecular Weight and PDI Results from Lab Reactor Testing of Supported Catalysts

Supported Catalyst	**Activity (g polymer/g**	**MW (kDa)**	**PDI (Mw/Mn)**

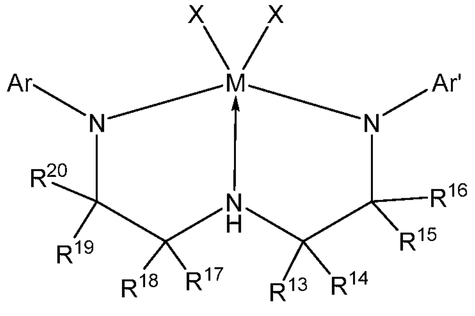
	supported cat)		
(HN5-K)ZrBn$_2$	580	443	9.01
(HN5-L)ZrBn$_2$	890	354	8.33
(HN5-M)ZrBn$_2$	1050	534	7.04
(HN5-N)ZrBn$_2$	1100	516	7.05
(HN5-O)ZrBn$_2$	ND	ND	ND
(HN5-P)ZrBn$_2$	930	352	9.62

[00129] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention can be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

CLAIMS

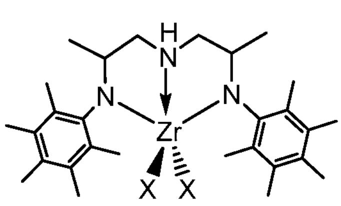
What is claimed is:

1. A polymerization catalyst system, comprising a non-metallocene catalyst having the structure:



wherein M is a group 4 element, each of R^{13}-R^{20} are independently a hydrogen or a methyl group, wherein at least one of R^{13}-R^{20} is a methyl group, Ar is an aryl group or a substituted aryl group, Ar' is an aryl group or a substituted aryl group, and each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

2. The polymerization catalyst system of claim 1, wherein the catalyst comprises a compound with the formula:



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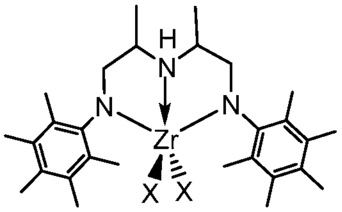

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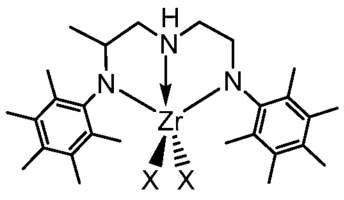

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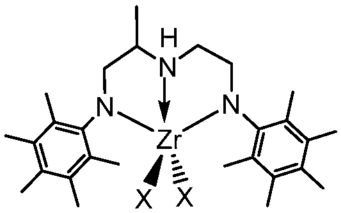

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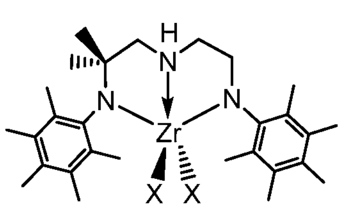
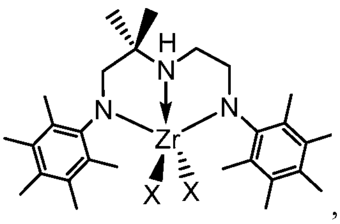


, or


,

wherein each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

3. The polymerization catalyst system of claim 1, comprising bis(n-butylcyclopentadienyl) zirconium$(X)_2$, wherein each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

4. The polymerization catalyst system of claim 1, comprising (n-propylcyclopentadienyl, tetramethylcyclopentadienyl) zirconium$(X)_2$, wherein each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

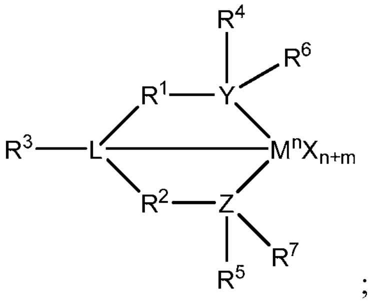
5. The polymerization catalyst system of claim 1, comprising [(pentamethylbenzylN(CH_2CH_2)(pentamethylbenzylN$CH_2CH(CH_3)$)NH]Zr$(X)_2$, wherein each X is, independently, a hydride group, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

6. The polymerization catalyst system of claim 1, comprising a catalyst of the formula:

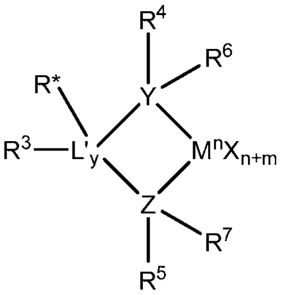
$$Cp^ACp^BMX_n \text{ or } Cp^A(A)Cp^BMX_n,$$

wherein M is a Group 4, 5, or 6 atom; Cp^A and Cp^B are each bound to M and are independently selected from the group consisting of cyclopentadienyl ligands, substituted cyclopentadienyl ligands, ligands isolobal to cyclopentadienyl and substituted ligands isolobal to cyclopentadienyl; (A) is a divalent bridging group bound to both Cp^A and Cp^B selected from the group consisting of divalent C_1 to C_{20} hydrocarbyls and C_1 to C_{20} heteroatom containing hydrocarbonyls, wherein the heteroatom containing hydrocarbonyls comprise from one to three heteroatoms; X is a leaving group selected from the group consisting of chloride ions, bromide ions, C_1 to C_{10} alkyls, and C_2 to C_{12} alkenyls, carboxylates, acetylacetonates, and alkoxides; and n is an integer from 1 to 3.

7. The polymerization catalyst system of claim 1, comprising a catalyst of the formula:



; or



,

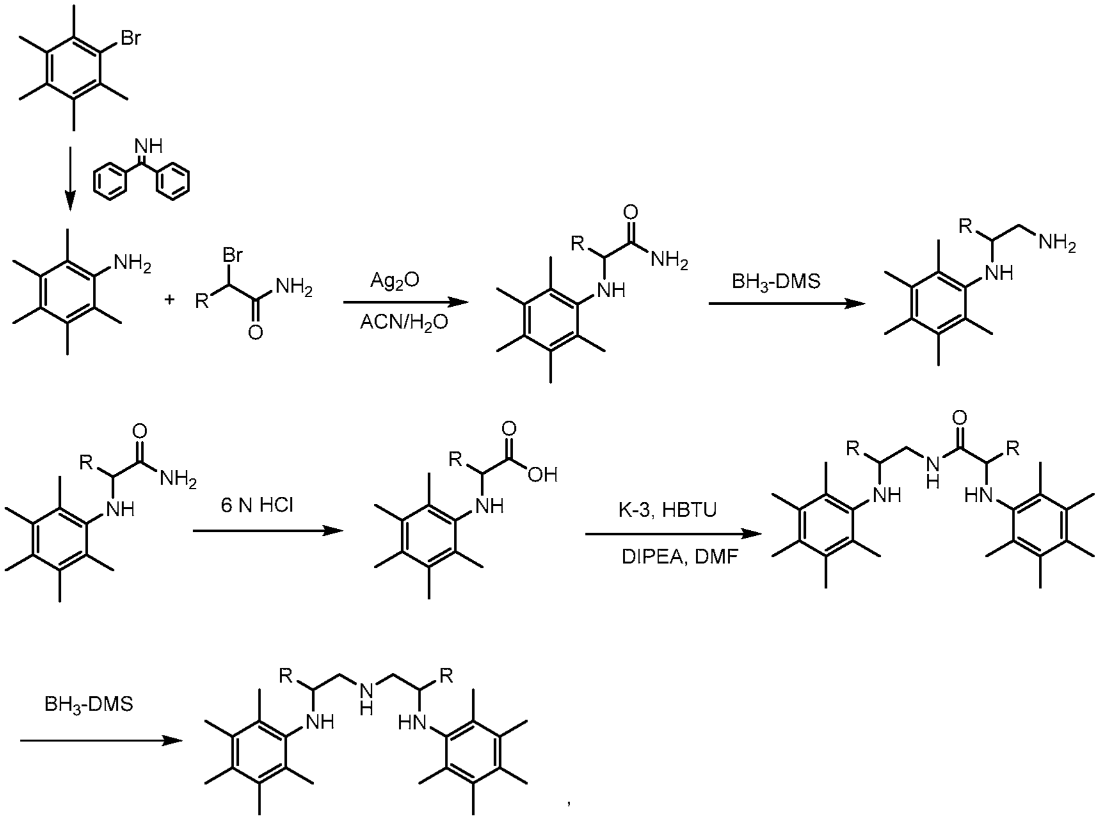
wherein M is a Group 3 to 12 transition metal or a Group 13 or 14 main group metal; each X is independently an anionic leaving group; y is 0 or 1; n is the oxidation state of M; m is the formal charge of the ligand represented by YZL or YZL'; L is a Group 15 or 16 element; L' is a group 15 or 16 element or Group 14 containing group; Y is a Group 15 element; Z is a Group 15 element; R^1 and R^2 are independently a C_1 to C_{20} hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus; R^1 and R^2 may be interconnected to each other; R^3 is absent, a hydrocarbon group, hydrogen, a halogen, or a heteroatom containing group; R^4 and R^5 are independently an alky group, 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 a multiple ring system; R^4 and R^5 may be interconnected to each other; R^6 and R^7 are independently absent, hydrogen, an alkyl group, a halogen, a heteroatom, or a hydrocarbyl group; and R^* is absent, hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group.

8. The polymerization catalyst system of claim 1, wherein two or more catalysts are co-supported on a single support.

9. The polymerization catalyst of claim 1, wherein a non metallocene catalyst and a metallocene catalyst are co-supported on a single support, and at least a portion of the metallocene catalyst is added as a trim feed to the support.

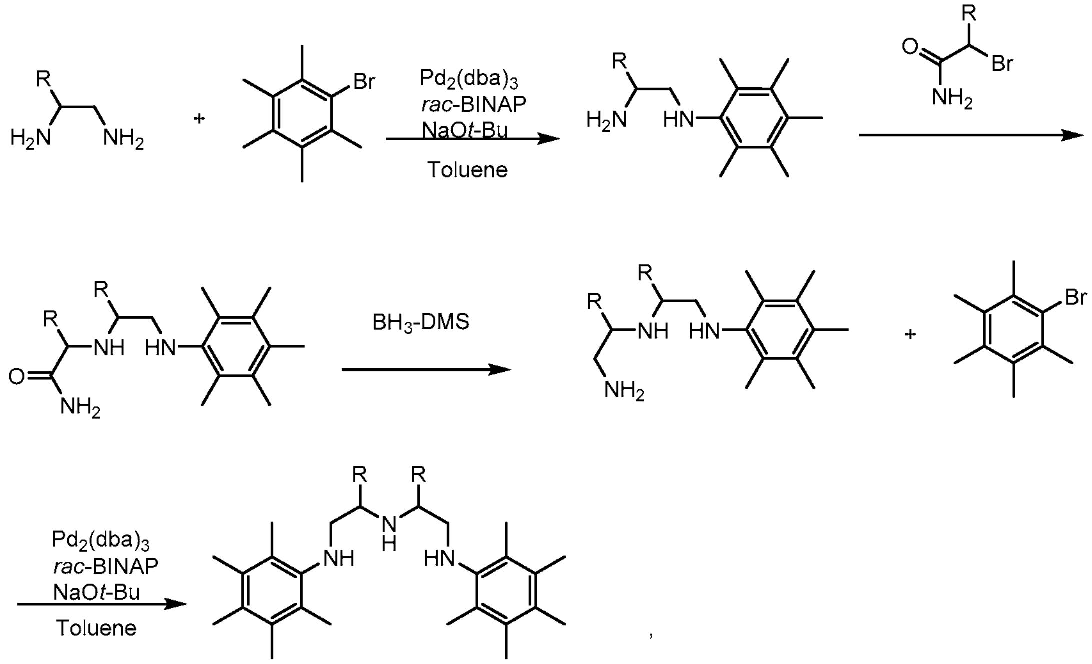
10. The polymerization catalyst system of claim 1, comprising a slurry mixture.

11. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:



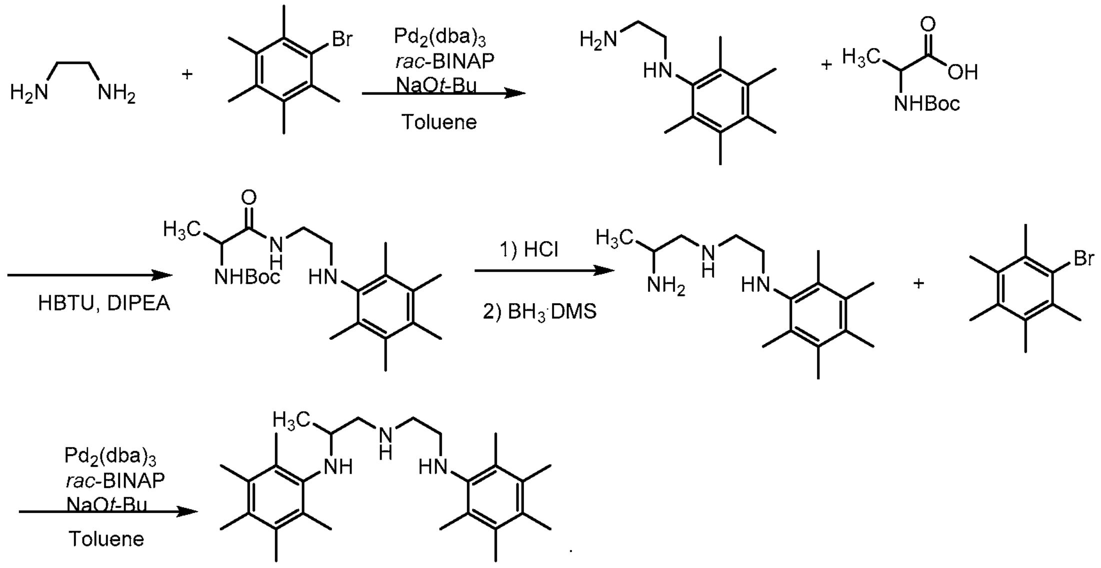
wherein each R is, independently, a methyl group or a hydrogen, and at least one R is a methyl group.

12. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:

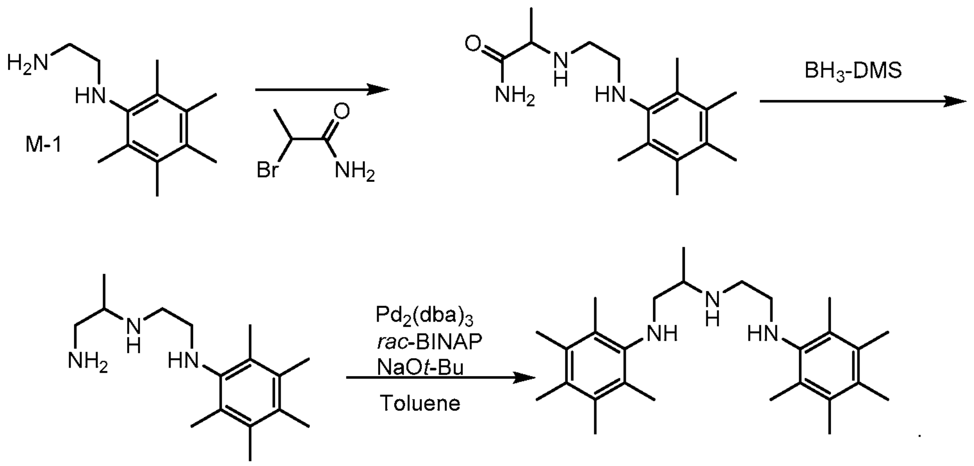


wherein each R is, independently, a methyl group or a hydrogen, and at least one R is a methyl group.

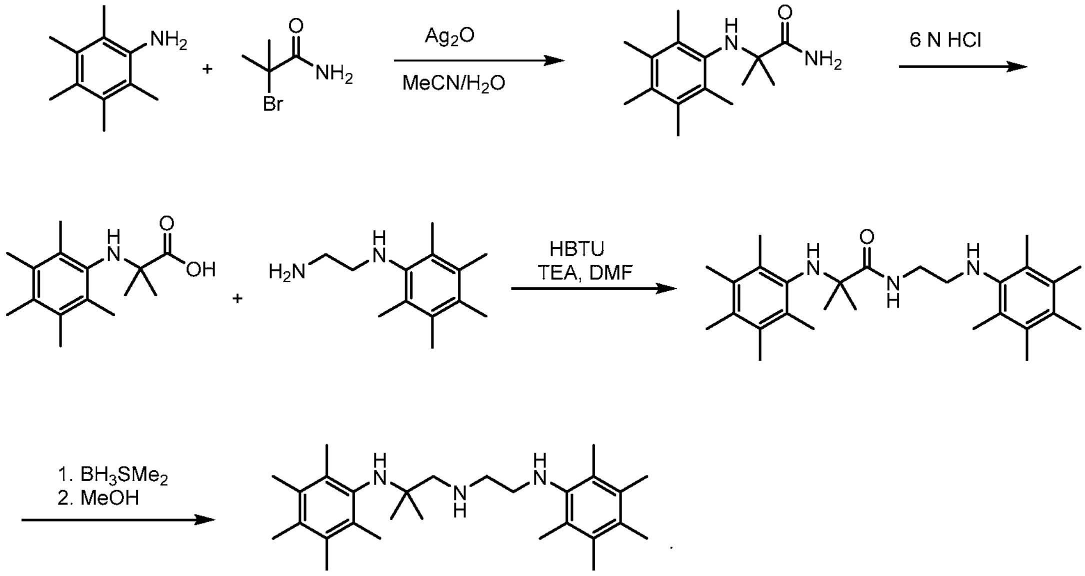
13. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:



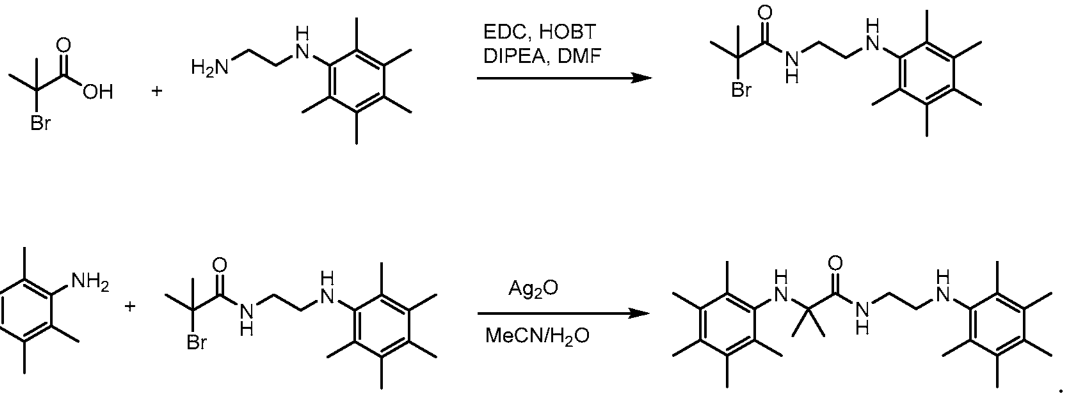
14. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:



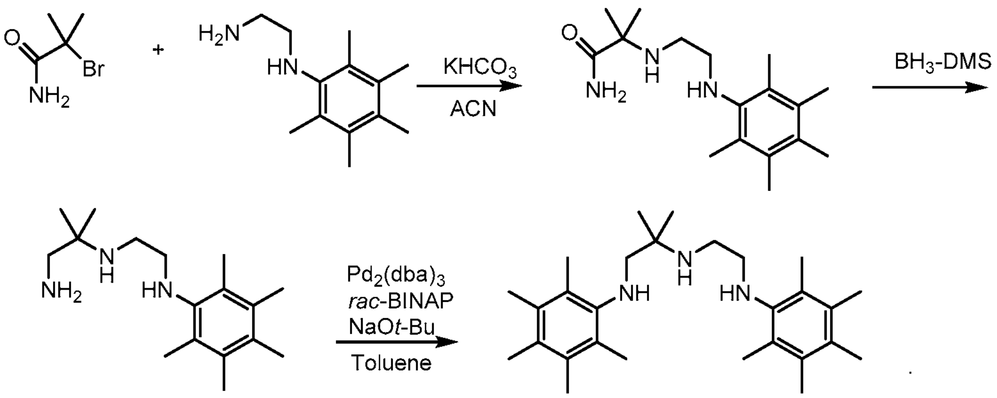
15. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:



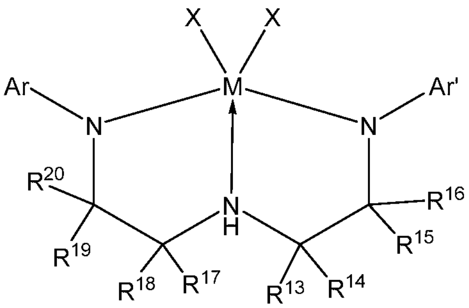
16. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:



17. The polymerization catalyst system of claim 1, comprising a component formed by a reaction sequence comprising:

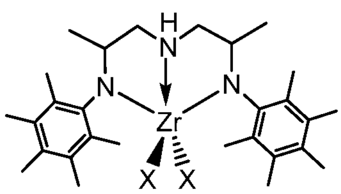


18. A method for generating a polyethylene polymer, comprising reacting at least ethylene with a catalyst system comprising:



wherein M is a group 4 element, each of R^{13}-R^{20} are independently a hydrogen or a methyl group, wherein at least one of R^{13}-R^{20} is a methyl group, Ar is an aryl group or a substituted aryl group, Ar’ is an aryl group or a substituted aryl group, and each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

19. The method of claim 18, wherein the catalyst system comprises a compound with the formula:



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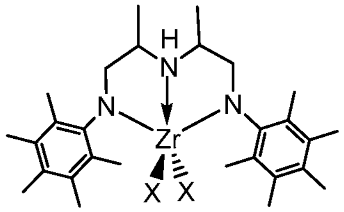

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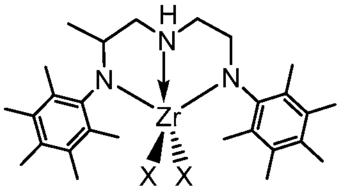

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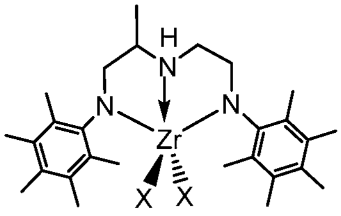

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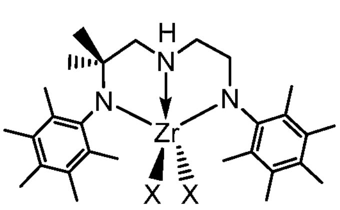

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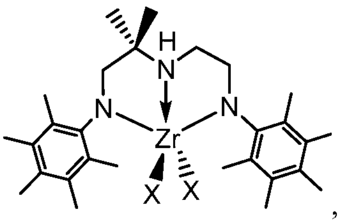


,

wherein each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

20. The method of claim 18, wherein the catalyst system comprises bis(n-butylcyclopentadienyl) zirconium$(X)_2$, wherein each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

21. The method of claim 18, wherein the catalyst system comprises (n-propylcyclopentadienyl, tetramethylcyclopentadienyl) zirconium$(X)_2$, wherein each X is, independently, a hydride group, an amide, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

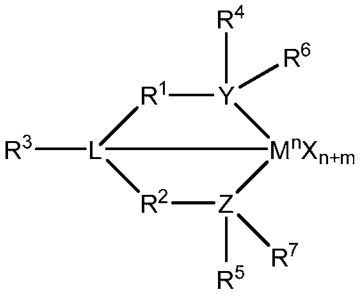
22. The method of claim 18, wherein the catalyst system comprises [(pentamethylbenzylN(CH_2CH_2))(pentamethylbenzylN$CH_2CH(CH_3)$)NH]Zr$(X)_2$, wherein each X is, independently, a hydride group, a benzyl group, a methyl group, a chloro group, a fluoro group, or a hydrocarbyl group.

23. The method of claim 18, wherein the catalyst system comprises a catalyst of the formula:

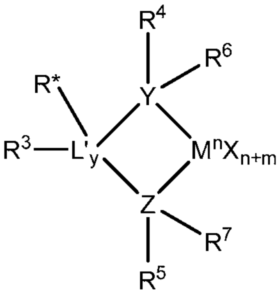
$$Cp^ACp^BMX_n \text{ or } Cp^A(A)Cp^BMX_n,$$

wherein M is a Group 4, 5, or 6 atom; Cp^A and Cp^B are each bound to M and are independently selected from the group consisting of cyclopentadienyl ligands, substituted cyclopentadienyl ligands, ligands isolobal to cyclopentadienyl and substituted ligands isolobal to cyclopentadienyl; (A) is a divalent bridging group bound to both Cp^A and Cp^B selected from the group consisting of divalent C_1 to C_{20} hydrocarbyls and C_1 to C_{20} heteroatom containing hydrocarbonyls, wherein the heteroatom containing hydrocarbonyls comprise from one to three heteroatoms; X is a leaving group selected from the group consisting of chloride ions, bromide ions, C_1 to C_{10} alkyls, and C_2 to C_{12} alkenyls, carboxylates, acetylacetonates, and alkoxides; and n is an integer from 1 to 3.

24. The method of claim 18, wherein the catalyst system comprises a catalyst of the formula:



; or



,

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; y is 0 or 1; n is the oxidation state of M; m is the formal charge of the ligand represented by YZL or YZL'; L is a Group 15 or 16 element; L' is a group 15 or 16 element or Group 14 containing group; Y is a Group 15 element; Z is a Group 15 element; R^1 and R^2 are independently a C_1 to C_{20} hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus; R^1 and R^2 may be interconnected to each other; R^3 is absent, a hydrocarbon group, hydrogen, a halogen, or a heteroatom containing group; R^4 and R^5 are independently an alky group, 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 a multiple ring system; R^4 and R^5 may be interconnected to each other; R^6 and R^7 are independently absent, hydrogen, an alkyl group, a halogen, a heteroatom, or a hydrocarbyl group; and R^* is absent, hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group.

25. The method of claim 18, comprising reacting a comonomer comprising an alpha olefin with the ethylene and the catalyst system.

26. The method of claim 25, wherein the comonomer comprises four to eight carbons.

27. The method of claim 18, comprising forming polymer in a gas phase polymerization reactor.

28. The method of claim 18, comprising forming polymer in a slurry phase polymerization reactor.

29. The method of claim 18, comprising:

measuring a sample of the polyethylene polymer to obtain an initial product property; and

changing a process parameter to obtain a second product property, based, at least in part, on the initial product property.

30. The method of claim 29, wherein measuring a sample of the polyolefin polymer comprises measuring comonomer incorporation as a function of a molecular weight.

31. The method of claim 29, wherein measuring a sample comprises determining a physical property of a plastic sample.

32. The method of claim 29, wherein measuring a sample comprises determining a flow index, a melt index, a density, a molecular weight distribution, a comonomer content, or any combinations thereof.

33. The method of claim 18, comprising adjusting the ratio of a comonomer to ethylene within a polymerization reactor to control at least one of the composition distribution, the molecular weight distribution, and the melt index (I_2) of a polyethylene.

34. The method of claim 18, comprising adjusting the ratio of the hydrogen to ethylene within a polymerization reactor to control at least one of the composition distribution, the molecular weight distribution, and the melt index (I_2) of a polyethylene.

35. The method of claim 18, comprising adjusting the ratio of a metallocene catalyst to the non-metallocene catalyst to control at least one of the composition distribution, the molecular weight distribution, and the melt index (I_2) of a polyethylene.

36. The method of claim 18, comprising forming a catalyst system comprising a metallocene catalyst and the non-metallocene catalyst.

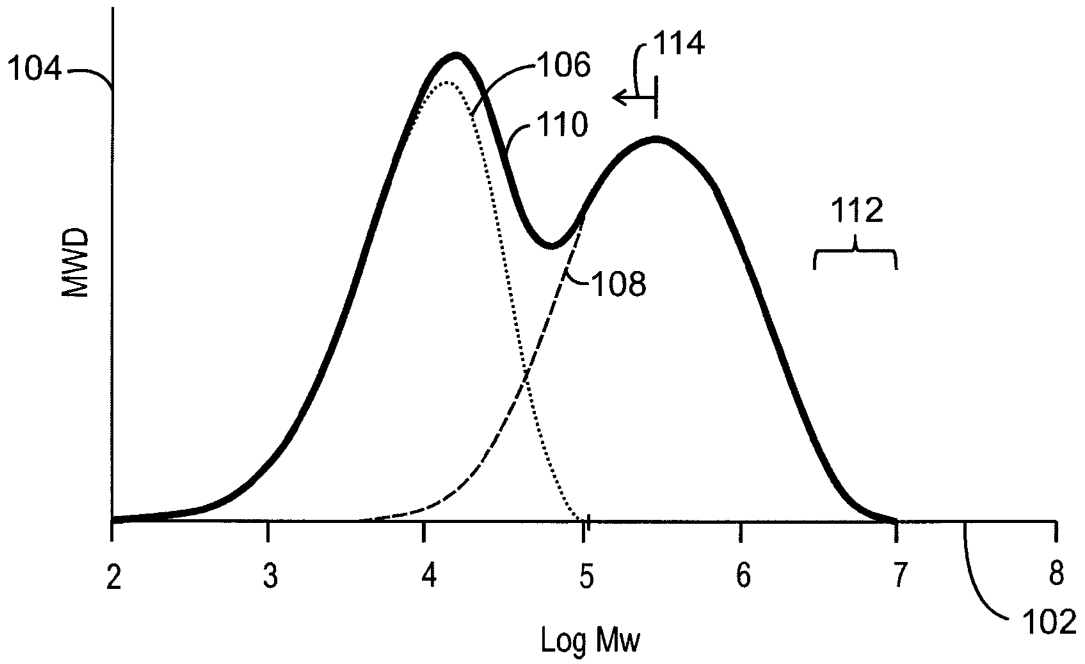


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FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/017671

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F10/00 C08F4/6592 C07F7/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/132811 A1 (UNIVATION TECH LLC [US]; KAO SUN-CHUEH [US]; RIX FRANCIS C [US]; LI DO) 18 November 2010 (2010-11-18) page 40 - page 44 paragraph [0176] - paragraph [0178] figure 5 6 -----	1-10, 18-28,36
A	WO 2011/103402 A1 (UNIVATION TECH LLC [US]; CANN KEVIN J [US]; HARLAN C JEFF [US]; MARIOT) 25 August 2011 (2011-08-25) examples -----	1-10, 18-28,36

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* 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

Date of the actual completion of the international search 16 May 2014	Date of mailing of the international search report 01/09/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Parry, Julian

International application No.
PCT/US2014/017671

INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-10, 18-28, 36(all partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10, 18-28, 36(all partially)

   the subject matter of claims 1-10, 18-28 and 36 excluding the subject matter of claims 11-17 and 29-35

   ---

2. claims: 11(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim 11

   ---

3. claims: 12(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim 12

   ---

4. claims: 13(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim 13

   ---

5. claims: 14(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim14

   ---

6. claims: 15(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim 15

   ---

7. claims: 16(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim 16

   ---

8. claims: 17(completely); 1-10, 18-28, 36(partially)

   the subject matter of claims 1-10,18-28 and 36 insofar as it relates to claim 17

   ---

9. claim: 29(partially)

   the subject matter of claim 29 excluding the subject matter of claims 30-35

---

10. claims: 30(completely); 29(partially)

    the subject matter of claim 29 insofar as it relates to claim 30

---

11. claims: 31(completely); 29(partially)

    the subject matter of claim 29 insofar as it relates to claim 31

---

12. claims: 32(completely); 29(partially)

    the subject matter of claim 29 insofar as it relates to claim 32

---

13. claims: 33(completely); 29(partially)

    the subject matter of claim 29 insofar as it relates to claim 33

---

14. claims: 34(completely); 29(partially)

    the subject matter of claim 29 insofar as it relates to claim 34

---

15. claims: 35(completely); 29(partially)

    the subject matter of claim 29 insofar as it relates to claim 35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/017671

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010132811 A1	18-11-2010	CA 2757045 A1	18-11-2010
		CN 102414228 A	11-04-2012
		EP 2430053 A1	21-03-2012
		US 2012046428 A1	23-02-2012
		WO 2010132811 A1	18-11-2010
WO 2011103402 A1	25-08-2011	AU 2011217940 A1	13-09-2012
		CA 2789687 A1	25-08-2011
		CN 102770467 A	07-11-2012
		EP 2539377 A1	02-01-2013
		JP 2013520556 A	06-06-2013
		KR 20130026531 A	13-03-2013
		RU 2012140372 A	27-03-2014
		SG 183293 A1	27-09-2012
		US 2013035463 A1	07-02-2013
		WO 2011103402 A1	25-08-2011