

ASYMMETRICAL METALLOCENES HAVING AN ISOBUTYL CYCLOPENTADIENYL LIGAND

Field of Disclosure

[0001] Embodiments of the present disclosure are directed towards asymmetrical metallocenes, catalyst compositions including asymmetrical metallocenes, methods of making and using same, and polyolefins made thereby.

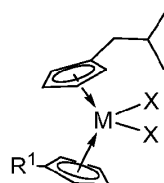
Background

[0002] Metallocenes can be used in various applications, including as polymerization catalysts. Polymers may be utilized for a number of products including films, among others. Polymers can be formed by reacting one or more types of monomer in a polymerization reaction. There is continued focus in the industry on developing new and improved materials and/or processes that may be utilized to form polymers.

Summary

[0003] The present disclosure provides various embodiments, including the following.

[0004] As asymmetrical metallocene represented by structure (I):



[0005] wherein: M is Hf or Zr; R¹, is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl; and each X is independently a leaving group; wherein the (C₄)alkyl except 2-methylpropyl is selected from butyl, 1-methylpropyl, and 1,1-dimethylethyl.

[0006] An asymmetrical metallocene catalyst composition comprising the asymmetrical metallocene and an activator.

[0007] A method of making the asymmetrical metallocene catalyst composition, the method comprising contacting the asymmetrical metallocene with the activator.

[0008] A method of making a polyolefin polymer, the method comprising polymerizing at least one olefin monomer with the asymmetrical metallocene catalyst composition to make the polyolefin polymer.

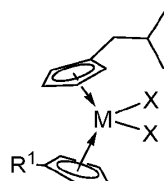
Brief Description of the Drawings

[0009] Figure 1A and Figure 1B show data plots utilized to determine molecular weight comonomer distribution index (MWCDI) in accordance a number of embodiments of the present disclosure.

Detailed Description

[0010] Asymmetrical metallocenes having an isobutyl cyclopentadienyl ligand are discussed herein. Advantageously, these asymmetrical metallocenes can be utilized to make catalyst compositions, for instance. These catalyst compositions can be utilized to make polymers having an improved, i.e., greater, molecular weight comonomer distribution index (MWCDI) as compared to other polymers, made from other metallocenes. These polymers are desirable for a number of applications, including films, among others. As such, providing an improved MWCDI is advantageous. Such polymers are advantageous for a number of applications.

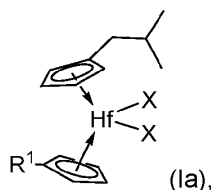
[0011] The asymmetrical metallocenes have an isobutyl cyclopentadienyl ligand and can be represented by structure (I):



wherein: M is Hf or Zr; R¹ is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl; and each X is independently a leaving group; wherein the (C₄)alkyl except 2-methylpropyl is selected from butyl, 1-methylpropyl, and 1,1-dimethylethyl. As shown in structure (I), the upper cyclopentadienyl ring is substituted with an isobutyl group, also called a 2-methylpropyl group, which has the monovalent structure -CH₂CH(CH₃)₂.

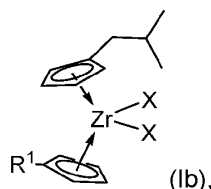
[0012] One or more embodiments of the present disclosure provide that M is Hf. One or more embodiments of the present disclosure provide that M is Zr.

[0013] For instance, one or more embodiments provide that M is Hf and the asymmetrical metallocene is represented by structure (Ia):



[0014] wherein: R¹ is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl; and each X is independently a leaving group selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl. One or more embodiments provide X is selected from Cl, (C₁-C₃)alkyl, and benzyl. One or more embodiments provide X is CH₃.

[0015] One or more embodiments provide that M is Zr and the asymmetrical metallocene is represented by structure (Ib):



[0016] wherein: R¹ is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl; and each X is independently a leaving group selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl. One or more embodiments provide X is selected from Cl, (C₁-C₃)alkyl, and benzyl. One or more embodiments provide X is CH₃.

[0017] One or more embodiments of the present disclosure provide that the ligands of the cyclopentadienyl ring having the isobutyl cyclopentadienyl ligand, shown in structure (I), are different than the ligands of the cyclopentadienyl ring including R¹. As such, the asymmetrical metallocenes discussed herein can be referred to as having nonidentical ligands. As an example, embodiments provide that R¹ is not an isobutyl group.

[0018] One or more embodiments provide that R¹ is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl. One or more embodiments provide that R¹ is a (C₅)alkyl. One or more embodiments provide that R¹ is a (C₄)alkyl except 2-methylpropyl. One or more embodiments provide that R¹ is a (C₁-C₃)alkyl. One or more embodiments provide that R¹ is a (C₁-C₂)alkyl. One or more embodiments provide that R¹ is a (C₃)alkyl. The (C₃)alkyl may be branched or linear. As used herein "Pr" and "n-

Pr" refer to CH₂CH₂CH₃. One or more embodiments of the present disclosure provide that R¹ is a (C₂)alkyl. One or more embodiments of the present disclosure provide that R¹ is a (C₂)alkyl. One or more embodiments of the present disclosure provide that R¹ is a (C₃)alkyl, ethyl, or methyl; wherein the (C₃)alkyl is selected from 1-methylethyl and propyl.

[0019] Embodiments of the present disclosure provide that X is a leaving group. One or more embodiments provide that X is selected from alkyls, aryls, hydrides, and halogens. One or more embodiments provide that X is selected from alkyls and halogens. One or more embodiments provide that X is Cl. One or more embodiments provide that X is methyl. One or more embodiments provide that X is selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl.

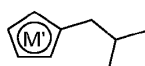
[0020] Examples of X include halogen ions, hydrides, (C₁ to C₁₂)alkyls, (C₂ to C₁₂)alkenyls, (C₆ to C₁₂)aryl, (C₇ to C₂₀)alkylaryl, (C₁ to C₁₂)alkoxys, (C₆ to C₁₆)aryloxys, (C₇ to C₈)alkylaryloxys, (C₁ to C₁₂)fluoroalkyls, (C₆ to C₁₂)fluoroaryl, and (C₁ to C₁₂)heteroatom-containing hydrocarbons and substituted derivatives thereof; one or more embodiments include hydrides, halogen ions, (C₁ to C₆)alkyls, (C₂ to C₆)alkenyls, (C₇ to C₁₈)alkylaryl, (C₁ to C₆)alkoxys, (C₆ to C₁₄)aryloxys, (C₇ to C₁₆)alkylaryloxys, (C₁ to C₆)alkylcarboxylates, (C₁ to C₆)fluorinated alkylcarboxylates, (C₆ to C₁₂)arylcarboxylates, (C₇ to C₁₈)alkylarylcarboxylates, (C₁ to C₆)fluoroalkyls, (C₂ to C₆)fluoroalkenyls, and (C₇ to C₁₈)fluoroalkylaryl; one or more embodiments include hydride, chloride, fluoride, methyl, phenyl, phenoxy, benzoxy, tosyl, fluoromethyls and fluorophenyls; one or more embodiments include (C₁ to C₁₂)alkyls, (C₂ to C₁₂)alkenyls, (C₆ to C₁₂)aryl, (C₇ to C₂₀)alkylaryl, substituted (C₁ to C₁₂)alkyls, substituted (C₆ to C₁₂)aryl, substituted (C₇ to C₂₀)alkylaryl, and (C₁ to C₁₂)heteroatom-containing alkyls, (C₁ to C₁₂)heteroatom-containing aryls, and (C₁ to C₁₂)heteroatom-containing alkylaryl; one or more embodiments include chloride, fluoride, (C₁ to C₆)alkyls, (C₂ to C₆)alkenyls, (C₇ to C₁₈)alkylaryl, halogenated (C₁ to C₆)alkyls, halogenated (C₂ to C₆)alkenyls, and halogenated (C₇ to C₁₈)alkylaryl; one or more embodiments include fluoride, methyl, ethyl, propyl, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl,

fluoromethyls (mono-, di- and trifluoromethyls) and fluorophenyls (mono-, di-, tri-, tetra- and pentafluorophenyls).

[0021] 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., $-\text{C}_6\text{F}_5$ (pentafluorophenyl), fluorinated alkylcarboxylates, e.g., $\text{CF}_3\text{C}(\text{O})\text{O}-$, hydrides, halogen ions and combinations thereof. Other examples of X ligands include alkyl groups such as cyclobutyl, cyclohexyl, methyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methylenedichloride, methoxy, ethoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, and dimethylphosphide radicals, among others. In one embodiment, two or more X's form a part of a fused ring or ring system. In one or more embodiments, X can be a leaving group selected from the group consisting of chloride ions, bromide ions, $(\text{C}_1 \text{ to } \text{C}_{10})$ alkyls, $(\text{C}_2 \text{ to } \text{C}_{12})$ alkenyls, carboxylates, acetylacetonates, and alkoxides. In one or more embodiments, X is methyl.

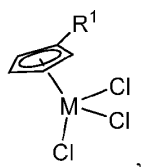
[0022] The asymmetrical metallocenes discussed herein can be made by contacting a Hf complex or a Zr complex with an alkali metal complex to make the asymmetrical metallocenes. As an example, the alkali metal complex can be a lithium complex, such as *iso*-butylcyclopentadienyl lithium, methylcyclopentadienyl lithium, ethylcyclopentadienyl lithium, *n*-propylcyclopentadienyl lithium, among others. The asymmetrical metallocenes discussed herein can be made by processes, e.g., with conventional solvents, reaction conditions, reaction times, and isolation procedures, utilized for making known metallocenes.

[0023] The alkali metal complex can be represented by the following structure:



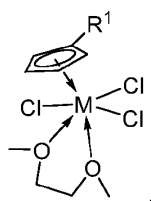
[0024] wherein M' is lithium, sodium, or potassium.

[0025] One or more embodiments provide that the hafnium complex or the zirconium complex can be represented by the following structure:



wherein M is Hf or Zr, respectively, and R¹ is as defined as discussed herein (e.g., R¹ is propyl).

[0026] One or more embodiments provide that the hafnium complex or the zirconium complex can be represented by the following structure:



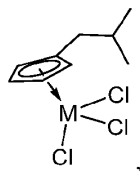
wherein M is Hf or Zr, respectively, and R¹ is as defined as discussed herein (e.g., R¹ is propyl).

[0027] The alkali metal complex can be represented by the following structure:



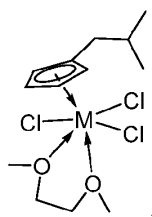
wherein M' is lithium, sodium, or potassium, and R¹ is as defined as discussed herein (e.g., R¹ is propyl).

[0028] One or more embodiments provide that the hafnium complex or the zirconium complex can be represented by the following structure:



wherein M is Hf or Zr, respectively.

[0029] One or more embodiments provide that the hafnium complex or the zirconium complex can be represented by the following structure:



wherein M is Hf or Zr, respectively.

[0030] One or more embodiments provide that a method of making the asymmetrical metallocene, e.g., where each X is Cl, comprises contacting the

asymmetrical metallocene with two mole equivalents of an organomagnesium halide of formula $\text{RMg}(\text{halide})$ or one mole equivalent of R_2Mg , wherein R is $(\text{C}_1\text{-C}_5)\text{alkyl}$, CH_2SiMe_3 , or benzyl; and the halide is Cl or Br, to make the asymmetrical metallocene of structure (I) wherein each X is a $(\text{C}_1\text{-C}_5)\text{alkyl}$, CH_2SiMe_3 , or benzyl. One or more embodiments provide X is CH_3 .

[0031] 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.

[0032] As used herein, an "alkyl" includes linear, branched and cyclic paraffin radicals that are deficient by one hydrogen. Thus, for example, CH_3 ("methyl") and CH_2CH_3 ("ethyl") are examples of alkyls.

[0033] As used herein, an "alkenyl" includes linear, branched and cyclic olefin radicals that are deficient by one hydrogen; alkynyl radicals include linear, branched and cyclic acetylene radicals deficient by one hydrogen radical.

[0034] As used herein, "aryl" groups include phenyl, naphthyl, pyridyl and other radicals whose molecules have the ring structure characteristic of benzene, naphthylene, phenanthrene, anthracene, etc. It is understood that an "aryl" group can be a C_6 to C_{20} aryl group. For example, a C_6H_5 aromatic structure is an "phenyl", a C_6H_4 2 aromatic structure is an "phenylene". An "arylalkyl" group is an alkyl group having an aryl group pendant therefrom. It is understood that an "aralkyl" group can be a $(\text{C}_7$ to $\text{C}_{20})$ aralkyl group. An "alkylaryl" is an aryl group having one or more alkyl groups pendant therefrom.

[0035] As used herein, an "alkylene" includes linear, branched and cyclic hydrocarbon radicals deficient by two hydrogens. Thus, CH_2 ("methylene") and CH_2CH_2 ("ethylene") are examples of alkylene groups. Other groups deficient by two hydrogen radicals include "arylene" and "alkenylene".

[0036] As used herein, the term "heteroatom" includes any atom selected from the group consisting of B, Al, Si, Ge, N, P, O, and S. A "heteroatom-containing group" is a hydrocarbon radical that contains a heteroatom and may contain one or more of the

same or different heteroatoms, and from 1 to 3 heteroatoms in a particular embodiment. Non-limiting examples of heteroatom-containing groups include radicals (monoradicals and diradicals) of imines, amines, oxides, phosphines, ethers, ketones, oxazolines, heterocyclics, oxazolines, and thioethers.

[0037] As used herein, the term "substituted" means that one or more hydrogen atoms in a parent structure has been independently replaced by a substituent atom or group.

[0038] The asymmetrical metallocenes discussed herein can be utilized to make catalyst compositions. These asymmetrical metallocene compositions include the asymmetrical metallocene having an isobutyl cyclopentadienyl ligand and an activator. One or more embodiments provide that the activator is an alkylaluminoxane such as methylaluminoxane. As used herein, "activator" refers to any compound or combination of compounds, supported, or unsupported, which can activate a complex or a catalyst 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, e.g., the "X" groups described herein, from the metal center of the complex/catalyst component, e.g., the asymmetrical metallocene of structure (I). The activator may also be referred to as a "co-catalyst". As used herein, "leaving group" refers to one or more chemical moieties bound to a metal atom and that can be abstracted by an activator, thus producing a species active towards olefin polymerization. Various catalyst compositions, e.g., olefin polymerization catalyst compositions, are known in the art and different known catalyst composition components may be utilized. Various amounts of known catalyst composition components may be utilized for different applications.

[0039] The asymmetrical metallocenes discussed herein can be utilized to make spray-dried compositions. As used herein, "spray-dried composition" refers to a composition that includes a number of components that have undergone a spray-drying process. Various spray-drying process are known in the art and are suitable for forming the spray-dried compositions disclosed herein. One or more embodiments provide that the spray-dried composition comprises a trim composition.

[0040] In one or more embodiments, the spray-drying process may comprise atomizing a composition including the asymmetrical metallocene having an isobutyl cyclopentadienyl ligand. A number of other known components may be utilized in the spray-drying process. An atomizer, such as an atomizing nozzle or a centrifugal high speed disc, for example, may be used to create a spray or dispersion of droplets of the

composition. The droplets of the composition may then be rapidly dried by contact with an inert drying gas. The inert drying gas may be any gas that is non-reactive under the conditions employed during atomization, such as nitrogen, for example. The inert drying gas may meet the composition at the atomizer, which produces a droplet stream on a continuous basis. Dried particles of the composition may be trapped out of the process in a separator, such as a cyclone, for example, which can separate solids formed from a gaseous mixture of the drying gas, solvent, and other volatile components.

[0041] A spray-dried composition may have the form of a free-flowing powder, for instance. After the spray-drying process, the spray-dried composition and a number of known components may be utilized to form a slurry. The spray-dried composition may be utilized with a diluent to form a slurry suitable for use in olefin polymerization, for example. In one or more embodiments, the slurry may be combined with one or more additional catalysts or other known components prior to delivery into a polymerization reactor.

[0042] In one or more embodiments, the spray-dried composition may be formed by contacting a spray dried activator particle, such as spray dried MAO, with a solution of the asymmetrical metallocene having an isobutyl cyclopentadienyl ligand. Such a solution typically may be made in an inert hydrocarbon solvent, for instance, and is sometimes called a trim solution. Such a spray-dried composition comprised of contacting a trim solution of the asymmetrical metallocene with a spray dried activator particle, such as spray-dried MAO, may be made *in situ* in a feed line heading into a gas phase polymerization reactor by contacting the trim solution with a slurry, typically in mineral oil, of the spray-dried activator particle.

[0043] Various spray-drying conditions may be utilized for different applications. For instance, the spray-drying process may utilize a drying temperature from 75 to 185 °C. Other drying temperatures are possible, where the temperature can depend on the metallocene and activator. Various sizes of orifices of the atomizing nozzle employed during the spray-drying process may be utilized to obtain different sizes. Alternatively, for other types of atomizers such as discs, rotational speed, disc size, and number/size of holes may be adjusted to obtain different sizes. One or more embodiments provide that a filler may be utilized in the spray-drying process. Different fillers and amounts thereof may be utilized for various applications.

[0044] The asymmetrical metallocenes discussed herein, e.g., catalyst compositions, such as the spray-dried asymmetrical metallocene composition, may be

utilized to make a polymer. For instance, the asymmetrical metallocene may be activated, i.e., with an activator, to make an asymmetrical metallocene catalyst. One or more embodiments provide that the spray-dried compositions include an activator. As used herein, "activator" refers to any compound or combination of compounds, supported, or unsupported, which can activate a complex or a catalyst component, such as by creating a cationic species of the catalyst component, e.g., to provide the catalyst. The activator may also be referred to as a "co-catalyst". 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. Activators include methylaluminoxane (MAO) and modified methylaluminoxane (MMAO), among others. One or more embodiments provide that the activator is methylaluminoxane. Activating conditions are well known in the art. Known activating conditions may be utilized.

[0045] A molar ratio of metal, e.g., aluminum, in the activator to Hf or Zr in the asymmetrical metallocene having an isobutyl cyclopentadienyl ligand may be 1500: 1 to 0.5: 1, 300: 1 to 1: 1, or 150: 1 to 1: 1. One or more embodiments provide that the molar ratio of in the activator to Hf or Zr in the asymmetrical metallocene is at least 75:1. One or more embodiments provide that the molar ratio of in the activator to Hf or Zr in the asymmetrical metallocene is at least 100:1. One or more embodiments provide that the molar ratio of in the activator to Hf or Zr in the asymmetrical metallocene is at least 150:1.

[0046] The asymmetrical metallocenes having an isobutyl cyclopentadienyl ligand, as well as a number of other components discussed herein, can be supported on the same or separate supports, or one or more of the components may be used in an unsupported form. Utilizing the support may be accomplished by any technique used in the art. One or more embodiments provide that the spray-dry process is utilized. The support may be functionalized. One or more embodiments provide that the spray-dried compositions include a support.

[0047] A "support", which may also be referred to as a "carrier", refers to any support material, including a porous support material, such as talc, inorganic oxides, and inorganic chlorides. Other support materials include resinous support materials, e.g., polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

[0048] Support materials include inorganic oxides that include Group 2, 3, 4, 5, 13 or 14 metal oxides. Some preferred supports include silica, fumed silica, alumina, silica-alumina, and mixtures thereof. Some other supports include magnesia, titania, zirconia, magnesium chloride, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like. One or more embodiments provide that the support is hydrophobic fumed silica. Additional support materials may include porous acrylic polymers, nanocomposites, aerogels, spherulites, and polymeric beads. An example of a support is fumed silica available under the trade name Cabosil™ TS- 610, or other TS- or TG-series supports, available from Cabot Corporation. Fumed silica is typically a silica with particles 7 to 30 nanometers in size that has been treated with dimethylsilyldichloride such that a majority of the surface hydroxyl groups are capped.

[0049] The asymmetrical metallocenes discussed herein, e.g., the catalyst compositions/spray-dried asymmetrical metallocene compositions, and an olefin can be contacted under polymerization conditions to make a polymer, e.g., a polyolefin polymer. The polymerization process may be a solution polymerization process, a suspension polymerization process, a slurry polymerization process, and/or a gas phase polymerization process. The polymerization process may utilize using known equipment and reaction conditions, e.g., known polymerization conditions. The polymerization process is not limited to any specific type of polymerization system. The polymer can be utilized for a number of articles such as films, fibers, nonwoven and/or woven fabrics, extruded articles, and/or molded articles.

[0050] One or more embodiments provide that the polymers are made utilizing a gas-phase reactor system. One or more embodiments provide that a single gas-phase reactor, e.g., in contrast to a series of reactors, is utilized. In other words, polymerization reaction occurs in only one reactor. For instance, the polymers can be made utilizing a fluidized bed reactor. Gas-phase reactors are known and known components may be utilized for the fluidized bed reactor.

[0051] As used herein an “olefin,” which may be referred to as an “alkene,” refers to a linear, branched, or cyclic compound including carbon and hydrogen and having at least one double bond. As used herein, when a polyolefin, polymer, and/or copolymer is referred to as comprising, e.g., being made from, an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an ethylene content of 75 wt% to 95 wt%, it is understood that

the polymer unit in the copolymer is derived from ethylene in the polymerization reaction(s) and the derived units are present at 75 wt% to 95 wt%, based upon the total weight of the polymer. A higher α -olefin refers to an α -olefin having 3 or more carbon atoms.

[0052] Polyolefins made with the compositions discussed herein can be made from olefin monomers such as ethylene (*i.e.*, polyethylene), or propylene (*i.e.*, polypropylene), among other provided herein, where the polyolefin is a homopolymer made only from the olefin monomer (e.g., made with 100 wt.% ethylene or 100 wt.% propylene). Alternatively, polyolefins made with the compositions discussed herein can be made from olefin monomers such as ethylene, *i.e.*, polyethylene, and linear or branched higher alpha-olefin monomers containing 3 to 20 carbon atoms. Examples of higher alpha-olefin monomers include, but are not limited to, propylene, butene, pentene, 1-hexene, and 1-octene. Examples of polyolefins include ethylene-based polymers, having at least 50 wt % ethylene, including ethylene-1-butene, ethylene-1-hexene, and ethylene-1-octene copolymers, among others. One or more embodiments provide that the polymer can include from 50 to 99.9 wt % of units derived from ethylene based on a total weight of the polymer. All individual values and subranges from 50 to 99.9 wt % are included; for example, the polymer can include from a lower limit of 50, 60, 70, 80, or 90 wt % of units derived from ethylene to an upper limit of 99.9, 99.7, 99.4, 99, 96, 93, 90, or 85 wt % of units derived from ethylene based on the total weight of the polymer. The polymer can include from 0.1 to 50 wt % of units derived from comonomer based on the total weight of the polymer. One or more embodiments provide that ethylene is utilized as a monomer and hexene is utilized as a comonomer.

[0053] As mentioned, the polymers made with the compositions disclosed herein can be made in a fluidized bed reactor. The fluidized bed reactor can have a reaction temperature from 10 to 130 °C. All individual values and subranges from 10 to 130 °C are included; for example, the fluidized bed reactor can have a reaction temperature from a lower limit of 10, 20, 30, 40, 50, or 55 °C to an upper limit of 130, 120, 110, 100, 90, 80, 70, or 60 °C.

[0054] The fluidized bed reactor can have an ethylene partial pressure from 30 to 250 pounds per square inch (psi). All individual values and subranges from 30 to 250 are included; for example, the fluidized bed reactor can have an ethylene partial pressure from a lower limit of 30, 45, 60, 75, 85, 90, or 95 psi to an upper limit of 250, 240, 220, 200, 150, or 125 psi.

[0055] One or more embodiments provide that ethylene is utilized as a monomer and hexene is utilized as a comonomer. The fluidized bed reactor can have a comonomer to ethylene mole ratio, e.g., C_6/C_2 , from 0.0001 to 0.100. All individual values and subranges from 0.0001 to 0.100 are included; for example, the fluidized bed reactor can have a comonomer to ethylene mole ratio from a lower limit of 0.0001, 0.0005, 0.0007, 0.001, 0.0015, 0.002, 0.007, or 0.010 to an upper limit of 0.100, 0.080, or 0.050.

[0056] When hydrogen is utilized for a polymerization process, the fluidized bed reactor can have a hydrogen to ethylene mole ratio (H_2/C_2) from 0.00001 to 0.90000, for instance. All individual values and subranges from 0.00001 to 0.90000 are included; for example, the fluidized bed reactor can have a H_2/C_2 from a lower limit of 0.00001, 0.00005, or 0.00008 to an upper limit of 0.90000, 0.500000, 0.10000, 0.01500, 0.00700, or 0.00500. One or more embodiments provide that hydrogen is not utilized.

[0057] A number of polymer properties may be determined utilizing Compositional Conventional Gel Permeation Chromatography. For instance, weight average molecular weight (M_w), number average molecular weight (M_n), Z-average molecular weight (M_z), and M_w/M_n (PDI) were determined using a chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 160 °C and the column compartment was set at 150 °C. The columns used were 4 Agilent "Mixed A" 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0058] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 g/mol and were arranged in 6 "cocktail" mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C for 30 minutes. The polystyrene standard peak

molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (EQ1)$$

where M is the molecular weight, A has a value of 0.4061 and B is equal to 1.0.

[0059] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[0060] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent "Mixed A" 30cm 20-micron linear mixed-bed columns.

[0061] Samples were prepared in a semi-automatic manner with the PolymerChar "Instrument Control" Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160 °C under "low speed" shaking.

[0062] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCONE software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

$$[0063] \quad Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (EQ 2)$$

$$[0064] \quad Mw_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ 3)$$

[0065]

$$Mz_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})}$$

(EQ 4)

[0066] To monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate_(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV_(FM Sample)) to that of the decane peak within the narrow standards calibration (RV_(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate_(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCONE Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

[0067]

Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample))

(EQ5)

[0068] IR5 GPC Octene Composition Calibration. A calibration for the IR5 detector rationing was performed using at least ten ethylene-based polymer standards (Octene as comonomer) made by single-site metallocene catalyst from a single reactor in solution process (polyethylene homopolymer and ethylene/octene copolymers) of a narrow SCB distribution and known comonomer content (as measured by ¹³C NMR Method, Qiu et al., Anal. Chem.2009, 81, 8585–8589), ranging from homopolymer (0 SCB/1000 total C) to approximately 40 SCB/1000 total C, where total C = carbons in backbone + carbons in branches. Each standard had a weight-average molecular weight from 36,000 g/mole to 126,000 g/mole measured by GPC. Each standard had a molecular weight distribution (Mw/Mn) from 2.0 to 2.5. Polymer properties for the SCB standards are shown in Table A.

Table A: "Copolymer" Standards

Wt % Comonomer	IR5 Area ratio	SCB / 1000 Total C	Mw	Mw/Mn
23.1	0.2411	28.9	37,300	2.22

14.0	0.2152	17.5	36,000	2.19
0.0	0.1809	0.0	38,400	2.20
35.9	0.2708	44.9	42,200	2.18
5.4	0.1959	6.8	37,400	2.16
8.6	0.2043	10.8	36,800	2.20
39.2	0.2770	49.0	125,600	2.22
1.1	0.1810	1.4	107,000	2.09
14.3	0.2161	17.9	103,600	2.20
9.4	0.2031	11.8	103,200	2.26

[0069] The “IR5 Area Ratio (or “IR5 Methyl Channel Area / IR5 Measurement Channel Area”)” of “the baseline-subtracted area response of the IR5 methyl channel sensor” to “the baseline-subtracted area response of IR5 measurement channel sensor” (standard filters and filter wheel as supplied by PolymerChar: Part Number IR5_FWM01 included as part of the GPC-IR instrument) was calculated for each of the “Copolymer” standards. A linear fit of the Wt% Comonomer frequency versus the “IR5 Area Ratio” was constructed in the form of the following Equation 6:

$$\text{Wt\% Comonomer} = A_0 + [A_1 \times (\text{IR5 Methyl Channel Area} / \text{IR5 Measurement Channel Area})] \quad (\text{EQ 6})$$

where A_0 is the “Wt% Comonomer” intercept at an “IR5 Area Ratio” of zero, and A_1 is the slope of the “Wt% Comonomer” versus “IR5 Area Ratio” and represents the increase in the Wt% Comonomer as a function of “IR5 Area Ratio.” The IR5 area ratio is equal to the IR5 height ratio for narrow PDI and narrow SCBD standard materials.

[0070] The comonomer distribution, or short chain branching distribution, in an ethylene/ α -olefin copolymer can be characterized as either normal (also referred to as having a Zeigler-Natta distribution), reverse, or flat. Several reported methods are utilized to quantify a Broad Orthogonal Composition Distribution (BOCD). Herein, a simple line fit is utilized such that the normal or reverse nature of the comonomer distribution can be quantified by the molecular weight comonomer distribution index (MWCDI), which is the slope of the linear regression of the comonomer distribution taken from a compositional GPC measurement, wherein the x-axis is Log(MW) and the y-axis is weight percent of comonomer. Figure 1A shows data plots utilized to determine MWCDI for Example 1-2 (MWCDI = 5.85) and Comparative Example A-2 (MWCDI = 3.60), as shown in Table 1 of the Examples section of the present application. Figure 1B shows data plots utilized to determine MWCDI for Example 1-2 (MWCDI = 2.13) and

Comparative Example A-2 (MWCDI = 1.67), as shown in Table 2 of the Examples section of the present application.

[0071] A reverse comonomer distribution is defined when the MWCDI > 0 and a normal comonomer distribution is defined when the MWCDI < 0. When the MWCDI = 0 the comonomer distribution is said to be flat. Additionally, the MWCDI quantifies the magnitude of the comonomer distribution. Comparing two polymers that have MWCDI > 0, the polymer with the greater MWCDI value is defined to have a greater, i.e., increased, BOCD; in other words, the polymer with the greater MWCDI value has a greater reverse comonomer distribution. For instance, as reported in respectively in Table 1 and Table 2, Example 1-2, Example 2-2, and Example 3-2 each has an increased BOCD as compared to Comparative Example A-2. Polymers with a relatively greater MWCDI, i.e. BOCD, can provide improved physical properties, such as improved film performance, as compared to polymers having a relatively lesser MWCDI.

[0072] The polymers made with the compositions disclosed herein can have a MWCDI from 0.05 to 10.00. All individual values and subranges from 0.10 to 10.00 are included; for example, the polymer can have a MWCDI from a lower limit of 0.05, 0.10, 0.30, 0.50, or 1.00 to an upper limit of 10.00, 9.00, 8.00, 8.50, 8.35, 7.00, or 6.00. For instance, one or more embodiments provide that the polymer can have a MWCDI from 0.05 to 6.00, 0.10 to 2.00, 0.50 to 3.00, 1.00 to 7.00, or 1.00 to 6.00, among other ranges.

[0073] The polymers made with the compositions disclosed herein can have a density from 0.8700 to 0.9700 g/cm³. All individual values and subranges from 0.8700 to 0.9700 g/cm³ are included; for example, the polymer can have a density from a lower limit of 0.8700, 0.9000, 0.9100, 0.9150, 0.9200, or 0.9250 g/cm³ to an upper limit of 0.9700, 0.9600, 0.9500, 0.9450, 0.9350, or 0.9300 g/cm³. Density can be determined by according to ASTM D792.

[0074] The polymers made with the compositions disclosed herein can have a melt index (I₂) from 0.0 to 10 dg/min. I₂ can be determined according to ASTM D1238 (190 °C, 2.16 kg). All individual values and subranges from 0.00 to 10 dg/min are included; for example, the polymer can have an I₂ from a lower limit of 0.0, 0.05, 0.07 or 0.10 dg/min to an upper limit of 10, 5, or 3 dg/min.

[0075] The polymers made with the compositions disclosed herein can have a melt index (I₅) from 0.05 to 15 dg/min. I₅ can be determined according to ASTM D1238

(190 °C, 5 kg). All individual values and subranges from 0.05 to 15 dg/min are included; for example, the polymer can have an I_5 from a lower limit of 0.05, 0.07 or 0.10 dg/min to an upper limit of 15, 10, or 5 dg/min.

[0076] The polymers made with the compositions disclosed herein can have a melt index (I_{21}) from 0.05 to 25 dg/min. I_{21} can be determined according to ASTM D1238 (190 °C, 21.6 kg). All individual values and subranges from 0.05 to 25 dg/min are included; for example, the polymer can have an I_{21} from a lower limit of 0.05, 0.07 or 0.10 dg/min to an upper limit of 25, 15, or 5 dg/min.

[0077] The polymers made with the compositions disclosed herein can have a weight average molecular weight (M_w) from 10,000 to 1,000,000 g/mol. All individual values and subranges from 10,000 to 1,000,000 g/mol are included; for example, the polymers can have an M_w from a lower limit of 10,000, 50,000, or 100,000 g/mol to an upper limit of 1,000,000, 750,000, or 500,000 g/mol. M_w can be determined by gel permeation chromatography (GPC), as is known in the art. GPC is discussed herein.

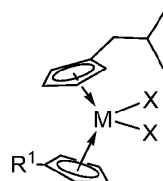
[0078] The polymers made with the compositions disclosed herein can have a number average molecular weight (M_n) from 5,000 to 300,000 g/mol. All individual values and subranges from 5,000 to 300,000 g/mol are included; for example, the polymers can have an M_n from a lower limit of 5,000, 20,000, or 40,000 g/mol to an upper limit of 300,000, 250,000, or 200,000 g/mol. M_n can be determined by GPC.

[0079] The polymers made with the compositions disclosed herein can have a Z-average molecular weight (M_z) from 40,000 to 2,000,000 g/mol. All individual values and subranges from 40,000 to 2,000,000 g/mol are included; for example, the polymers can have an M_z from a lower limit of 40,000, 100,000, or 250,000 g/mol to an upper limit of 2,000,000, 1,800,000, or 1,650,000 g/mol. M_z can be determined by GPC.

[0080] The polymers made with the compositions disclosed herein can have a weight average molecular weight to number average molecular weight ratio (M_w/M_n) from 2.00 to 6.00. All individual values and subranges from 2.00 to 6.00 are included; for example, the polymers can have an M_w/M_n from a lower limit of 2.00, 2.50, or 3.00 to an upper limit of 6.00, 5.50, or 4.50.

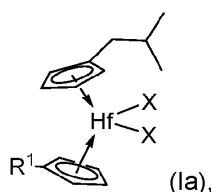
[0081] A number of aspects of the present disclosure are provided as follows.

[0082] Aspect 1 provides an asymmetrical metallocene represented by structure (I):



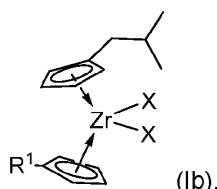
[0083] wherein: M is Hf or Zr; R¹ is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl; and each X is independently a leaving group; wherein the (C₄)alkyl except 2-methylpropyl is selected from butyl, 1-methylpropyl, and 1,1-dimethylethyl.

[0084] Aspect 2 provides the asymmetrical metallocene of aspect 1, wherein M is Hf and the asymmetrical metallocene is represented by structure (Ia):



wherein: R¹ is as defined in claim 1; and wherein each X is independently a leaving group selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl.

[0085] Aspect 3 provides the asymmetrical metallocene of aspect 1, wherein M is Zr and the asymmetrical metallocene is represented by structure (Ib):



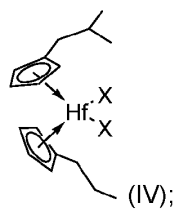
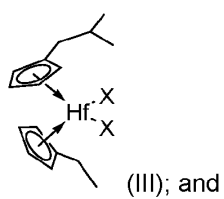
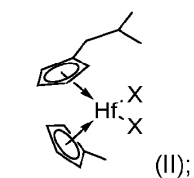
[0086] wherein: R¹ is as defined in claim 1; and wherein each X is independently a leaving group selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl.

[0087] Aspect 4 provides the asymmetrical metallocene of any one of aspects 1 to 3, wherein R¹ is the (C₁-C₃)alkyl, wherein the (C₁-C₃)alkyl is a (C₃)alkyl, ethyl, or methyl; and wherein the (C₃)alkyl is selected from 1-methylethyl and *n*-propyl; or wherein R¹ is the (C₄)alkyl that is not 2-methylpropyl; or wherein R¹ is the (C₅)alkyl.

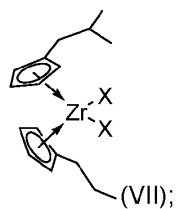
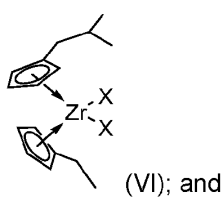
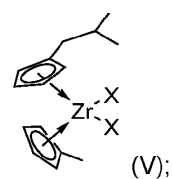
[0088] Aspect 5 provides the asymmetrical metallocene of any one of aspects 1 to 4, wherein each X is Cl or each X is CH₃.

[0089] Aspect 6 provides the asymmetrical metallocene of aspect 1, wherein the asymmetrical metallocene is selected from the group consisting of:

hafnium asymmetrical metallocenes represented by structures (II) to (IV):



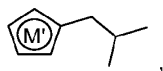
or zirconium asymmetrical metallocenes represented by structures (V) to (VII):



[0090] wherein in structures (II) to (VII) each X is Cl or each X is CH₃.

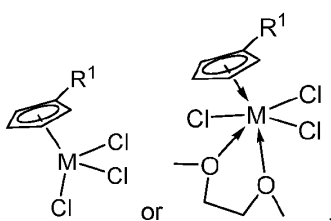
[0091] Aspect 7 provides a method synthesizing the asymmetrical metallocene of any one of aspects 1-6, the method comprising either:

contacting a hafnium complex or a zirconium complex with an alkali metal complex, wherein the alkali metal complex is represented by the following structure:



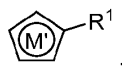
wherein M' is lithium, sodium, or potassium, and

the hafnium complex or the zirconium complex is represented by one of the following structures:



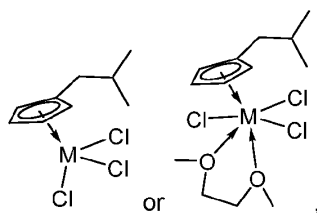
wherein M is Hf or Zr, respectively, and R¹ is as defined in the above claims (e.g., R¹ is propyl); or

contacting a hafnium complex or a zirconium complex with an alkali metal complex, wherein the alkali metal complex is represented by the following structure:



wherein M' is lithium, sodium, or potassium and R¹ is as defined in the above claims; and

the hafnium complex or the zirconium complex is represented by one of the following structures:



wherein M is Hf or Zr, respectively;

to make the asymmetrical metallocene.

[0092] Aspect 8 provides the method of aspect 7, comprising contacting the asymmetrical metallocene with two mole equivalents of an organomagnesium halide of

formula $\text{RMg}(\text{halide})$ or one mole equivalent of R_2Mg , wherein R is $(\text{C}_1\text{-C}_5)\text{alkyl}$, CH_2SiMe_3 , or benzyl; and the halide is Cl or Br, to make the asymmetrical metallocene of structure (I) wherein each X is $(\text{C}_1\text{-C}_5)\text{alkyl}$, CH_2SiMe_3 , or benzyl.

[0093] Aspect 9 provides a metallocene catalyst composition comprising: the asymmetrical metallocene of any one of aspects 1-6, or the asymmetrical metallocene made by the method of aspect 7 or aspect 8; and an activator (e.g., an alkylaluminumoxane such as methylaluminumoxane).

[0094] Aspect 10 provides metallocene catalyst composition of aspect 9 further comprising a support (e.g., silica such as a hydrophobic fumed silica or a dehydrated silica).

[0095] Aspect 11 provides the metallocene catalyst composition of aspect 10, wherein the composition is a spray-dried metallocene catalyst composition.

[0096] Aspect 12 provides a method of making the metallocene catalyst composition of any one of aspects 9 to 11, the method comprising either: contacting the asymmetrical metallocene with the activator but not the support, to give the metallocene catalyst composition of aspect 9 without a support; or contacting the asymmetrical metallocene with the activator and the support to give the metallocene catalyst composition of aspect 10 with the support; or contacting the asymmetrical metallocene with the activator and the support in an inert solvent to give a suspension thereof and spray-drying the suspension to give the spray-dried metallocene catalyst composition of aspect 11, or contacting the asymmetrical metallocene in an inert solvent with a supported or spray dried activator (or slurry thereof) to give a spray-dried metallocene catalyst composition of aspect 11.

[0097] Aspect 13 provides a method of making a polyolefin polymer, the method comprising: polymerizing at least one olefin monomer with either the metallocene catalyst composition of any one of aspects 9-11, or the metallocene catalyst composition made by the method of aspect 12, to make the polyolefin polymer; wherein preferably the at least one olefin monomer comprises ethylene and, optionally, a comonomer selected from the group consisting of propene and a $(\text{C}_4\text{-C}_{20})\alpha\text{-olefin}$.

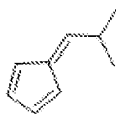
[0098] Aspect 14 provides the method of aspect 13, wherein the at least one olefin monomer comprises ethylene and the comonomer; and wherein the polyolefin polymer has a molecular weight comonomer distribution index (MWCDI) from 0.10 to 10.00, as measured by the MWCDI Test Method described herein; wherein preferably

the comonomer is selected from the group consisting of 1-butene, 1-hexene, and 1-octene.

[0099] Aspect 15 provides a polyolefin polymer made by the method of any one of aspects 13-14.

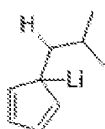
EXAMPLES

[00100] 5-(2-methylpropylidene)cyclopenta-1,3-diene, which may be represented by the following formula:



was synthesized as follows. In a glove box, pyrrolidine (1.45 g, 10 mol%) was added to a glass container that contained a solution of isobutyraldehyde (14.6 g, 203 mmol) and cyclopentadiene (13.4 g, 203 mmol) in MeOH-H₂O (200 mL 4/1). The contents of the container were transferred to an ice-cold mixture of brine solution and 10 mol% AcOH in a narrow graduated cylinder. The organic phase was isolated and dried over molecular sieves. The product (5-(2-methylpropylidene)cyclopenta-1,3-diene) was filtered to yield a bright yellow oil, which was subsequently used without further purification (16.0 g, 65 %). ¹H NMR (400 MHz, CDCl₃) δ: 6.54 (tdd, J = 5.4, 3.8, 2.5 Hz, 2H), 6.51 – 6.44 (m, 1H), 6.29 – 6.17 (m, 2H), 3.02 (dp, J = 10.0, 6.6 Hz, 1H), 1.15 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ: 149.88, 143.69, 133.08, 130.87, 126.06, 119.36, 30.58, 23.24.

[00101] Iso-butylcyclopentadienyl lithium, which may be represented by the following formula:

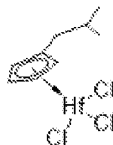


was synthesized as follows.

[00102] Et₂O (250 mL) was added to a container. 5-(2-methylpropylidene)cyclopenta-1,3-diene (16.0 g, 133 mmol) was added to the contents of the container while stirring. LiAlH₄ (33 mL, 4 M Et₂O solution) was added dropwise to the contents of the container while stirring. Bubbling was observed. Over the course of the addition a white solid precipitated, a yellow color gradually receded as the LiAlH₄ addition continued. The addition was stopped once the solution became only slightly

yellow. The product, iso-butylcyclopentadienyl lithium, observed to be white solid, was collected by filtration, rinsed with Et₂O, and dried under vacuum (13.7 g, 80 %).

[00103] Hafnium complex I, which may be represented by the following formula:

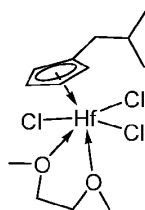


[00104] was synthesized as follows.

[00105] Hafnium tetrachloride (0.33 g, 1.0 mmol) and bis(*iso*-butylcyclopentadienyl)hafnium dichloride (0.50 g, 1.0 mmol) were combined in a large screw-cap container. The contents of the container evolved into a viscous brown liquid upon heating. A colorless vapor started to appear on the sides of the container at approximately 150 °C. The heating was adjusted to 150 °C at that point. A white solid began to form at a colorless vapor line. After approximately 5 minutes, the container was removed from the heat and cooled under a nitrogen atmosphere. A white solid was manually scraped from the container and transferred to a second container. After removing most of the white solid the container was placed under vacuum and reheated to 150 °C for 5 minutes. A second crop of the white solid was obtained and combined with the first set of isolated material to obtain Complex I (0.59 g, 72 %). ¹H NMR (400 MHz, C₆D₆) δ 5.81 (t, J = 2.7 Hz, 2H), 5.75 (t, J = 2.7 Hz, 2H), 2.27 (d, J = 7.0 Hz, 3H), 1.35 (dq, J = 13.5, 6.7 Hz, 1H), 0.59 (d, J = 6.6 Hz, 8H).

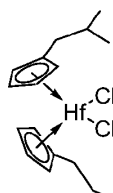
[00106] ¹³C NMR (101 MHz, C₆D₆) δ 134.94, 116.61, 116.04, 38.83, 30.18, 21.67. ¹³C NMR (101 MHz, C₆D₆) δ 134.94, 116.61, 116.04, 38.83, 30.18, 21.67.

[00107] Hafnium complex II: (*n*-propylcyclopentadienyl)hafnium trichloride, dimethoxyethane adduct, which may be represented by the following formula:



[00108] was synthesized as follows. The (*n*-propylcyclopentadienyl)hafnium trichloride, dimethoxyethane adduct, was synthesized by adapting the procedure described in WO2016/168448A1 by Harlan.

[00109] Example 1-1, an asymmetrical metallocene, which may be represented by the following formula:

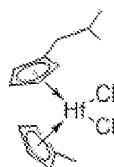


[00110] was synthesized as follows.

[00111] The (*n*-propylcyclopentadienyl)hafnium trichloride, dimethoxyethane adduct (0.15 g, 0.311 mmol) and *iso*-butylcyclopentadienyl lithium (0.022 g, 0.311 mmol) were added to a container. Et₂O was then added to the container and the contents of the container were stirred for approximately 12 hours at approximately 20 °C. The contents of the container were filtered and then concentrated under vacuum to yield Example 1-1, observed to be a white solid (0.145 g, 98 %). Example 1-1 can be further purified by extraction with a 1:1 hexane, toluene solution followed by filtration and concentration of filtrate under vacuum. ¹H NMR (400 MHz, C₆D₆): δ 5.81 (q, J = 2.7 Hz, 4H), 5.65 (dt, J = 3.8, 2.7 Hz, 4H), 2.67 – 2.59 (m, 2H), 2.56 (d, J = 7.0 Hz, 2H), 1.62 (dp, J = 13.5, 6.7 Hz, 1H), 1.45 (h, J = 7.5 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H), 0.79 (d, J = 6.7 Hz, 6H). ¹³C NMR (101 MHz, C₆D₆): δ 116.49, 115.52, 110.70, 110.62, 39.88, 32.47, 30.71, 24.41, 22.47, 14.03.

[00112] Example 1-2, a spray-dried composition, was made as follows. In a nitrogen-purged glovebox, hydrophobic fumed silica (CABOSIL TS-610; 0.665 grams) and toluene (19 grams) were added to a container and mixed, followed by addition of a 10 % solution (5.5 grams) by weight of methylaluminoxane (MAO) in toluene. Then the contents of the container were stirred for approximately 15 minutes. Then, Example 1-1 (0.024 grams) was added to the container and the contents of the container were stirred for approximately 45 minutes. Then, the contents of the container were spray-dried utilizing a Buchi Mini Spray Drier B-290 (185 °C set temperature; 100 °C outlet temperature; 150 rpm pump speed) to provide Example 1-2.

[00113] Example 2-1, an asymmetrical metallocene, which may be represented by the following formula:



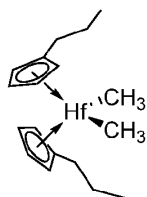
[00114] was synthesized as follows.

[00115] Hafnium complex I (0.100 g, 246 mmol) and methylcyclopentadienyl lithium (0.021 g, 0.246 mmol) were added to a container. Et₂O was then added to the container and contents of the container were stirred for approximately 12 hours at approximately 20 °C. The contents of the container were filtered and then concentrated under vacuum to obtain Example 2-1 (0.098 g, 88 %). ¹H NMR (400 MHz, C₆D₆) δ 5.79 (t, J = 2.7 Hz, 2H), 5.75 – 5.70 (m, 1H), 5.62 (t, J = 2.7 Hz, 1H), 5.60 (t, J = 2.7 Hz, 1H), 2.54 (d, J = 7.0 Hz, 2H), 2.25 (d, J = 2.5 Hz, 1H), 2.18 (s, 3H), 1.60 (dq, J = 13.5, 6.7 Hz, 1H), 0.78 (d, J = 6.7 Hz, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 116.43, 116.23, 110.71, 110.66, 39.86, 30.71, 22.46.

[00116] Example 2-2, a spray-dried composition, was made as follows. In a nitrogen-purged glovebox, hydrophobic fumed silica (CABOSIL TS-610; 0.665 grams) and toluene (19 grams) were added to a container and mixed, followed by addition of a 10 % solution (5.5 grams) by weight of methylaluminoxane (MAO) in toluene. Then the contents of the container were stirred for approximately 15 minutes. Then, Example 2-1 (0.022 grams) was added to the container and the contents of the container were stirred for approximately 45 minutes. Then, the contents of the container were spray-dried utilizing a Buchi Mini Spray Drier B-290 (185 °C set temperature; 100 °C outlet temperature; 150 rpm pump speed) to provide Example 2-2.

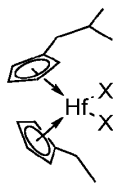
[00117] Comparative Example A-1, a hafnium metallocene having identical ligands, was made as follows. Bis-(*n*-propylcyclopentadienyl)-hafnium dichloride was commercially obtained from TCI; this is readily converted to bis-(*n*-propylcyclopentadienyl)-hafnium dimethyl by someone skilled in the art by reaction with a methylating agent, such as a Grignard reagent, for example, methylmagnesium bromide.

[00118] Comparative Example A-1 may be represented by the following formula:



[00119] Comparative Example A-2, a spray-dried composition, was made as follows. In a nitrogen-purged glovebox, hydrophobic fumed silica (CABOSIL TS-610; 2.65 grams) and toluene (75.0 grams) were added to a container and mixed, followed by addition of a 10 % solution (22 grams) by weight of methylaluminoxane (MAO) in toluene. Then the contents of the container were stirred for approximately 15 minutes. Then, Comparative Example A-1 (0.110 grams) was added to the container and the contents of the container were stirred for approximately 45 minutes. Then, the contents of the container were spray-dried utilizing a Buchi Mini Spray Drier B-290 (185 °C set temperature; 100 °C outlet temperature; 150 rpm pump speed) to provide Comparative Example A-2.

[00120] Example 3-1 is a prophetic example of an asymmetrical metallocene that may be represented by the following formula:



[00121] One or more embodiments provide that for Example 3-1, X is Cl.

[00122] Polymerizations were performed as follows. For respective polymerizations, a lab-scale gas phase polymerization reactor (2-liter, stainless steel autoclave equipped with a variable speed mechanical agitator) was charged with dried NaCl (200 g) and heated to 100 °C under a stream of nitrogen for one hour. Then the reactor was purged with nitrogen, silica supported methylaluminoxane was added as a scavenger to the reactor, the reactor temperature was adjusted to approximately a desired temperature, the reactor was sealed, and the contents of the reactor were stirred. The reactor was preloaded with hydrogen, ethylene, and 1-hexene to a desired pressure. Upon reaching steady state, catalyst was charged into the reactor (at a temperature indicated below) to start polymerization. The reactor temperature was maintained at a desired temperature for the 60-minute polymerization, where hydrogen,

C₆/C₂ ratio and ethylene pressure were maintained constant. At the end of the 60-minute polymerization, the reactor was cooled down, vented and opened. The resulting mixture was washed with water and methanol, and dried. Polymerization conditions are reported in Tables 1-6.

[00123] A number of properties were determined for polymers made with Example 1-2, Example 2-2, Example 4-2, Example 5-2, Example 6-2, and Comparative Example A-2, the results are reported in Tables 1-6. Catalyst productivity (grams polymer/gram catalyst-hour) was determined as a ratio of polymer produced to an amount of catalyst added to the reactor. Melt index (I₂) was determined according to ASTM D1238 (190 °C, 2.16 kg), melt index (I₅) was determined according to ASTM D1238 (190 °C, 5 kg), melt index (I₂₁) was determined according to ASTM D1238 (190 °C, 21.6 kg); melt temperatures were determined using a Differential Scanning Calorimetry according to ASTM D 3418-08, with a scan rate of 10 °C/min on a sample of 10 mg was used, and the second heating cycle was used to determine T_m. M_w, M_n, M_z, M_w/M_n (PDI), and M_z/M_w were determined as discussed above in the detailed description. The comonomer content, e.g., 1-hexene, incorporated in the polymers was determined by rapid FT-IR spectroscopy on the dissolved polymer in a GPC measurement as discussed above in the detailed description. Molecular weight comonomer distribution index (MWCDI) was determined as discussed herein.

Table 1

	Example 1-2	Example 2-2	Comp. Example A-2
Reaction Temp (°C)	80	80	80
C ₆ /C ₂	0.016	0.016	0.016
H ₂ /C ₂	0.0005	0.0005	0.0005
C ₂ Partial Pressure (psi)	220	220	220
Catalyst loading (mg)	5	5	10
Yield (g)	53.6	26.2	109.9
Catalyst productivity	8,734	4,403	10,579
Mn	64,059	49,193	37,995

Mw	167,150	152,984	121,132
Mz	340,705	-	280,366
Mw/Mn	2.61	3.11	3.19
C ₆ (wt %)	13.8	7.5	10.8
Melt Index (I ₂)	0.2	0.3	0.9
Melt Index (I ₅)	0.6	1.1	2.2
Melt Index (I ₂₁)	4.0	7.9	17.5
Melt Temp (°C)	118.4	121.1	117.9
MWCDI	5.85	5.05	3.60

[00124] The data of Table 1 illustrate that polymer made with each of Example 1-2 and Example 2-2 had an improved, i.e., greater, molecular weight comonomer distribution index (MWCDI) as compared to polymer made with Comparative Example A-2.

[00125] Figure 1A shows data plots utilized to determine MWCDI for Example 1-2 (MWCDI = 5.85) and Comparative Example A-2 (MWCDI = 3.60), as shown in Table 1. Data plot 102 corresponds the determination of MWCDI for Example 1-2. Data plot 104 corresponds the determination of MWCDI for Comparative Example A-2.

Table 2

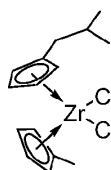
	Example 1-2	Example 2-2	Comparative Example A-2
Reaction Temp (°C)	90	90	90
C ₆ /C ₂	0.016	0.016	0.016
H ₂ /C ₂	0.0005	0.0005	0.0005
C ₂ Partial Pressure (psi)	220	220	220
Catalyst loading (mg)	2.5	5	10
Yield (g)	44.6	58.5	100.9

Catalyst productivity	13,975	10,637	9,165
Mn	45,328	88,462	60,675
Mw	108,560	220,814	163,442
Mz	204,586	449,453	323,504
Mw/Mn	2.40	2.50	2.69
C ₆ (wt %)	14.8	9.4	12.9
Melt Index (I ₂)	1.1	0.0	0.3
Melt Index (I ₅)	2.5	0.3	0.7
Melt Index (I ₂₁)	16.0	1.9	4.8
Melt Temp (°C)	101.2	113.3	99.4
MWCDI	2.13	1.87	1.67

[00126] The data of Table 2 illustrate that polymer made with each of Example 1-2 and Example 2-2 had an improved, i.e., greater, molecular weight comonomer distribution index (MWCDI) as compared to polymer made with Comparative Example A-2.

[00127] Figure 1B shows data plots utilized to determine MWCDI for Example 1-2 (MWCDI = 2.13) and Comparative Example A-2 (MWCDI = 1.67), as shown in Table 2. Data plot 106 corresponds the determination of MWCDI for Example 1-2. Data plot 106 corresponds the determination of MWCDI for Comparative Example A-2.

[00128] Example 4-1, an asymmetrical metallocene, which may be represented by the following formula:



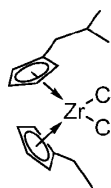
[00129] was synthesized as follows. A solution of *iso*-butylcyclopentadienyl lithium (0.10 g, 0.72 mmol) in THF (5 mL) was slowly added to a vial containing a solution of (methylcyclopentadienyl)zirconium trichloride (0.2 g, 0.72 mmol) in THF (5 mL) and stirred at room temperature for approximately 12 hours. Then, solvent was removed with

vacuum and the residual was re-dissolved in toluene (10 mL) and filtered through a syringe filter. The solution was then concentrated to about ~2 mL with vacuum and addition of pentane (10 mL) resulted in formation of white precipitate. Solids were collected, washed with pentane (2x5 mL) and dried with vacuum to give Example 4-1 (0.22 g, 84%).

[00130] ^1H NMR (400 MHz, Benzene- d_6) δ 5.88 (t, J = 2.56 Hz, 2H), 5.81 (t, J = 2.68 Hz, 2H), 5.70 (t, J = 2.83 Hz, 2H), 5.67 (t, J = 2.83 Hz, 2H), 2.52 (d, J = 7.10 Hz, 2H), 2.13 (s, 3H), 1.61 (tq, 1H), 0.78 (d, J = 6.72 Hz, 6H).

[00131] Example 4-2, a spray-dried composition, was made as follows. In a nitrogen-purged glovebox, slurry Cabosil TS-610 hydrophobic fumed silica (1.38 g) in toluene (36 g) until well dispersed. Then add of a 10 wt% solution (11 g) of MAO in toluene and stir for 15 minutes. Then added Example 4-1 (0.030 g) and stirred for 30 to 60 minutes. Spray-dry the mixture using a Büchi Mini Spray Dryer B-290 with the following operating parameters: set temperature 185° C, outlet temperature 100 °C, aspirator 95, and pump speed 150 rotations per minute (rpm) to provide Example 4-2.

[00132] Example 5-1, an asymmetrical metallocene, which may be represented by the following formula:

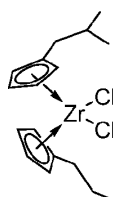


[00133] was synthesized as follows. A solution of *iso*-butylcyclopentadienyl lithium (0.09 g, 0.57 mmol) in THF (5 mL) was slowly added to a vial containing a solution of (ethylcyclopentadienyl)zirconium trichloride (0.2 g, 0.59 mmol) in THF (5 mL) and stirred at room temperature for approximately 12 hours. Then, solvent was removed with vacuum and the residual was re-dissolved in toluene (10 mL) and filtered through a syringe filter. The solution was then concentrated to about ~2 mL with vacuum and addition of pentane (10 mL) resulted in formation of white precipitate. Solids were collected, washed with pentane (2x5 mL) and dried with vacuum to give Example 5-1 (0.13 g, 58%).

[00134] ^1H NMR (400 MHz, Benzene- d_6) δ 5.87 (m, 4H), 5.70 (m, 4H), 2.61 (q, 2H), 2.52 (d, J = 7.10 Hz, 2H), 1.61 (tq, 1H), 1.04 (t, J = 7.36 Hz, 3H), 0.78 (d, J = 6.66 Hz, 6H).

[00135] Example 5-2, a spray-dried composition, was made as follows. In a nitrogen-purged glovebox, slurry Cabosil TS-610 hydrophobic fumed silica (1.32 g) in toluene (34 g) until well dispersed. Then add of a 10 wt% solution (10.5 g) of MAO in toluene and stir for 15 minutes. Then added Example 5-1 (0.030 g) and stirred for 30 to 60 minutes. Spray-dry the mixture using a Büchi Mini Spray Dryer B-290 with the following operating parameters: set temperature 185° C, outlet temperature 100 °C, aspirator 95, and pump speed 150 rotations per minute (rpm) to provide Example 5-2.

[00136] Example 6-1, an asymmetrical metallocene, which may be represented by the following formula:



[00137] was synthesized as follows. A solution of *iso*-butylcyclopentadienyl lithium (0.08 g, 0.57 mmol) in THF (5 mL) was slowly added to a vial containing a solution of (*n*-propylcyclopentadienyl)hafnium trichloride dimethoxyethane adduct (0.2 g, 0.57 mmol) in THF (5 mL) and stirred at room temperature for approximately 12 hours. Then, solvent was removed with vacuum and the residual was re-dissolved in toluene (10 mL) and filtered through a syringe filter. The solution was then concentrated to about ~2 mL with vacuum and addition of pentane (10 mL) resulted in formation of white precipitate. Solids were collected, washed with pentane (2x5 mL) and dried with vacuum to give Example 6-1 (0.20 g, 90%).

[00138] ¹H NMR (400 MHz, Benzene-*d*₆) δ 5.89 (m, 4H), 5.72 (m, 4H), 2.60 (t, J = 7.74 Hz, 2H), 2.54 (d, J = 6.97 Hz, 2H), 1.62 (septet, 1H), 1.45 (tq, 2H), 0.81 (t, J = 7.42 Hz, 3H), 0.79 (d, J = 6.58 Hz, 6H).

[00139] Example 6-2, a spray-dried composition, was made as follows. In a nitrogen-purged glovebox, slurry Cabosil TS-610 hydrophobic fumed silica (1.28 g) in toluene (33 g) until well dispersed. Then add of a 10 wt% solution (10.2 g) of MAO in toluene and stir for 15 minutes. Then added Example 6-1 (0.030 g) and stirred for 30 to 60 minutes. Spray-dry the mixture using a Büchi Mini Spray Dryer B-290 with the following operating parameters: set temperature 185° C, outlet temperature 100 °C, aspirator 95, and pump speed 150 rotations per minute (rpm) to provide Example 6-2.

Table 3

	Example 4-2	Example 5-2	Example 6-2
Reaction Temp (°C)	80	80	80
C ₆ /C ₂	0.016	0.016	0.016
H ₂ /C ₂	0.0005	0.0005	0.0005
C ₂ Partial Pressure (psi)	220	220	220
Catalyst loading (mg)	5.1	4.7	5.1
Yield (g)	30.6	65.8	118.0
Catalyst productivity	5,995	14,144	22,910
C ₆ (wt %)	3.5	3.4	4.2
Melt Index (I ₂)	7.94	10.50	12.43
Melt Index (I ₅)	19.35	26.68	31.63
Melt Index (I ₂₁)	120.91	182.98	204.71
Melt Temp (°C)	122.7	123.3	122.5
MWCDI	0.92	0.85	1.73

[00140] The data of Table 3 illustrate that polymer made with each of Example 4-2, Example 5-2, and Example 6-2 had a reverse comonomer distribution (MWCDI > 0).

Table 4

	Example 4-2	Example 5-2	Example 6-2
Reaction Temp (°C)	90	90	90
C ₆ /C ₂	0.016	0.016	0.016
H ₂ /C ₂	0.0005	0.0005	0.0005
C ₂ Partial Pressure (psi)	220	220	220
Catalyst loading	4.8	5.2	5.1

(mg)			
Yield (g)	72.76	130.18	160.39
Catalyst productivity	15,159	25,036	31,761
C ₆ (wt %)	3.66	3.91	4.64
Melt Index (I ₂)	6.12	8.17	10.72
Melt Index (I ₅)	15.11	19.41	27.08
Melt Index (I ₂₁)	95.45	126.46	171.60
Melt Temp (°C)	121.9	122.2	121.5
MWCDI	0.97	1.07	0.91

[00141] The data of Table 4 illustrate that polymer made with each of Example 4-2, Example 5-2, and Example 6-2 had a reverse comonomer distribution (MWCDI > 0).

Table 5

	Example 4-2	Example 5-2	Example 6-2
Reaction Temp (°C)	80	80	80
C ₆ /C ₂	0.004	0.004	0.004
H ₂ /C ₂	0.0005	0.0005	0.0005
C ₂ Partial Pressure (psi)	220	220	220
Catalyst loading (mg)	5.2	5.1	4.9
Yield (g)	39.98	97.37	147.98
Catalyst productivity	7,762	19,092	30,199
C ₆ (wt %)	1.16	1.18	1.31
Melt Index (I ₂)	13.40	17.62	23.17
Melt Index	35.50	46.07	59.72

(I ₅)			
Melt Index (I ₂₁)	244.69	323.05	405.40
Melt Temp (°C)	129.11	129.49	129.15
MWCDI	0.94	0.77	0.73

[00142] The data of Table 5 illustrate that polymer made with each of Example 4-2, Example 5-2, and Example 6-2 had a reverse comonomer distribution (MWCDI > 0).

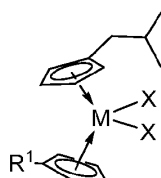
Table 6

	Example 4-2	Example 5-2	Example 6-2
Reaction Temp (°C)	100	100	100
C ₆ /C ₂	0.004	0.004	0.004
H ₂ /C ₂	0.0016	0.0016	0.0016
C ₂ Partial Pressure (psi)	230	230	230
Catalyst loading (mg)	5.4	5.4	5.1
Yield (g)	66.9	115.0	133.2
Catalyst productivity	12,405	21,296	26,371
C ₆ (wt %)	1.11	1.23	1.63
Melt Index (I ₂)	48.53	98.93	142.90
Melt Index (I ₅)	133.39	254.50	375.90
Melt Index (I ₂₁)	-	-	-
Melt Temp (°C)	129.30	129.6	129.0
MWCDI	0.89	-	-

[00143] The data of Table 6 illustrate that polymer made with each of Example 4-2, Example 5-2, and Example 6-2 had a reverse comonomer distribution (MWCDI > 0).

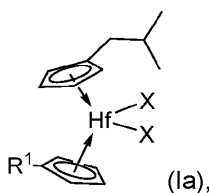
What is claimed is:

1. An asymmetrical metallocene represented by structure (I):



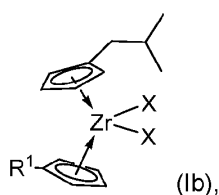
wherein: M is Hf or Zr; R¹ is a (C₁-C₃)alkyl, a (C₄)alkyl except 2-methylpropyl, or a (C₅)alkyl; and each X is independently a leaving group; wherein the (C₄)alkyl except 2-methylpropyl is selected from butyl, 1-methylpropyl, and 1,1-dimethylethyl.

2. The asymmetrical metallocene of claim 1, wherein M is Hf and the asymmetrical metallocene is represented by structure (Ia):



wherein: R¹ is as defined in claim 1; and wherein each X is independently a leaving group selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl.

3. The asymmetrical metallocene of claim 1, wherein M is Zr and the asymmetrical metallocene is represented by structure (Ib):



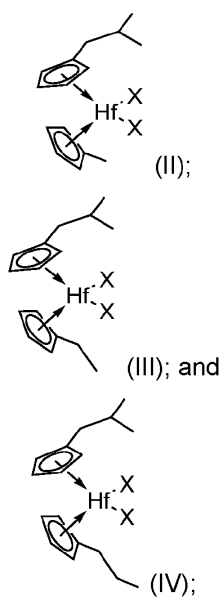
wherein: R¹ is as defined in claim 1; and wherein each X is independently a leaving group selected from a halogen, (C₁-C₅)alkyl, CH₂SiMe₃, and benzyl.

4. The asymmetrical metallocene of any one of claims 1 to 3, wherein R¹ is the (C₁-C₃)alkyl, wherein the (C₁-C₃)alkyl is a (C₃)alkyl, ethyl, or methyl; and wherein the

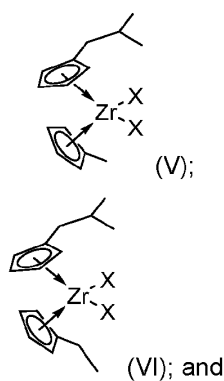
(C₃)alkyl is selected from 1-methylethyl and *n*-propyl; or wherein R¹ is the (C₄)alkyl that is not 2-methylpropyl; or wherein R¹ is the (C₅)alkyl.

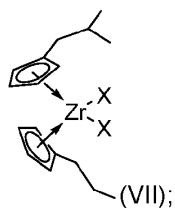
5. The asymmetrical metallocene of any one of claims 1 to 4, wherein each X is Cl or each X is CH₃.

6. The asymmetrical metallocene of claim 1 selected from the group consisting of: hafnium asymmetrical metallocenes represented by structures (II) to (IV):



or zirconium asymmetrical metallocenes represented by structures (V) to (VII):

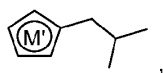




wherein in structures (II) to (VII) each X is Cl or each X is CH₃.

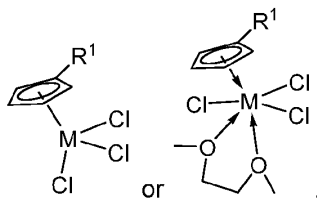
7. A method of synthesizing the asymmetrical metallocene of any one of claims 1-6 wherein each X is Cl, the method comprising either:

contacting a hafnium complex or a zirconium complex with an alkali metal complex, wherein the alkali metal complex is represented by the following structure:



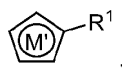
wherein M' is lithium, sodium, or potassium, and

the hafnium complex or the zirconium complex is represented by one of the following structures:



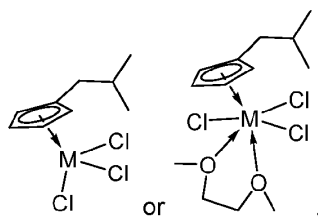
wherein M is Hf or Zr, respectively, and R¹ is as defined in the above claims; or

contacting a hafnium complex or a zirconium complex with an alkali metal complex, wherein the alkali metal complex is represented by the following structure:



wherein M' is lithium, sodium, or potassium and R¹ is as defined in the above claims; and

the hafnium complex or the zirconium complex is represented by one of the following structures:



wherein M is Hf or Zr, respectively;

to make the asymmetrical metallocene.

8. The method of claim 7 comprising contacting the asymmetrical metallocene with two mole equivalents of an organomagnesium halide of formula $\text{RMg}(\text{halide})$ or one mole equivalent of R_2Mg , wherein R is $(\text{C}_1\text{-C}_5)\text{alkyl}$, CH_2SiMe_3 , or benzyl; and the halide is Cl or Br, to make the asymmetrical metallocene of structure (I) wherein each X is $(\text{C}_1\text{-C}_5)\text{alkyl}$, CH_2SiMe_3 , or benzyl.

9. A metallocene catalyst composition comprising:
 the asymmetrical metallocene of any one of claims 1-6, or the asymmetrical metallocene made by the method of claim 7 or claim 8; and
 an activator.

10. The metallocene catalyst composition of claim 9 further comprising a support.

11. The metallocene catalyst composition of claim 10, wherein the composition is a spray-dried metallocene catalyst composition.

12. A method of making the metallocene catalyst composition of any one of claims 9 to 11, the method comprising either: contacting the asymmetrical metallocene with the activator but not the support, to give the metallocene catalyst composition of claim 9 without a support; or contacting the asymmetrical metallocene with the activator and the support to give the metallocene catalyst composition of claim 10 with the support; or contacting the asymmetrical metallocene with the activator and the support in an inert solvent to give a suspension thereof and spray-drying the suspension to give the spray-dried metallocene catalyst composition of claim 11, or contacting the asymmetrical

metallocene in an inert solvent with a supported or spray dried activator (or slurry thereof) to give a spray-dried metallocene catalyst composition of claim 11.

13. A method of making a polyolefin polymer, the method comprising:
polymerizing at least one olefin monomer with either the metallocene catalyst composition of any one of claims 9-11, or the metallocene catalyst composition made by the method of claim 12, to make the polyolefin polymer; wherein preferably the at least one olefin monomer comprises ethylene and, optionally, a comonomer selected from the group consisting of propene and a (C₄-C₂₀)alpha-olefin.
14. The method of claim 13, wherein the at least one olefin monomer comprises ethylene and the comonomer; and wherein the polyolefin polymer has a molecular weight comonomer distribution index (MWCDI) from 0.10 to 10.00, as measured by the MWCDI Test Method described herein; wherein preferably the comonomer is selected from the group consisting of 1-butene, 1-hexene, and 1-octene.

15. A polyolefin polymer made by the method of any one of claims 13-14.