GERMANIUM BRIDGED GROUP IV METALLOCENES

Field of Disclosure

[0001] Embodiments of the present disclosure are directed towards Ge bridged Group IV metallocenes, supported catalyst systems, including spray-dried compositions of Ge bridged Group IV metallocenes, and methods utilizing supported as well as spray-dried catalyst systems including Ge bridged Group IV metallocenes.

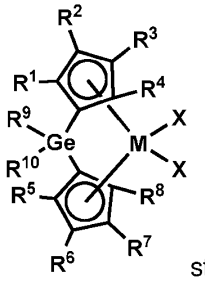
Background

[0002] Metallocenes can be used in various applications, including as polymerization catalysts. Polymers may be utilized for a number of products including films, fibers, pipes, nonwoven and/or woven fabrics, extruded articles, and/or molded articles, 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] A germanium bridged Group IV metallocene represented by structure (1):



structure (1),

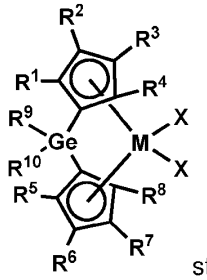
wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen or a C1 to C8 alkyl, M is a Group IV atom, and each X is independently a leaving group.

Detailed Description

[0005] Ge bridged Group IV metallocenes are discussed herein. Advantageously, these Ge bridged Group IV metallocenes can be utilized to make supported catalyst systems as well as spray-dried compositions. These supported, and spray-dried compositions can be utilized to make polymers that surprisingly provide an improved, i.e. greater, productivity and/or an improved, i.e. greater, efficiency, as

compared to polymers made from other spray-dried bridged Group IV metallocene compositions.

[0006] The Ge bridged Group IV metallocenes, which can be utilized for the spray-dried compositions disclosed herein, can be represented by a compound of structure (1):



structure (1).

[0007] Embodiments provide that R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen or a C1 to C8 alkyl, M is a Group IV atom, and each X is independently a leaving group.

[0008] One or more embodiments provide that M is Ti. One or more embodiments provide that M is selected from Zr and Hf. One or more embodiments provide that M is Zr. One or more embodiments provide that M is Hf.

[0009] One or more embodiments provide that each of R^1-R^4 is a C1 to C8 alkyl and each of R^5-R^8 is a C1 to C8 alkyl. One or more embodiments provide that each of R^1-R^4 is a C1 to C3 alkyl and each of R^5-R^8 is a C1 to C3 alkyl. One or more embodiments provide that each of R^1-R^4 is a C1 and each of R^5-R^8 is a C1 alkyl.

[0010] One or more embodiments provide that only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C1 to C8 alkyl while three of R^5-R^8 are H. One or more embodiments provide that only one of R^1-R^4 is a C1 to C3 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C1 to C3 alkyl while three of R^5-R^8 are H. One or more embodiments provide that only one of R^1-R^4 is a C3 alkyl while three of R^1-R^4 are H and only one of of R^5-R^8 is a C3 alkyl while three of R^5-R^8 are H.

[0011] One or more embodiments provide that only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H and each of R^5-R^8 is a C1 to C8 alkyl. One or more embodiments provide that only one of R^1-R^4 is a C1 to C3 alkyl while three of R^1-R^4 are H and each of R^5-R^8 is a C1 to C3 alkyl. One or more embodiments provide that only one of R^1-R^4 is a C3 alkyl while three of R^1-R^4 are H and each of R^5-R^8 is a C1 alkyl.

[0012] Embodiments provide that R^9-R^{10} are each independently hydrogen or a C1 to C6 alkyl. One or more embodiments provide that R^9-R^{10} are each independently a C1 to C3 alkyl. One or more embodiments provide that R^9-R^{10} are each independently a C1 to C2 alkyl. One or more embodiments provide that R^9-R^{10} are each independently a C1 alkyl.

[0013] 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. Examples of X include halogen ions, hydrides, (C1 to C12)alkyls, (C2 to C12)alkenyls, (C5 to C12)aryls, (C7 to C20)alkylaryls, (C1 to C12)alkoxys, (C6 to C16)aryloxys, (C7 to C8)alkylaryloxys, (C1 to C12)fluoroalkyls, (C6 to C12)fluoroaryls, 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)alkylaryls, (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)fluoroalkylaryls; 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, (C5 to C12)aryls, (C6 to C20)alkylaryls, substituted (C1 to C12)alkyls, substituted (C6 to C12)aryls, substituted (C7 to C20)alkylaryls, and (C1 to C12)heteroatom-containing alkyls, (C1 to C12)heteroatom-containing aryls, and (C1 to C12)heteroatom-containing alkylaryls; one or more embodiments include chloride, fluoride, (C1 to C6)alkyls, (C2 to C6)alkenyls, (C7 to C18)alkylaryls, halogenated (C1 to C6)alkyls, halogenated (C2 to C6) alkenyls, and halogenated (C7 to C18)alkylaryls; 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).

[0014] 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., -C6F5 (pentafluorophenyl), fluorinated alkylcarboxylates, e.g., CF3C(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, 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, (C1 to C10)alkyls, (C2 to C12)alkenyls, carboxylates, acetylacetonates, and alkoxides.

[0015] 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.

[0016] 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.

[0017] 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.

[0018] 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_5 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 C_7 to C_{20} aralkyl group. An “alkylaryl” is an aryl group having one or more alkyl groups pendant therefrom.

[0019] 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".

[0020] The Ge bridged Group IV metallocenes discussed herein can be made by processes, i.e. with conventional solvents, reaction conditions, reaction times, and isolation procedures, utilized for making known metallocenes.

[0021] As mentioned, the Ge bridged Group IV metallocenes can be utilized to make supported catalyst systems or compositions. In some embodiments the Ge bridged Group IV metallocene and support material are contacted together in an inert hydrocarbon liquid to give a suspension in the inert hydrocarbon liquid, then the suspension is contacted with the activator to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0022] In other embodiments the Ge bridged Group IV metallocene and activator are contacted together in an inert hydrocarbon liquid to give a solution of a catalyst in the inert hydrocarbon liquid, then the solution is contacted with the support material to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0023] In other embodiments the activator and the support material are contacted together in an inert hydrocarbon liquid to give a suspension of a supported activator in the inert hydrocarbon liquid, then the suspension is contacted with the Ge bridged Group IV metallocene to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0024] In other embodiments the Ge bridged Group IV metallocene, activator, and support material are contacted together simultaneously in an inert hydrocarbon liquid to give a suspension of the supported catalyst, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0025] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may include a step of decanting some of the inert hydrocarbon liquid from the suspension. In some embodiments the decanting method comprises pouring off excess inert hydrocarbon liquid from the suspension to give a concentrated suspension of the supported catalyst system.

[0026] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may comprise a step of drying the supported catalyst system. The drying step may comprise a conventional drying method or a spray-drying method.

[0027] A conventional drying method comprises a method of slowly increasing the mass or molar amount of less volatile chemical constituent(s) per unit volume of a continuous mixture comprising more volatile and less volatile chemical constituent(s) by gradually removing the more volatile chemical constituent(s) from the less volatile constituent(s) of the continuous mixture to give a concentrate having a higher mass or molar amount of the less volatile chemical constituent(s) per unit volume than did the continuous mixture, wherein the rate of gradual removing is limited by a relatively small evaporative surface area to mass ratio (compared to spray-drying). The concentrate may be a precipitated solid.

[0028] As mentioned, the Ge bridged Group IV metallocenes can be utilized to make spray-dried compositions, i.e., spray-dried Ge bridged Group IV metallocene 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.

[0029] In one or more embodiments, the spray-drying process may comprise atomizing a composition including the Ge bridged Group IV metallocene. 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.

[0030] 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.

[0031] In one or more embodiments, the spray-dried composition may be formed by contacting a spray dried activator particle, such as spray dried fumed silica (*e.g.* Cabosil) and methylaluminoxane(MAO), with a solution of the Ge bridged Group IV metallocene. Such a solution of the Ge bridged Group IV metallocenes 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 Ge bridged Group IV metallocene with a spray dried activator particle, such as spray-dried MAO, may be made *in situ* in a feed line heading into a slurry or gas phase polymerization reactor by contacting the trim solution with a slurry, typically in mineral oil, of the spray-dried activator particle.

[0032] As an example, various spray-drying conditions may be utilized for different applications. For instance, the spray-drying process may utilize a drying temperature from 115 to 185 °C. Various sizes of orifices of the atomizing nozzle employed during the spray-drying process may be utilized to obtain different particle 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 particle 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.

[0033] The spray-dried Ge bridged Group IV metallocene compositions may be utilized to make a polymer. For instance, the Ge bridged Group IV metallocene may be activated, i.e. with an activator, to make a Ge bridged Group IV 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.

[0034] The activator used in the heterogenization method may be any compound capable of reacting with the precatalyst of formula (I) to yield an active olefin polymerization catalyst. The activator may be a Lewis acid, a non-coordinating ionic activator, or an ionizing activator, or a Lewis base.

[0035] A molar ratio of metal, e.g., aluminum, in the activator to Group IV metal in the Ge bridged Group IV metallocene may be 3500: 1 to 0.5: 1, 1500 : 1 to 0.5: 1, 750 : 1 to 0.5 : 1, 300 : 1 to 0.5 : 1, or 150: 1 to 1 : 1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 75:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 100:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 150:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 300:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 750:1. Suitable activators are commercially available. In some embodiments the aluminum based activator is an alkylaluminum or an alkylaluminoxane (alkylalumoxane). Any alkyl group may be utilized. In some embodiments, each alkyl of the alkylaluminum or alkylaluminoxane independently may be a $(C_1$-$C_8)$alkyl, alternatively a $(C_1$-$C_7)$alkyl, alternatively a $(C_1$-$C_6)$alkyl, alternatively a $(C_1$-$C_4)$alkyl.

[0036] The alkylaluminum may be a trialkylaluminum, alkylaluminum halide, or alkylaluminum alkoxide (diethylaluminum ethoxide). The trialkylaluminum may be trimethylaluminum, triethylaluminum ("TEAl"), tripropylaluminum, or tris(2-methylpropyl)aluminum. The alkylaluminum halide may be diethylaluminum chloride. The alkylaluminum alkoxide may be diethylaluminum ethoxide.

[0037] The Ge bridged Group IV metallocenes, as well as a number of other components discussed herein, can be supported on the same or on 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.

[0038] 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.

[0039] Support materials include inorganic oxides that include Group 2, 3, 4, 5, 13 or 14 metal oxides. The terms "support", "solid support", "support material", and "solid support material" may be used interchangeably, and herein refer to a porous inorganic substance or organic substance. 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. 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.

[0040] Embodiments provide that the inorganic oxide support material is porous and has variable surface area, pore volume, and average particle size. In some embodiments, the surface area is from 50 to 1000 square meter per gram (m^2/g) and the average particle size is from 1 to 300 micrometers (μm), alternatively 20 to 300 μm. Alternatively, the pore volume is from 0.5 to 6.0 cubic centimeters per gram (cm^3/g) and the surface area is from 200 to 600 m^2/g. Alternatively, the pore volume is from 1.1 to 1.8 cm^3/g and the surface area is from 245 to 375 m^2/g. Alternatively, the pore volume is from 2.4 to 3.7 cm^3/g and the surface area is from 410 to 620 m^2/g. Alternatively, the pore volume is from 0.9 to 1.4 cm^3/g and the surface area is from 390 to 590 m^2/g. Each of the above properties are measured using conventional techniques known in the art.

[0041] The support material may comprise silica, alternatively amorphous silica (not quartz), alternatively a high surface area amorphous silica, e.g., from 500 to 1000 m^2/g. Such silicas are commercially available from several sources including the Davison Chemical Division of W.R. Grace and Company, e.g., Davison 952 and Davison 955 products, and PQ Corporation, e.g., ES70 product. The silica may be in the form of spherical particles, which may be obtained by a spray-drying process. Alternatively, MS3050 product is a silica from PQ Corporation that is not spray-dried. As procured, these silicas are not calcined (i.e., not dehydrated). Silica that is calcined prior to purchase may also be used as the support material.

[0042] In some embodiments the solid support is a hydrophobic fumed silica. The hydrophobic fumed silica is made by contacting an untreated fumed silica, having surfaces containing silicon-bonded hydroxyl groups (Si-OH groups), with a hydrophobing agent, described later. In some embodiments the hydrophobing agent is a silicon-based hydrophobing agent, containing on average per molecule one or more functional groups reactive with a Si-OH group, to give the hydrophobic fumed silica. The silicon-based hydrophobing agent may be selected from $(CH_3)_2SiCl_2$, a polydimethylsiloxane, hexamethyldisilazane (HMDZ), and a $(C_1\text{-}C_{10})$alkylSi$((C_1\text{-}C_{10})$alkoxy$)_3$ (e.g., an octyltrialkoxysilane such as octyltriethoxysilane, i.e., $CH_3(CH_2)_7Si(OCH_2CH_3)_3$). In some embodiments the silicon-based hydrophobing agent is dimethyldichlorosilane, i.e., $(CH_3)_2SiCl_2$. In some embodiments the support material is a dimethyldichlorosilane-treated fumed silica, such as that sold as product TS-610 from Cabot Corporation.

[0043] The support material may be uncalcined or calcined. The calcined support material is made prior to being contacted with a precatalyst, activator, and/or hydrophobing agent, by heating the support material in air to give a calcined support material. The calcining comprises heating the support material at a peak temperature from 350 °C to 850 °C, alternatively from 400 °C to 800 °C, alternatively from 400 °C to 700 °C, alternatively from 500° to 650° C and for a time period from 2 to 24 hours, alternatively from 4 to 16 hours, alternatively from 8 to 12 hours, alternatively from 1 to 4 hours, thereby making the calcined support material. If the support material has not been heated in this way it is an uncalcined support material.

[0044] The Ge bridged Group IV metallocenes, a catalyst system made from the Ge bridged Group IV metallocenes, and/or the spray-dried Ge bridged Group IV metallocene compositions, and an olefin can be contacted under polymerization

conditions to make a polymer, e.g., a polyolefin polymer. The catalyst system can include the germanium bridged Group IV metallocene; an activator; and a support, which are discussed herein. The polymerization process may be a suspension polymerization process, a slurry polymerization process, and/or a gas phase polymerization process. The polymerization process may utilize 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, pipes, nonwoven and/or woven fabrics, extruded articles, and/or molded articles.

[0045] 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.

[0046] 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.

[0047] Polyolefins made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can 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 (which can be referred to more simply as 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 1-hexene is utilized as a comonomer.

[0048] As mentioned, the polymers made with the spray-dried Ge bridged Group IV metallocene 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.

[0049] The fluidized bed reactor can have an ethylene partial pressure from 30 to 300 pounds per square inch (psi). All individual values and subranges from 30 to 300 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 300, 240, 220, 200, 150, or 125 psi.

[0050] 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.

[0051] 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.

[0052] The polymers made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can have a density from 0.8700 to 0.9700

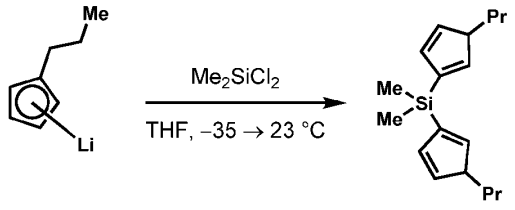
g/cm^3. All individual values and subranges from 0.8700 to 0.9700 g/cm^3 are included; for example, the polymer can have a density from a lower limit of 0.8700, 0.9000, 0.9100, 0.9150, 0.9200, or 0.9250 g/cm^3 to an upper limit of 0.9700, 0.9600, 0.9500, 0.9450, 0.9350, or 0.9300 g/cm^3. Density can be determined by according to ASTM D792.

[0053] The polymers made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can have a melt index (I_2) from 0.05 to 400 dg/min. I_2 can be determined according to ASTM D 3418-08 (190 °C, 2.16 kg). All individual values and subranges from 0.05 to 400 dg/min are included; for example, the polymer can have an I_2 from a lower limit of 0.05, 0.07 or 0.10 dg/min to an upper limit of 400, 375, or 350 dg/min.

[0054] The polymers made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can have a weight average molecular weight (Mw) 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 Mw from a lower limit of 10,000, 15,000, or 20,000 g/mol to an upper limit of 1,000,000, 800,000, 600,000, or 350,000 g/mol. Mw can be determined by gel permeation chromatography (GPC), as is known in the art. GPC is discussed herein.

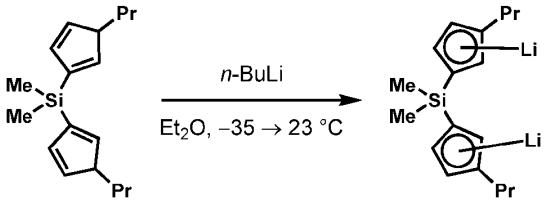
[0055] The polymers made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can have a weight average molecular weight to number average molecular weight ratio (Mw/Mn), which may be referred to as polydispersity index or molecular weight distribution, from 2.0 to 30.0. All individual values and subranges from 2.0 to 30.0 are included; for example, the polymers can have an Mw/Mn from a lower limit of 2.0, 2.2, or 2.3 to an upper limit of 30.0, 28.0, or 26.0.

EXAMPLES

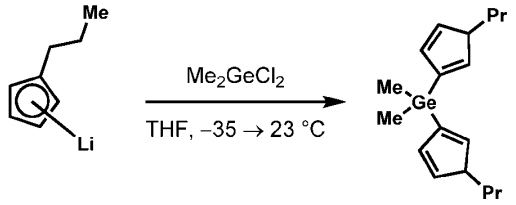


[0056] In a continuous purge nitrogen filled glovebox, a red-orange mixture of PrCpLi (0.250 g, 2.191 mmol, 2.05 eq) in anhydrous deoxygenated THF (10 mL) was placed in a freezer (-35 °C) for 16 hrs, and then neat Me_2SiCl_2 (0.13 mL, 1.069 mmol,

1.00 eq) was added. The red-orange mixture was maintained in the freezer for 2 hrs, then removed, and the red-orange solution was stirred (300 rpm) for 2 hrs. The solution was concentrated, suspended in hexanes (5 mL), concentrated, and then repeated 1x more. The mixture was suspended in hexanes (10 mL), stirred (300 rpm) for 2 mins, filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 3 mL), concentrated, suspended in hexanes (5 mL), and filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 3 mL), and concentrated to provide the bridged bis-cyclopentadiene, which was observed as a red-brown oil (0.256 g, 0.9394 mmol, 88%). NMR indicated product was a complex mixture of isomers. *Chemical Shifts of the Major Isomer Listed. ^{1}H NMR (500 MHz, C_6D_6) δ 6.62 – 6.32 (m, 4H), 6.26 – 6.05 (m, 2H), 3.43 – 3.16 (m, 2H), 2.38 (td, J = 7.6, 2.9 Hz, 4H), 1.56 (hept, J = 7.6 Hz, 4H), 0.97 – 0.80 (m, 6H), -0.20 (s, 6H).

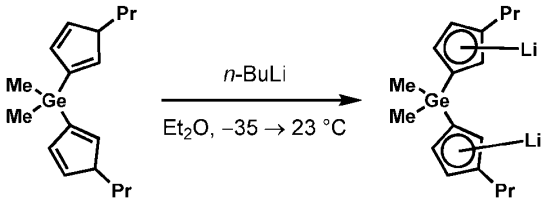


[0057] In a continuous purge nitrogen filled glovebox, a red-orange mixture of the starting bis-cyclopentadiene (0.256 g, 0.9394 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 16 hrs, and then *n*-BuLi (0.83 mL, 2.067 mmol, 2.20 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 30 mins, then removed from the freezer and stirred (500 rpm) for 4 hrs. The white mixture was suction filtered, rinsed with Et_2O (4 x 10 mL), and dried *in vacuo* to afford the dilithio salt, which was observed to be a white solid (0.197 g, 0.6928 mmol, 74%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (500 MHz, C_6D_6) δ 6.06 (t, J = 2.7 Hz, 2H), 5.97 – 5.88 (m, 4H), 2.70 – 2.63 (m, 4H), 1.77 (hd, J = 7.7, 2.6 Hz, 4H), 1.11 (dd, J = 8.6, 6.6 Hz, 6H), 0.75 (s, 6H).

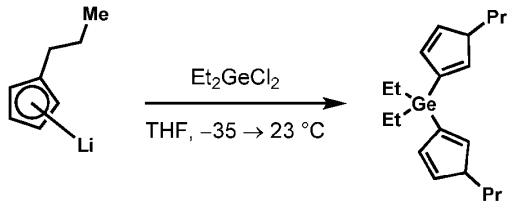


[0058] In a continuous purge nitrogen filled glovebox, a red-orange mixture of PrCpLi (0.250 g, 2.191 mmol, 2.25 eq) in anhydrous deoxygenated THF (15 mL) was

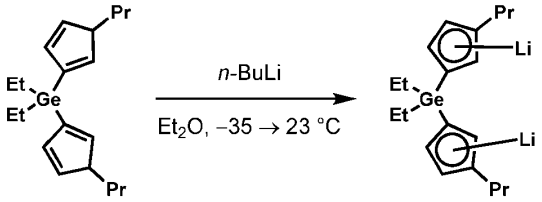
placed in a freezer (-35 °C) for 12 hrs, and then neat Me_2GeCl_2 (0.11 mL, 0.9738 mmol, 1.00 eq) was added. The red-orange mixture was allowed to sit in the freezer for 30 mins, removed, and the red-orange solution was stirred (500 rpm) at 23 °C for 4 hrs. The solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 3 mL), and concentrated to provide the bridged bis-cyclopentadiene, which was observed to be a clear golden yellow oil (0.303 g, 0.9524 mmol, 98%). NMR indicated product exists as a mixture of isomers. ^{1}H NMR (400 MHz, C_6D_6) δ 6.82 – 5.91 (m, 6H), 4.31 – 2.83 (m, 2H), 2.39 (t, J = 7.6 Hz, 4H), 1.57 (h, J = 7.4 Hz, 4H), 0.92 (t, J = 7.4 Hz, 6H), -0.08 (s, 6H).



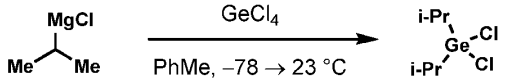
[0059] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.303 g, 0.9524 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 16 hrs, and then *n*-BuLi (0.86 mL, 2.143 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 30 mins, removed from the freezer, and stirred (500 rpm) at 23 °C for 2 hrs. The white mixture was suction filtered, the white solid was rinsed with Et_2O (4 x 10 mL), and dried *in vacuo* to provide the dilithio salt, which was observed to be a white solid (0.273 g, 0.8269 mmol, 87%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (400 MHz, C_6D_6 with THF) δ 6.05 – 6.02 (m, 2H), 5.94 (t, J = 2.1 Hz, 2H), 5.91 (t, J = 2.6 Hz, 2H), 2.69 – 2.60 (m, 4H), 1.75 – 1.66 (m, 4H), 1.05 – 0.99 (m, 6H), 0.63 (s, 6H).



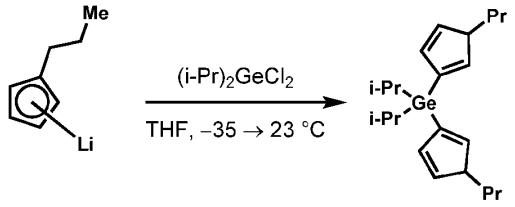
[0060] In a continuous purge nitrogen filled glovebox, a red-orange mixture of PrCpLi (0.250 g, 2.191 mmol, 2.25 eq) in anhydrous deoxygenated THF (20 mL) was placed in a freezer (-35 °C) for 12 hrs, and then neat Et_2GeCl_2 (0.14 mL, 0.9738 mmol, 1.00 eq) was added. The red-orange mixture was maintained in the freezer for 30 mins, removed, and the red-orange solution was stirred (500 rpm) at 23 °C for 4 hrs. The solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 5 mL), and concentrated to provide the bridged bis-cyclopentadiene, which was observed to be a clear amber oil (0.318 g, 0.9186 mmol, 94%). NMR indicated product exists as a mixture of isomers. ^{1}H NMR (400 MHz, C_6D_6) δ 6.84 – 5.87 (m, 6H), 4.00 – 3.50 (br s, 2H), 2.50 – 2.36 (m, 4H), 1.59 (h, J = 7.4 Hz, 4H), 0.99 – 0.92 (m, 12H), 0.59 (q, J = 8.0 Hz, 4H).



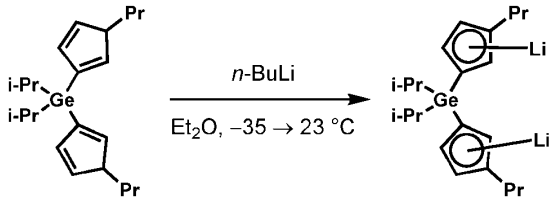
[0061] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.318 g, 0.9186 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 2.5 hrs, and then *n*-BuLi (0.83 mL, 2.067 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 30 mins, removed from the freezer, and stirred (500 rpm) at 23 °C for 3 hrs. The white mixture was suction filtered, the white solid was rinsed with Et_2O (4 x 10 mL), and dried with vacuum to provide the dilithio salt as a white solid (0.280 g, 0.7817 mmol, 85%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (400 MHz, C_6D_6) δ 6.15 (dd, J = 2.9, 2.1 Hz, 2H), 6.07 (t, J = 2.1 Hz, 2H), 6.05 – 6.01 (m, 2H), 2.77 – 2.66 (m, 4H), 1.83 – 1.69 (m, 4H), 1.44 – 1.36 (m, 6H), 1.28 – 1.19 (m, 6H), 1.06 (td, J = 7.2, 1.9 Hz, 4H).



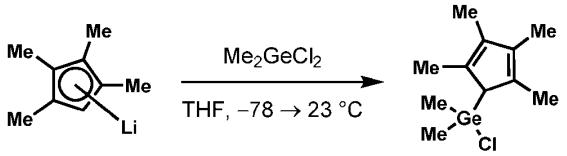
[0062] To a round-bottomed flask equipped with a stirbar under N_2 was added $GeCl_4$ (2.470 g, 11.518 mmol, 1.00 eq), which was then diluted with anhydrous deoxygenated PhMe (60 mL), and the solution was placed in a bath cooled to -78 °C. After stirring (300 rpm) for 1 hr, i-PrMgCl (12.1 mL, 24.187 mmol, 2.10 eq, 2 M in THF) was added in a dropwise manner over 20 minutes. The white mixture was stirred for 90 mins at -78 °C, then the cooling bath was removed and the mixture was stirred at 23 °C for 3 hrs, and brought into a continuous purge nitrogen filled glovebox. The mixture was then diluted with hexanes (30 mL), stirred (300 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (3 x 10 mL), and the clear colorless filtrate solution was used in the subsequent reaction without further purification or concentration. NMR indicated product. 1H NMR (500 MHz, C6D6) δ 1.20 – 1.13 (m, 2H), 0.96 (d, J = 6.7 Hz, 12H).



[0063] In a continuous purge nitrogen filled glovebox, a pale yellow solution of $(i\text{-}Pr)_2GeCl_2$ (0.224 g, 0.9738 mmol, 1.00 eq) in anhydrous deoxygenated THF (20 mL) was placed in a freezer (-35 °C) for 16 hrs, and then solid PrCpLi (0.250 g, 2.191 mmol, 2.25 eq) was added all at once. The red-orange mixture was stirred (500 rpm) at 23 °C for 3 hrs, upon which the resultant solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 5 mL), and concentrated to provide the bridged bis-cyclopentadiene, observed as a clear amber oil (0.272 g, 0.7269 mmol, 75%). NMR indicated product exists as a mixture of isomers. ^1H NMR (400 MHz, C_6D_6) δ 6.94 – 6.03 (m, 6H), 4.05 – 3.20 (br s, 2H), 2.42 (t, J = 7.6 Hz, 4H), 1.61 (hept, J = 7.3 Hz, 4H), 1.26 – 1.15 (m, 2H), 1.06 (d, J = 7.2 Hz, 12H), 0.95 (t, J = 7.3 Hz, 6H).

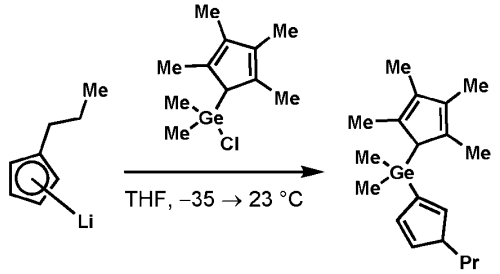


[0064] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.272 g, 0.7269 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (20 mL) was placed in a freezer (-35 °C) for 16 hrs, and then *n*-BuLi (0.65 mL, 1.635 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was allowed to sit in the freezer for 30 mins, removed from the freezer, stirred (500 rpm) at 23 °C for 2 hrs, the clear pale yellow solution was concentrated, the resultant off-white mixture was suspended in hexanes (5 mL), concentrated, re-suspended in hexanes (5 mL), the white mixture was suction filtered, the white solid was rinsed with hexanes (3 x 5 mL), dried with vacuum, collected, dissolved in Et_2O (10 mL), and placed in the freezer (-35 °C) for 20 hrs. The resultant white mixture was suction filtered cold, the white solid was rinsed with cold hexanes (3 x 5 mL), and dried with vacuum to provide the dilithio salt as a white solid (0.217 g, 0.5679 mmol, 77%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (500 MHz, C_6D_6) δ 6.22 (t, J = 2.6 Hz, 2H), 6.14 (t, J = 2.1 Hz, 2H), 6.09 (t, J = 2.5 Hz, 2H), 2.82 – 2.71 (m, 4H), 1.79 (h, J = 7.5 Hz, 4H), 1.69 (h, J = 7.3 Hz, 2H), 1.49 (d, J = 7.4 Hz, 12H), 1.10 (t, J = 7.4 Hz, 6H).

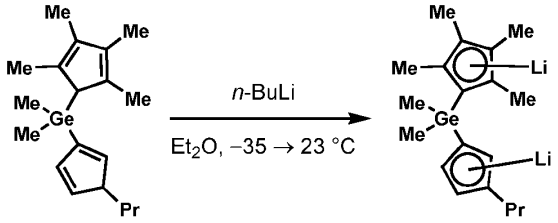


[0065] In a round-bottomed flask equipped with a stirbar under N_2 was added $GeCl_4$ (1.00 mL, 8.668 mmol, 4.44 eq) and then anhydrous deoxygenated THF (50 mL). The solution was placed in a bath cooled to -78 °C for 1 hr, then solid lithium tetramethyl cyclopentadiene (0.250 g, 1.951 mmol, 1.00 eq) was added all at once, and the white heterogeneous mixture was stirred (500 rpm) for 16 hrs warming to 23 °C gradually over time. The clear colorless solution was brought into a continuous purge, nitrogen filled glovebox, concentrated, suspended in hexanes (5 mL), concentrated, re-suspended in hexanes (10 mL), stirred for 2 mins, suction filtered through Celite, rinsed with hexanes (3 x 10 mL), and the filtrate was concentrated. The resultant filtrate mixture was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 5 mL), and concentrated to provide the germanyl mono-tetramethylcyclopentadiene as a clear pale-yellow oil (0.297 g, 1.142 mmol, 59%). NMR indicated product exists as a mixture of isomers. *Only chemical shifts of the major

isomer are listed. ^{1}H NMR (500 MHz, C_6D_6) δ 3.18 (t, J = 43.9 Hz, 1H), 1.86 (s, 6H), 1.69 (s, 6H), 0.32 (s, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 134.89, 57.65, 13.45, 10.84, 1.70.

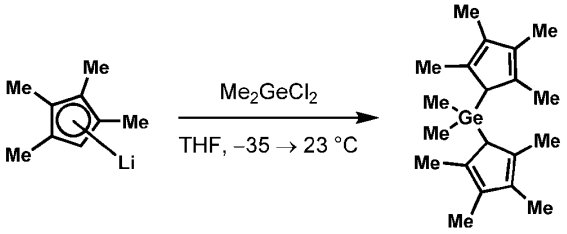


[0066] In a continuous purge nitrogen filled glovebox, a pale-yellow solution of the mono-tetramethyl Cp-Ge(Me)Cl_2 (0.297 g, 1.142 mmol, 1.00 eq) in anhydrous deoxygenated THF (25 mL) was placed in a freezer (-35 °C) for 16 hrs, and then solid PrCpLi (0.150 g, 1.313 mmol, 1.15 eq) was added all at once. The red-orange mixture was stirred (500 rpm) at 23 °C for 3 hrs, upon which the resultant solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 5 mL), and concentrated to provide the bridged bis-cyclopentadiene as a clear amber oil (0.327 g, 0.9845 mmol, 86%). NMR indicated product. ^{1}H NMR (500 MHz, C_6D_6) δ 6.74 – 5.84 (m, 3H), 3.06 – 2.84 (m, 1H), 2.46 – 2.34 (m, 2H), 1.91 (s, 6H), 1.83 (s, 6H), 1.59 (h, J = 7.5 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H), -0.02 (s, 6H).

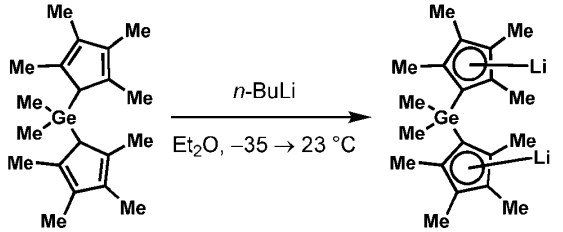


[0067] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.327 g, 0.9845 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (20 mL) was placed in a freezer (-35 °C) for 1 hr, and then *n*-BuLi (0.89 mL, 2.215 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was allowed to sit in the freezer for 10 mins, removed from the freezer, stirred (500 rpm) at 23 °C for 2 hrs, the resultant off-white mixture was placed in the freezer for 20 hrs, suction filtered through a fritted filter cold,

rinsed with cold hexanes (4 x 5 mL), and the amorphous solid was dried with vacuum to provide the dilithio salt as a white solid (0.219 g, 0.6363 mmol, 65%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (400 MHz, C_6D_6) δ 5.89 – 5.75 (m, 3H), 2.59 (t, J = 7.9 Hz, 2H), 2.23 (s, 6H), 2.01 (s, 6H), 1.70 – 1.55 (m, 2H), 1.06 – 0.95 (m, 3H), 0.87 (s, 6H).



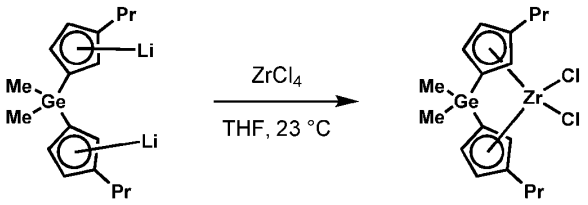
[0068] In a continuous purge nitrogen filled glovebox, a solution of Me2GeCl2 (0.846 g, 4.873 mmol, 1.00 eq) in anhydrous deoxygenated THF (50 mL) was placed in a freezer (-35 °C) for 16 hrs, upon which solid lithium tetramethylcyclopentadiene (1.405 g, 10.964 mmol, 2.25 eq) was added all at once. The white mixture was manintained in the freezer for 30 mins, removed from the freezer, and the golden yellow solution was stirred (500 rpm) at 23 °C for 3 hrs, then concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 3 mL), and concentrated to provide the bridged bis-cyclopentadiene as a pale yellow solid (1.672 g, 4.829 mmol, 99%). NMR indicated product. 1H NMR (400 MHz, C6D6) δ 3.27 (d, J = 4.7 Hz, 2H), 1.93 (s, 12H), 1.84 (s, 12H), -0.06 (s, 6H).



[0069] In a continuous purge nitrogen filled glovebox, a clear pale golden yellow solution of the starting bis-cyclopentadiene (1.672 g, 4.829 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (30 mL) was placed in a freezer (-35 °C) for 16 hrs, and then *n*-BuLi (4.40 mL, 10.865 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 20 mins, removed from the

freezer, and stirred (500 rpm) at 23 °C for 2 hrs. The white mixture was suction filtered, the white solid was rinsed with Et_2O (4 x 10 mL), and dried with vacuum to provide the dilithio salt as a white solid (1.417 g, 3.955 mmol, 82%). NMR (in THF & C_6D_6) indicated product. ^1H NMR (500 MHz, C_6D_6) δ 2.38 (s, 6H), 2.30 (s, 6H), 2.18 (s, 6H), 2.04 (s, 6H), 0.82 (s, 6H).

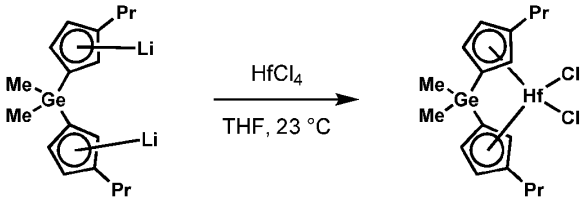
[0070] Example 1, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Zr, and each X is Cl, was made as follows.



[0071] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of ZrCl4 (67.5 mg, 0.2896 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.3040 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 1, which was observed to be a pale-yellow oil (0.130 g, 0.2725 mmol, 94%). NMR indicated product exists as a mixture of rac- and meso isomers. *Denotes chemical shifts of the meso isomer. 1H NMR (500 MHz, C6D6) δ 6.68 – 6.64 (m, 2H), *6.60 (dd, J = 2.8, 2.1 Hz, 2H), *5.64 (t, J = 2.7 Hz, 2H), 5.50 (t, J = 2.7 Hz, 2H), 5.31 (t, J = 2.3 Hz, 2H), *5.22 (t, J = 2.3 Hz, 1H), 2.86 – 2.67 (m, 4H), 1.61 – 1.48 (m, 4H), 0.87 (td, J = 7.3, 5.9 Hz, 6H), *0.31 (s, 3H), 0.28 (s, 6H), *0.25 (s, 3H). 13C NMR (101 MHz, C6D6) δ 141.82, *141.73, *126.61, 126.03, 113.42, *113.29, *112.82,

112.45, *106.01, 105.88, 32.30, *31.59, *23.51, 23.44, *13.82, 13.79, *-6.18, -6.23, *-6.27.

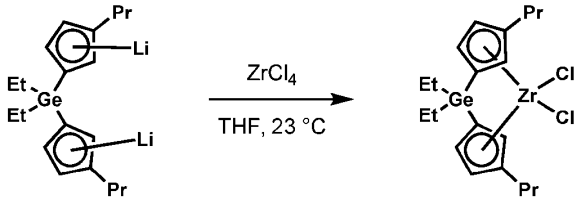
[0072] Example 2, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Hf, and each X is Cl, was made as follows.



[0073] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $HfCl_4$ (92.8 mg, 0.2896 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.3040 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant pale-golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 2, observed to be a pale-yellow oil (95.4 mg, 0.1686 mmol, 58%). NMR indicated product exists as a mixture of *rac-* and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. ^{1}H NMR (500 MHz, C_6D_6) δ 6.59 – 6.56 (m, 2H), *6.53 – 6.49 (m, 2H), *5.57 (t, J = 2.7 Hz, 2H), 5.43 (t, J = 2.7 Hz, 2H), 5.25 (t, J = 2.4 Hz, 2H), *5.16 (t, J = 2.3 Hz, 2H), 2.88 – 2.70 (m, 4H), 1.61 – 1.47 (m, 4H), 0.87 (td, J = 7.4, 5.5 Hz, 6H), *0.33 (s, 3H), 0.29 (s, 6H), 0.26 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ *140.01, 139.99, *125.30, 124.83, *111.29, 111.22, *110.74, 110.43, *107.83, 107.70, 32.25, *23.67, 23.62, 13.85, *13.83, *-6.18, -6.22, *-6.24.

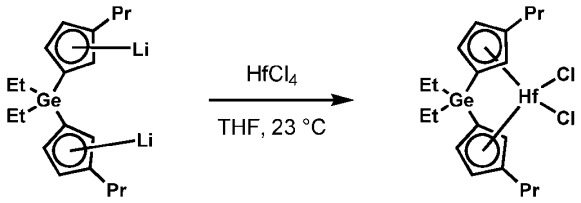
[0074] Example 3, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are

each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C2 alkyl, M is Zr, and each X is Cl, was made as follows.



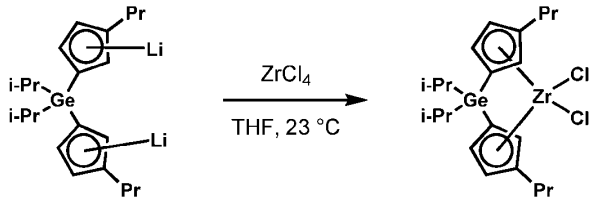
[0075] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $ZrCl_4$ (62.0 mg, 0.2659 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.2792 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 3, observed to be a pale golden yellow oil (0.117 g, 0.2312 mmol, 87%). NMR indicated product exists as a mixture of *rac-* and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. ^{1}H NMR (500 MHz, C_6D_6) δ 6.68 (dd, J = 2.8, 2.0 Hz, 2H), 6.62 (dd, J = 2.8, 2.1 Hz, 2H), 5.69 (t, J = 2.7 Hz, 2H), *5.56 (t, J = 2.7 Hz, 2H), *5.38 (t, J = 2.3 Hz, 2H), 5.30 (t, J = 2.3 Hz, 2H), 2.88 – 2.65 (m, 4H), 1.67 – 1.45 (m, 4H), 0.99 – 0.92 (m, 6H), 0.87 (td, J = 7.4, 5.6 Hz, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 141.85, *141.65, 126.72, *126.06, 114.16, *113.93, *113.61, 113.13, *105.15, 105.02, 32.34, *32.33, *23.53, 23.47, 13.86, *13.83, 8.22, *3.08, 3.03, *2.99.

[0076] Example 4, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C2 alkyl, M is Hf, and each X is Cl, was made as follows.



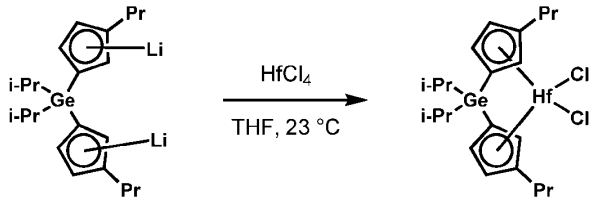
[0077] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of HfCl4 (85.2 mg, 0.2659 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.2792 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant pale-golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 4, observed to be a clear pale golden brown oil (0.156 g, 0.2633 mmol, 99%). NMR indicated product exists as a mixture of rac- and meso isomers. *Denotes chemical shifts of the meso isomer. 1H NMR (500 MHz, C6D6) δ 6.59 (dd, J = 2.8, 2.0 Hz, 2H), *6.53 (dd, J = 2.8, 2.1 Hz, 2H), *5.63 (t, J = 2.7 Hz, 2H), 5.49 (t, J = 2.7 Hz, 2H), 5.32 (t, J = 2.3 Hz, 2H), 5.24 (t, J = 2.4 Hz, 2H), 2.89 – 2.72 (m, 4H), 1.62 – 1.46 (m, 4H), 1.03 – 0.95 (m, 10H), 0.87 (td, J = 7.3, 5.4 Hz, 6H). 13C NMR (126 MHz, C6D6) δ 140.02, *139.92, *125.51, 125.40, 112.05, *111.87, *111.57, 111.13, *106.88, 106.76, 32.28, *32.27, *23.68, 23.64, 13.89, *13.86, 8.25, *3.10, 3.05, *3.02.

[0078] Example 5, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C3 alkyl, M is Zr, and each X is Cl, was made as follows.



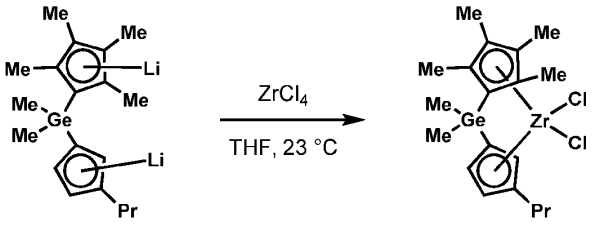
[0079] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of ZrCl4 (57.9 mg, 0.2486 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.8 mg, 0.2610 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 5, observed to be a clear pale-golden yellow amorphous oil (88.1 mg, 0.1652 mmol, 66%). NMR indicated product exists as a mixture of rac- and meso isomers. *Denotes chemical shifts of the meso isomer. 1H NMR (400 MHz, C6D6) δ 6.69 (t, J = 2.5 Hz, 2H), *6.64 (t, J = 2.4 Hz, 2H), *5.73 (t, J = 2.7 Hz, 2H), 5.61 (t, J = 2.7 Hz, 2H), 5.46 (t, J = 2.3 Hz, 2H), *5.38 (t, J = 2.4 Hz, 2H), 2.92 – 2.66 (m, 4H), 1.67 – 1.43 (m, 4H), 1.32 – 1.16 (m, 2H), 1.12 (ddd, J = 7.5, 4.9, 3.7 Hz, 12H), 0.88 (td, J = 7.4, 4.3 Hz, 6H). 13C NMR (101 MHz, C6D6) δ 141.81, *141.49, *126.78, 126.03, 114.80, *114.44, *114.32, 113.68, *105.44, 105.31, 32.36, *32.33, 30.11, *23.52, 23.46, *19.28, 19.26, 19.25, *19.22, *14.71, 14.66, *14.63, 13.89, *13.86.

[0080] Example 6, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C3 alkyl, M is Hf, and each X is Cl, was made as follows.



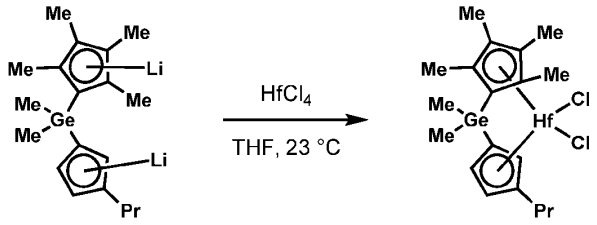
[0081] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of HfCl4 (67.0 mg, 0.2091 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (84.8 mg, 0.2196 mmol, 1.05 eq) in THF (6 mL, rinse 3 x 3 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant pale-golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 6, observed to be a clear pale-yellow oil (0.128 g, 0.2058 mmol, 98%). NMR indicated product exists as a mixture of rac- and meso isomers. *Denotes chemical shifts of the meso isomer. 1H NMR (400 MHz, C6D6) δ 6.60 (t, J = 2.4 Hz, 2H), *6.55 (t, J = 2.4 Hz, 2H), *5.67 (t, J = 2.7 Hz, 2H), 5.54 (t, J = 2.7 Hz, 2H), 5.40 (t, J = 2.3 Hz, 2H), *5.32 (t, J = 2.4 Hz, 2H), 2.95 – 2.70 (m, 4H), 1.67 – 1.46 (m, 4H), 1.26 – 1.18 (m, 2H), 1.13 (ddd, J = 7.8, 4.8, 3.4 Hz, 12H), 0.88 (td, J = 7.3, 4.2 Hz, 6H).

[0082] Example 7, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, R^7, and R^8 are each a C1 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Zr, and each X is Cl, was made as follows.



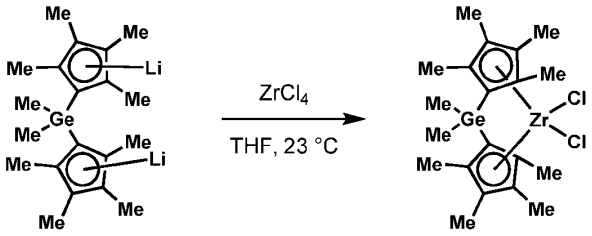
[0083] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $ZrCl_4$ (68.6 mg, 0.2944 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (106.4 mg, 0.3092 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 3 mL). The resultant golden yellow solution was stirred (500 rpm) for 20 hrs. The resultant pale-yellow solution was concentrated, suspended in PhMe-hexanes (10 mL, 1:20), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), filtrate concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 7, observed to be a clear pale-golden yellow amorphous solid (87.4 mg, 0.1779 mmol, 60%). NMR indicated product. ^{1}H NMR (400 MHz, C_6D_6) δ 6.70 (t, J = 2.2 Hz, 1H), 5.42 (t, J = 2.7 Hz, 1H), 5.14 (t, J = 2.4 Hz, 1H), 2.78 (h, J = 7.1 Hz, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 1.74 (s, 3H), 1.67 (s, 3H), 1.60 – 1.49 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H), 0.49 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 141.43, 134.16, 134.08, 125.60, 123.70, 123.66, 112.35, 111.67, 105.42, 97.58, 32.40, 23.57, 14.41, 14.24, 13.86, 12.15, 12.09, -1.14, -1.20.

[0084] Example 8, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, R^7, and R^8 are each a C1 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Hf, and each X is Cl, was made as follows.



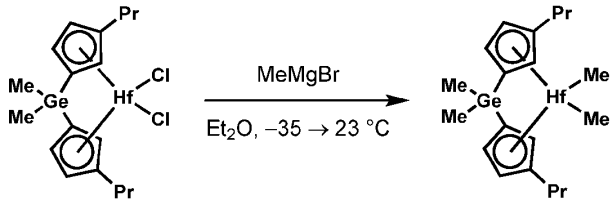
[0085] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $HfCl_4$ (83.8 mg, 0.2615 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (94.5 mg, 0.2746 mmol, 1.05 eq) in THF (5 mL, rinse 3 x 3 mL). The resultant golden yellow solution was stirred (500 rpm) for 20 hrs. The resultant pale-yellow solution was concentrated, suspended in PhMe-hexanes (10 mL, 1:20), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), filtrate concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Example 8, observed to be a clear pale-golden yellow amorphous foam (100.5 mg, 0.1733 mmol, 66%). NMR indicated product. ^{1}H NMR (400 MHz, C_6D_6) δ 6.67 – 6.56 (m, 1H), 5.39 (t, J = 2.7 Hz, 1H), 5.10 (t, J = 2.4 Hz, 1H), 2.79 (hept, J = 7.3 Hz, 2H), 2.09 (s, 3H), 2.07 (s, 3H), 1.83 (s, 3H), 1.75 (s, 3H), 1.55 (tdd, J = 10.8, 8.1, 4.3 Hz, 3H), 0.88 (t, J = 7.3 Hz, 8H), 0.50 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 139.96, 132.41, 132.25, 124.68, 120.69, 120.60, 109.89, 109.31, 107.89, 99.80, 32.36, 23.69, 14.12, 13.94, 13.89, 11.99, 11.91, -1.14, -1.19.

[0086] Example 9, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, R^3, and R^4 are each a C1 alkyl, R^5, R^6, R^7, and R^8 are each a C1 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Zr, and each X is Cl, was made as follows.



[0087] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $ZrCl_4$ (77.9 mg, 0.3341 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (135.5 mg, 0.3508 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 3 mL). The resultant golden yellow solution was stirred (500 rpm) for 20 hrs. The resultant pale-yellow solution was concentrated, suspended in PhMe (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with PhMe (4 x 10 mL), filtrate concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, and the pale yellow solid was rinsed with hexanes (4 x 10 mL). The pale golden yellow solid was suspended in hexanes (10 mL), placed in the freezer (-35 °C) for 4 hrs, suction filtered cold through a fritted filter, rinsed with cold hexanes (3 x 5 mL), and the solid was dried. The resultant pale golden yellow solid was dissolved in PhMe (3 mL), placed in the freezer for 18 hrs, suction filtered cold through a fritted filter, rinsed with cold PhMe (3 x 3 mL), and the solid was dried with vacuum to provide Example 9, observed to be a pale-golden yellow solid (28.0 mg, 0.0554 mmol, 17%). NMR indicated product. ^{1}H NMR (400 MHz, C_6D_6) δ 2.07 (s, 12H), 1.77 (s, 12H), 0.69 (s, 6H).

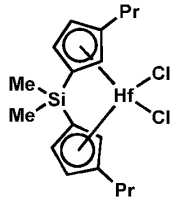
[0088] Example 10, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Hf, and each X is Me, was made as follows.



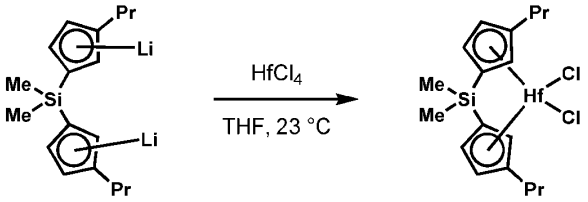
[0089] In a continuous purge nitrogen filled glovebox, a solution of the dichloride (90.2 mg, 0.1594 mmol, 1.00 eq) in anhydrous deoxygenated Et2O (10 mL) was placed in a freezer (-35 °C) for 16 hrs, a solution of MeMgBr (0.13 mL, 0.3665 mmol, 2.30 eq,

3.0 M in Et2O) was then added in a quick dropwise manner, the pale golden brown solution was removed from the freezer, stirred (500 rpm) at 23 °C for 8 hrs, and concentrated. Pentane (10 mL) was added, the mixture was stirred for 2 mins, filtered using a double 0.45 µm PTFE filter, rinsed with pentane (4 x 5 mL), and concentrated. The resultant pale yellow oil was diluted in pentane (5 mL), filtered using a double 0.45 µm PTFE filter, rinsed with pentane (4 x 5 mL), and concentrated to provide Example 10, observed to be a clear colorless oil (76.6 mg, 0.1456 mmol, 91%). NMR indicated product exists as a mixture of rac- and meso isomers. *Denotes chemical shifts of the meso isomer. 1H NMR (400 MHz, C6D6) δ 6.38 (dt, J = 6.5, 2.4 Hz, 2H), *5.41 (t, J = 2.7 Hz, 2H), 5.33 (t, J = 2.6 Hz, 2H), 5.21 (t, J = 2.3 Hz, 2H), *5.17 (t, J = 2.2 Hz, 2H), 2.68 – 2.50 (m, 4H), 1.62 (qd, J = 7.5, 1.3 Hz, 4H), 0.95 (td, J = 7.4, 2.9 Hz, 6H), *0.33 (s, 3H), 0.31 (s, 6H), *0.29 (s, 3H), *-0.24 (s, 3H), -0.32 (s, 6H), *-0.38 (s, 3H). 13C NMR (101 MHz, C6D6) δ 133.10, *132.97, *118.89, 118.67, 110.67, *110.64, *110.31, 110.04, *100.75, 100.69, 37.30, 32.07, *24.78, 24.75, 13.87, *13.86, *-5.88, -6.02, *-6.13.

[0090] Comparative Example A may be represented by the following structure:



[0091] Comparative Example A was made as follows.



[0092] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of HfCl4 (0.166 g, 0.5191 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (0.155 g, 0.5451 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant canary yellow solution was stirred (500 rpm) for 18 hrs. The resultant golden brown solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden brown amorphous foam was suspended in hexanes (10 mL), suction filtered, rinsed with hexanes (4 x 10 mL), and concentrated. The

resultant golden brown amorphous oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant pale golden brown oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Comparative Example A, observed to be a pale brown oil (0.157 g, 0.3019 mmol, 58%). NMR indicated product exists as a mixture of rac- and meso isomers. *Denotes chemical shifts of the meso isomer. 1H NMR (400 MHz, C6D6) δ 6.57 (t, J = 2.4 Hz, 2H), *6.49 (t, J = 2.4 Hz, 2H), *5.56 (t, J = 2.8 Hz, 2H), 5.41 (t, J = 2.8 Hz, 2H), 5.23 (t, J = 2.3 Hz, 2H), *5.12 (t, J = 2.4 Hz, 2H), 2.86 – 2.65 (m, 4H), 1.61 – 1.44 (m, 4H), 0.86 (td, J = 7.3, 4.5 Hz, 6H), *0.22 (s, 3H), 0.19 (s, 6H), *0.16 (s, 3H). 13C NMR (101 MHz, C6D6) δ *141.01, 140.67, *125.66, 125.46, *112.25, 112.03, 110.98, *110.96, *107.22, 107.10, *32.11, 32.07, *23.55, 23.50, 13.83, *13.81, *-5.86, -5.94, *-6.02.

[0093] Example 11, a spray-dried Ge bridged Group IV metallocene composition (e.g. a supported catalyst system), was made as follows. In a nitrogen-purged glovebox, hydrophobic fumed silica (CAB-O-SIL TS-610; 1.160 grams) and toluene (37.5 grams) were added to a container and mixed, followed by addition of a 10 % solution (9.30 grams) by weight of methylaluminoxane (MAO) in toluene. Then the contents of the container were stirred for approximately 15 minutes. Then, Example 1 (0.051 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 (140 °C set temperature; 75 °C outlet temperature; 150 rpm pump speed) to provide Example 11.

[0094] Examples 12-21, spray-dried Ge bridged Group IV metallocene compositions, and Comparative Example B were made as Example 11 with changes shown in Table 1.

Table 1

Spray-dried composition	Metallocene	Fumed silica	10 % MAO solution	Toluene
Example 11	Example 1 0.051 g	1.160 g	9.30 g	37.5 g
Example 12	Example 2 0.095 g	1.815 g	14.60 g	37.5 g
Example 13	Example 2	0.583 g	4.60 g	37.5 g

	0.018 g			
Example 14	Example 3 0.059 g	1.255 g	10.05 g	37.5 g
Example 15	Example 4 0.071 g	1.295 g	10.40 g	37.5 g
Example 16	Example 5 0.088 g	1.785 g	14.30 g	37.5 g
Example 17	Example 6 0.090 g	1.555 g	12.60 g	37.5 g
Example 18	Example 7 0.087 g	1.930 g	15.40 g	37.5 g
Example 19	Example 8 0.095 g	1.760 g	14.20 g	37.5 g
Example 20	Example 9 0.078 g	1.675 g	13.40 g	37.5 g
Example 21	Example 10 0.045 g	1.570 g	12.35 g	75.0 g
Comparative Example B	Comparative Example A 0.064 g	1.340 g	10.70 g	37.5 g

[0095] Polymerizations respectively utilizing Examples 11-21 and Comparative Example B 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, C_6/C_2 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 and a number of properties are reported in the following Tables.

Table 2

Spray-dried composition	Reaction Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Melt Index (dg/min)
Ex. 11	80	0.004	0.0005	3.3	31.2	26,500	5,810,100	107
Ex. 12	80	0.004	0.0005	2.3	27.1	10,800	1,207,900	3.6
Ex. 13	80	0.004	0.0005	3.0	23.9	6,500	1,213,800	N.F.
Ex. 14	80	0.004	0.0005	2.2	11.6	35,700	7,832,700	99
Ex. 16	80	0.004	0.0005	2.4	116.3	49,000	10,743,200	49
Ex. 17	80	0.004	0.0005	2.2	18.8	8,200	916,200	6.7
Ex. 18	80	0.004	0.0005	2.8	104.4	36,300	7,955,200	10
Ex. 19	80	0.004	0.0005	2.5	36.8	13,900	1,554,100	9.6
Ex. 20	80	0.004	0.0005	2.0	25.7	12,700	2,781,900	4.3
Ex. 21	80	0.004	0.0005	2.9	23.5	7,300	1,363,200	N.F.
Comp. Ex. B	80	0.004	0.0005	4.8	27.6	5,000	560,200	1.3

Table 3

Spray-dried composition	Reaction Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Melt Index (dg/min)
Ex. 11	80	0.004	0.002	2.5	29.0	28,700	6,292,500	198
Ex. 12	80	0.004	0.002	2.6	40.7	16,300	1,826,700	63
Ex. 14	80	0.004	0.002	2.3	17.1	30,000	6,576,800	171
Ex. 15	80	0.004	0.002	2.6	40.0	16,700	1,871,100	107

Ex. 16	80	0.004	0.002	2.4	17.1	32,200	7,068,600	214
Ex. 17	80	0.004	0.002	2.2	45.8	18,900	2,118,400	49
Ex. 18	80	0.004	0.002	2.5	85.4	34,100	7,469,400	286
Ex. 19	80	0.004	0.002	2.2	36.9	15,600	1,749,500	184
Ex. 20	80	0.004	0.002	2.6	30.4	10,500	2,300,900	43
Comp. Ex. B	80	0.004	0.002	5.0	41.7	7,100	795,500	25

Table 4

Spray-dried composition	Reaction Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Melt Index (dg/min)
Ex. 11	80	0.02	0.0005	2.0	140.8	70,500	15,457,100	95
Ex. 12	80	0.02	0.0005	1.9	40.9	17,000	1,907,000	0.27
Ex. 14	80	0.02	0.0005	1.9	98.0	70,000	15,345,600	83
Ex. 16	80	0.02	0.0005	2.5	36.9	54,400	11,936,800	56
Ex. 17	80	0.02	0.0005	1.9	32.5	13,700	1,532,700	0.41
Ex. 18	80	0.02	0.0005	2.2	59.5	26,000	5,697,900	10
Ex. 19	80	0.02	0.0005	2.2	14.1	3,400	384,300	0.21
Ex. 20	80	0.02	0.0005	2.3	18.3	9,200	2,019,900	0.41
Comp. Ex. B	80	0.02	0.0005	5.1	20.8	2,200	246,500	0.11

Table 5

Spray-dried composition	Reaction Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Melt Index (dg/min)
Ex. 11	90	0.02	0.0005	1.8	13.3	66,700	14,624,000	111

Ex. 12	90	0.02	0.0005	2.2	43.8	16,900	1,896,400	0.37
Ex. 14	90	0.02	0.0005	2.0	19.2	61,300	13,443,300	78
Ex. 15	90	0.02	0.0005	2.3	31.1	29,900	3,350,900	0.74
Ex. 16	90	0.02	0.0005	2.6	13.8	46,200	10,126,800	64
Ex. 17	90	0.02	0.0005	2.3	36.2	13,300	1,493,100	0.47
Ex. 18	90	0.02	0.0005	2.7	100.4	35,600	7,809,400	9.7
Ex. 19	90	0.02	0.0005	2.4	12.5	2,700	304,600	0.38
Ex. 20	90	0.02	0.0005	2.5	26.3	10,400	2,272,000	1.6
Comp. Ex. B	90	0.02	0.0005	5.0	14.9	1,700	190,500	-

Table 6

Spray-dried composition	Reaction Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Melt Index (dg/min)
Ex. 11	100	0.004	0.002	3.1	12.3	26,200	5,744,400	286
Ex. 12	100	0.004	0.002	2.9	17.8	26,800	3,002,800	29
Ex. 13	100	0.004	0.002	3.2	16.8	23,400	4,369,700	5
Ex. 14	100	0.004	0.002	2.3	11.6	26,400	5,787,300	257
Ex. 15	100	0.004	0.002	2.2	19.8	22,700	2,543,400	20
Ex. 16	100	0.004	0.002	2.4	9.3	36,600	8,019,600	234
Ex. 17	100	0.004	0.002	2.6	70.6	31,900	3,575,900	46
Ex. 18	100	0.004	0.002	2.5	138.3	52,500	11,502,200	184
Ex. 19	100	0.004	0.002	2.5	46.1	16,300	1,828,900	107
Ex. 20	100	0.004	0.002	2.2	39.2	14,900	3,266,600	60
Ex. 21	100	0.004	0.002	2.8	49.5	19,900	3,716,200	12
Comp. Ex. B	100	0.004	0.002	3.0	49.2	15,300	1,714,300	11

Table 7

Spray-dried composition	Reaction Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Melt Index (dg/min)
Ex. 12	80	0.016	0.0005	2.5		25,100	2,812,300	0.42
Ex. 13	80	0.016	0.0005	3.3		6,900	1,288,500	0.08
Ex. 15	80	0.016	0.0005	2.3	25.5	17,100	1,916,000	0.11
Ex. 21	80	0.016	0.0005	2.8		13,300	2,483,700	N.F.

[0096] The data of Tables 2-7 illustrate that Examples 11-21 provided polymers with and an improved, i.e. greater, Productivity and/or an improved, i.e. greater, Efficiency, as compared to polymers made with Comparative Example B.

Table 8

Additional Properties Corresponding Spray-dried compositions and polymers of Table 2					
Spray-dried composition	Mp (g /mol)	Mw (g /mol)	Poly dispersity index	C6 (wt %)	Tm (°C)
Ex. 11	27,400	32,700	4.7	2.4	126
Ex. 12	62,700	185,700	21.3	2.2	126
Ex. 13	71,300	227,100	6.7	2.4	125
Ex. 14	27,400	31,900	4.7	2.3	122
Ex. 16	32,700	47,800	2.9	2.6	127
Ex. 17	50,500	194,500	7.4	2.4	126
Ex. 18	49,500	67,800	3.1	1.7	129
Ex. 19	44,100	124,100	6.9	2.1	128
Ex. 20	48,400	125,100	7.6	0.8	132
Ex. 21	72,400	222,300	5.9	2.3	124

Comp. Ex. B	73,700	176,300	29.9	3.1	123

Table 9

Additional Properties Corresponding Spray-dried compositions and polymers of Table 3					
Spray-dried composition	Mp (g /mol)	Mw (g /mol	Poly dispersity index	C6 (wt %)	Tm (°C)
Ex. 11	23,100	26,000	3.9	2.5	126
Ex. 12	28,500	62,700	8.7	2.7	126
Ex. 14	23,900	45,700	7.1	2.8	130
Ex. 15	30,100	51,900	4.1	3.3	126
Ex. 16	22,900	31,200	2.7	3.1	127
Ex. 17	22,600	81,100	7.2	2.9	127
Ex. 18	21,100	38,700	6.0	2.3	129
Ex. 19	17,100	93,300	26.7	2.7	128
Ex. 20	23,400	82,600	18.9	1.7	130
Comp. Ex. B	35,500	75,900	10.4	3.2	125

Table 10

Additional Properties Corresponding Spray-dried compositions and polymers of Table 4

Spray-dried composition	Mp (g /mol)	Mw (g /mol	Poly dispersity index	C6 (wt %)	Tm (°C)
Ex. 11	27,000	44,600	6.6	12.0	113
Ex. 12	117,500	170,500	3.4	24.5	73
Ex. 14	29,200	40,300	5.1	11.8	-
Ex. 16	29,700	34,000	2.3	12.2	115
Ex. 17	111,200	187,000	3.7	21.9	76
Ex. 19	95,300	323,100	7.4	16.7	86
Ex. 20	62,000	191,700	7.9	3.2	125
Comp. Ex. B	105,400	151,000	13.5	29.9	62

Table 11

Additional Properties Corresponding Spray-dried compositions and polymers of Table 5					
Spray-dried composition	Mp (g /mol)	Mw (g /mol	Poly dispersity index	C6 (wt %)	Tm (°C)
Ex. 11	24,100	51,400	7.8	9.7	116
Ex. 12	113,500	182,500	21.1	19.6	-
Ex. 14	25,700	45,500	7.6	10.1	116
Ex. 15	108,400	168,600	4.0	18.6	86
Ex. 16	27,200	64,800	4.4	10.3	115
Ex. 17	103,900	157,300	3.6	17.9	88
Ex. 19	98,200	293,100	6.8	14.3	94
Ex. 20	52,300	139,000	6.5	2.4	126

Comp. Ex. B	114,300	248,500	21.6	23.8	74

Table 12

Additional Properties Corresponding Spray-dried compositions and polymers of Table 6					
Spray-dried composition	Mp (g /mol)	Mw (g /mol	Poly dispersity index	C6 (wt %)	Tm (°C)
Ex. 11	20,700	28,000	4.8	2.6	127
Ex. 12	38,600	58,900	3.4	3.6	123
Ex. 13	41,900	79,800	4.3	4.3	122
Ex. 14	20,800	37,700	7.0	2.3	126
Ex. 15	40,000	70,100	3.7	2.9	124
Ex. 16	22,100	37,900	3.3	3.2	127
Ex. 17	31,800	64,900	4.1	3.2	126
Ex. 19	22,900	62,800	9.4	2.6	128
Ex. 20	22,400	83,600	20.2	1.7	130
Ex. 21	40,600	97,600	5.2	3.9	123
Comp. Ex. B	47,600	99,000	13.3	3.6	123

Table 13

Additional Properties Corresponding Spray-dried compositions and polymers of Table 7

Spray-dried composition	Mp (g /mol)	Mw (g /mol	Poly dispersity index	C6 (wt %)	Tm (°C)
Ex. 12	130,000	194,700	3.6	22.6	80
Ex. 13	99,600	205,700	4.4	17.9	87
Ex. 15	112,300	212,100	4.5	19.0	-
Ex. 21	120,100	274,700	5.0	21.1	79

[0097] Productivity (grams polymer/grams catalyst-hour) was determined as a calculated ratio of polymer produced, based upon C2 and C6 uptake/consumption, as a ratio to an amount of catalyst added to the reactor

[0098] Efficiency (grams polymer/grams catalyst metal) was determined as a ratio of polymer produced, based upon C2 and C6 uptake/consumption, as a ratio to an amount of catalyst metal added to the reactor.

[0099] Melt index (I_2) was determined according to ASTM D 3418-08 (190 °C, 2.16 kg).

[00100] Melt temperature (Tm) was determined via Differential Scanning Calorimetry according to ASTM D 3418-08. In general, a scan rate of 10° C/min on a sample (10 mg) was used, and the second heating cycle was used to determine Tm.

[00101] Mw, Mn, Mp, and Polydispersity Index (Mw/Mn) were determined by GPC. Mp is reported as the molecular weight of the peak maxima.

[00102] GPC was determined as follows.

[00103] The 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 165 ºC and the column compartment was set at 155 ºC. The columns used were 4 TOSOH TSK GMHHR-H (30) HT 30-micron sized, mixed pore size 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.

[00104] 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 ºC with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160 ºC 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)).:

[00105] $$M_{polyethylene} = A \times \left(M_{polystyrene}\right)^{B} \quad \text{(EQ1)}$$

[00106] where M is the molecular weight, A has a value of 0.3992 and B is equal to 1.0.

[00107] A third order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[00108] 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 12,000 for the 4 TOSOH TSK GMHHR-H (30) HT 30-micron sized, mixed pore size columns.

[00109] 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 3 hours at 165 ºC under low speed shaking.

[00110] 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.

[00111] $$Mn_{(GPC)} = \frac{\sum^{i} IR_i}{\sum^{i}\left(IR_i / M_{polyethylene_i}\right)} \quad \text{(EQ 2)}$$

[00112] $$Mw_{(GPC)} = \frac{\sum^{i}\left(IR_i * M_{polyethylene_i}\right)}{\sum^{i} IR_i} \quad \text{(EQ 3)}$$

[00113] $$Mz_{(GPC)} = \frac{\sum^{i}\left(IR_i * M_{polyethylene_i}{}^{2}\right)}{\sum^{i}\left(IR_i * M_{polyethylene_i}\right)} \quad \text{(EQ 4)}$$

[00114] 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.

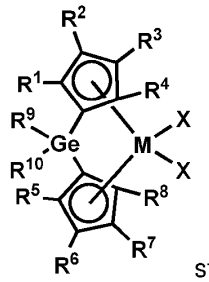
[00115] Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample)) (EQ5).

[00116] The comonomer content (C6 wt%), e.g., 1-hexene, incorporated in the polymers was determined by rapid FT-IR spectroscopy on the dissolved polymer in a GPC measurement. Comonomer content was determined with respect to polymer molecular weight by use of an infrared detector (an IR5 detector) in a gel permeation chromatography measurement, as described in Analytical Chemistry 2014, 86(17), 8649-8656. “Toward Absolute Chemical Composition Distribution Measurement of Polyolefins by High-Temperature Liquid Chromatography Hyphenated with Infrared Absorbance and Light Scattering Detectors” by Dean Lee, Colin Li Pi Shan, David M.

Meunier, John W. Lyons, Rongjuan Cong, and A. Willem deGroot. *Analytical Chemistry* 2014 *86* (17), 8649-8656.

What is claimed is:

1. A germanium bridged Group IV metallocene represented by structure (1):



structure (1),

wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen or a C1 to C8 alkyl, M is a Group IV atom, and each X is independently a leaving group.

2. The germanium bridged Group IV metallocene of claim 1, wherein M is selected from Hf and Zr.

3. The germanium bridged Group IV metallocene of claim 1, wherein each of R^1-R^4 is a C1 to C8 alkyl and each of R^5-R^8 is a C1 to C8 alkyl.

4. The germanium bridged Group IV metallocene of claim 1, wherein only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C1 to C8 alkyl while three of R^5-R^8 are H.

5. The germanium bridged Group IV metallocene of claim 1, wherein only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H and each of R^5-R^8 is a C1 to C8 alkyl.

6. A supported catalyst system comprising:
the germanium bridged Group IV metallocene of any one of claims 1-5;
an activator; and
a support.

7. The supported catalyst system of claim 6, wherein a molar ratio of metal in the activator to Group IV metal in the germanium bridged Group IV metallocene is from 3500 : 1 to 0.5 : 1.

8. The supported catalyst system of any one of claims 6-7, wherein the support comprises silica.

9 The supported catalyst system of any one of claims 6-8, wherein the activator comprises methylaluminoxane.

10. A spray-dried catalyst made by contacting a spray-dried activator particle with a trim solution including the germanium bridged Group IV metallocene of any one of claims 1-5.

11. A method of making a polymer, the method comprising:

contacting the supported catalyst system of any one of claims 6-9 and an olefin under polymerization conditions to make the polymer.

12. The method of claim 11, wherein contacting the supported catalyst system and the olefin is in a gas-phase reactor.

13. A method of making the supported catalyst system of claim 6 comprising step (a) or comprising steps (b) and (c):

(a) spray drying a mixture of an inert hydrocarbon solvent, the germanium bridged Group IV metallocene (I), the support material, and the activator to make the supported catalyst system; or

(b) spray drying a mixture of an inert hydrocarbon solvent, the support material and the activator to make a spray-dried supported activator, and

(c) mixing the germanium bridged Group IV metallocene (I) with the spray-dried supported activator and an inert hydrocarbon solvent to make the supported catalyst system.