

ORGANOMETALLIC CHAIN TRANSFER AGENTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority to U.S. provisional application no. 62/786,110, filed on December 28, 2018, which is incorporated herein by reference in its entirety.

FIELD

[0002] Embodiments relate to organometallic compositions that are useful for chain transfer during olefin polymerization.

BACKGROUND

[0003] Polyolefins are one of the most important and widely used polymeric materials in the world. Certain polyolefins are prepared by polymerization of unsaturated monomers via use of an active catalyst in combination with a chain transfer agent. While simple chain transfer agents such as diethyl zinc are known, more complex chain transfer agents can lead to preparation of novel polyolefins, such as novel telechelic polyolefins. This disclosure relates to a novel chain transfer agent that is useful for preparation of such novel polyolefins.

SUMMARY

[0004] The present disclosure relates to a chain transfer agent comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$, wherein:

Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group;

and

A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

[0005] The present disclosure further relates to processes for preparing the chain transfer agent comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIGS. 1A and 1B provide the ^1H NMR and GC/MS spectra for the synthesis of CTA 1, respectively.

[0007] FIG. 2 provides the ^1H NMR spectrum for the synthesis of CTA 2.

[0008] FIG. 3 provides the ^1H NMR spectrum for the synthesis of CTA 6.

DETAILED DESCRIPTION

Definitions

[0009] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

[0010] The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges containing explicit values (e.g., 1, or 2, or 3 to 5, or 6, or 7), any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.). The numerical ranges disclosed herein further include the fractions between any two explicit values.

[0011] The terms “comprising,” “including,” “having” and their derivatives are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term “comprising” may include any additional additive, adjuvant, component, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step, or procedure, excepting those that are not essential to operability. The term “consisting of” excludes any component, step, or procedure not specifically delineated or listed. The term “or,” unless stated otherwise, refers to the listed members individually as well as in any combination.

[0012] The term “hindered double bond” refers to a carbon-carbon double bond that cannot readily participate in coordination polymerization. In other words, a hindered double bond has negligible reactivity to participate in coordination polymerization. Examples of hindered double bonds include but are not limited to the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a

vinyl group attached to a branched alpha carbon. The term “hindered double bond,” as defined herein, excludes the double bonds of strained cyclic olefins that can readily participate in coordination polymerization. As one of ordinary skill in the art would understand, examples of such strained cyclic olefins include but are not limited to norbornene, ethylidene norbornene (ENB), 5-vinyl-2-norbornene (VNB), dicyclopentadiene, norbornadiene, 5-methylene-2-norbornene (MNB), 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, etc. The term “hindered double bond,” as defined herein, further excludes the double bond of a vinyl group attached to an unbranched alpha carbon.

[0013] The term “composition” refers to a mixture of materials or components which comprise the composition. Accordingly, the term “a composition comprising” and similar terms are not intended to exclude the presence of any additional components of the composition, whether or not the same is specifically disclosed.

[0014] The term “acyclic” refers to a series of atoms in a polymer or compound where such a series is linear or branched. Accordingly, the term “acyclic hydrocarbyl group” refers to a hydrocarbyl group that is linear or branched.

[0015] The term “cyclic” refers to a series of atoms in a polymer or compound where such a series includes one or more rings. Accordingly, the term “cyclic hydrocarbyl group” refers to a hydrocarbyl group that contains one or more rings. A “cyclic hydrocarbyl group,” as used herein, may contain acyclic (linear or branched) portions in addition to the one or more rings.

[0016] The term “substituted” refers to a substitution of one or more hydrogen atoms with, for example, an alkyl group. The term “unsubstituted” refers to the absence of such a substitution.

[0017] The term “heteroatom,” as one of ordinary skill in the art would understand, refers to any main group atom that is not carbon or hydrogen. Suitable heteroatoms include but are not limited to nitrogen, oxygen, sulfur, phosphorus, and the halogens.

[0018] As used herein, the terms “hydrocarbyl,” “hydrocarbyl group,” and like terms refer to compounds composed entirely of hydrogen and carbon, including aliphatic, aromatic, acyclic, cyclic, polycyclic, branched, unbranched, saturated, and unsaturated compounds.

[0019] The terms “hydrocarbyl,” “hydrocarbyl group,” “alkyl,” “alkyl group,” “aryl,” “aryl group,” “cycloalkene” and like terms are intended to include every possible isomer, including every structural isomer or stereoisomer. The same applies for like terms including but not limited to heterohydrocarbyl, hydrocarbylene, heterohydrocarbylene, alkylene, heteroalkyl,

heteroalkylene, arylene, heteroaryl, heteroarylene, cycloalkyl, cycloalkylene, heterocycloalkyl, and heterocycloalkylene.

[0020] The term “endocyclic double bond” refers to a double bond between two carbon atoms that are members of a ring. The term “exocyclic double bond” refers to a double bond between two carbon atoms where only one of the carbon atoms is a member of a ring.

[0021] “Active catalyst,” “active catalyst composition,” and like terms refer to a transition metal compound that is, with or without a co-catalyst, capable of polymerization of unsaturated monomers. An active catalyst may be a “procatalyst” that becomes active to polymerize unsaturated monomers without a co-catalyst. Alternatively, an active catalyst may be a “procatalyst” that becomes active, in combination with a co-catalyst, to polymerize unsaturated monomers.

[0022] The term “procatalyst” is used interchangeably with “catalyst,” “precatalyst,” “catalyst precursor,” “transition metal catalyst,” “transition metal catalyst precursor,” “polymerization catalyst,” “polymerization catalyst precursor,” “transition metal complex,” “transition metal compound,” “metal complex,” “metal compound,” “complex,” “metal-ligand complex,” and like terms.

[0023] “Co-catalyst” refers to a compound that can activate certain procatalysts to form an active catalyst capable of polymerization of unsaturated monomers. The term “co-catalyst” is used interchangeably with “activator” and like terms.

[0024] “Polymer” refers to a compound prepared by polymerizing monomers, whether of the same or a different type. The generic term “polymer” thus embraces the term “homopolymer” that refers to polymers prepared from only one type of monomer and the terms “interpolymer” or “copolymer” as defined herein. Trace amounts of impurities, for example, catalyst residues, may be incorporated into and/or within the polymer.

[0025] “Interpolymer” or “copolymer” refer to a polymer prepared by polymerizing at least two different types of monomers. These generic terms include both polymers prepared from two different types of monomers and polymers prepared from more than two different types of monomers (e.g., terpolymers, tetrapolymers, etc.). These generic terms embrace all forms of interpolymers or copolymers, such as random, block, homogeneous, heterogeneous, etc.

[0026] An “ethylene-based polymer” or “ethylene polymer” is a polymer that contains a majority amount (greater than 50 wt%) of polymerized ethylene, based on the weight of the polymer, and, optionally, may further contain polymerized units of at least one comonomer. An “ethylene-based interpolymer” is an interpolymer that contains, in polymerized form, a

majority amount (greater than 50 wt%) of ethylene, based on the weight of the interpolymer, and further contains polymerized units of at least one comonomer. Preferably, the ethylene-based interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). An “ethylene homopolymer” is a polymer that comprises repeating units derived from ethylene but does not exclude residual amounts of other components.

[0027] A “propylene-based polymer” or “propylene polymer” is a polymer that contains a majority amount (greater than 50 wt%) of polymerized propylene, based on the weight of the polymer, and, optionally, may further contain polymerized units of at least one comonomer. A “propylene-based interpolymer” is an interpolymer that contains, in polymerized form, a majority amount (greater than 50 wt%) of propylene, based on the weight of the interpolymer, and further contains polymerized units of at least one comonomer. Preferably, the propylene-based interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). A “propylene homopolymer” is a polymer that comprises repeating units derived from propylene but does not exclude residual amounts of other components.

[0028] An “ethylene/alpha-olefin interpolymer” is an interpolymer that contains a majority amount (greater than 50 wt%) of polymerized ethylene, based on the weight of the interpolymer, and further contains polymerized units of at least one alpha-olefin. Preferably, the ethylene/alpha-olefin interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). An “ethylene/alpha-olefin copolymer” is a copolymer that contains a majority amount (greater than 50 wt%) of polymerized ethylene, based on the weight of the copolymer, and further contains polymerized units of an alpha-olefin. Preferably, the ethylene/alpha-olefin copolymer is a random copolymer (i.e., comprises a random distribution of its monomeric constituents).

[0029] A “propylene/alpha-olefin interpolymer” is an interpolymer that contains a majority amount (greater than 50 wt%) of polymerized propylene, based on the weight of the interpolymer, and further contains polymerized units of at least one alpha-olefin. Preferably, the propylene/alpha-olefin interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). A “propylene/alpha-olefin copolymer” is an interpolymer that contains a majority amount (greater than 50 wt%) of polymerized propylene, based on the weight of the copolymer, and further contains polymerized units of an alpha-olefin. Preferably, the propylene/alpha-olefin copolymer is a random copolymer (i.e., comprises a random distribution of its monomeric constituents).

[0030] “Polyolefin” refers to a polymer produced from olefin monomers, where an olefin monomer (also called an alkene) is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond.

[0031] The terms “chain transfer agent component” and “chain transfer agent” as used herein, refers to a compound or mixture of compounds that is capable of causing reversible or irreversible polymeryl exchange with active catalyst sites. Irreversible chain transfer refers to a transfer of a growing polymer chain from the active catalyst to the chain transfer agent that results in termination of polymer chain growth. Reversible chain transfer refers to transfers of growing polymer chain back and forth between the active catalyst and the chain transfer agent.

[0032] The term “olefin block copolymer” or “OBC” refers to an ethylene/alpha-olefin multi-block interpolymer and includes ethylene and one or more copolymerizable alpha-olefin comonomers in polymerized form, characterized by multiple blocks or segments of two or more (preferably three or more) polymerized monomer units, the blocks or segments differing in chemical or physical properties. Specifically, the term “olefin block copolymer” refers to a polymer comprising two or more (preferably three or more) chemically distinct regions or segments (referred to as “blocks”) joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined (covalently bonded) end-to-end with respect to polymerized functionality, rather than in pendent or grafted fashion. The blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the type of crystallinity (e.g., polyethylene versus polypropylene), the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), region-regularity or region-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, and/or any other chemical or physical property. The block copolymers are characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn) and block length distribution, e.g., based on the effect of the use of a shuttling agent(s) in combination with catalyst systems. Non-limiting examples of the olefin block copolymers of the present disclosure, as well as the processes for preparing the same, are disclosed in U.S. Patent Nos. 7,858,706 B2, 8,198,374 B2, 8,318,864 B2, 8,609,779 B2, 8,710,143 B2, 8,785,551 B2, and 9,243,090 B2, which are all incorporated herein by reference in their entirety.

[0033] The term “block composite” (“BC”) refers to a polymer comprising three polymer components: (i) an ethylene-based polymer (EP) having an ethylene content from 10 mol% to

90 mol% (a soft copolymer), based on the total moles of polymerized monomer units in the ethylene-based polymer (EP); (ii) an alpha-olefin-based polymer (AOP) having an alpha-olefin content of greater than 90 mol% (a hard copolymer), based on the total moles of polymerized monomer units in the alpha-olefin-based polymer (AOP); and (iii) a block copolymer (diblock copolymer) having an ethylene block (EB) and an alpha-olefin block (AOB); wherein the ethylene block of the block copolymer is the same composition as the EP of component (i) of the block composite and the alpha-olefin block of the block copolymer is the same composition as the AOP of component (ii) of the block composite. Additionally, in the block composite, the compositional split between the amount of EP and AOP will be essentially the same as that between the corresponding blocks in the block copolymer. Non-limiting examples of the block composites of the present disclosure, as well as processes for preparing the same, are disclosed in U.S. Patent Nos. 8,686,087 and 8,716,400, which are incorporated herein by reference in their entirety.

[0034] The term "specified block composite" ("SBC") refers to a polymer comprising three polymer components: (i) an ethylene-based polymer (EP) having an ethylene content from 78 mol% to 90 mol% (a soft copolymer), based on the total moles of polymerized monomer units in the ethylene-based polymer (EP); (ii) an alpha-olefin-based polymer (AOP) having an alpha-olefin content of from 61 mol% to 90 mol% (a hard copolymer), based on the total moles of polymerized monomer units in the alpha-olefin-based polymer (AOP); and (iii) a block copolymer (diblock copolymer) having an ethylene block (EB) and an alpha-olefin block (AOB); wherein the ethylene block of the block copolymer is the same composition as the EP of component (i) of the specified block composite and the alpha-olefin block of the block copolymer is the same composition as the AOP of component (ii) of the specified block composite. Additionally, in the specified block composite, the compositional split between the amount of EP and AOP will be essentially the same as that between the corresponding blocks in the block copolymer. Non-limiting examples of the specified block composites of the present disclosure, as well as processes for preparing the same, are disclosed in WO 2017/044547, which is incorporated herein by reference in its entirety.

[0035] The term "crystalline block composite" ("CBC") refers to polymers comprising three components: (i) a crystalline ethylene based polymer (CEP) having an ethylene content of greater than 90 mol%, based on the total moles of polymerized monomer units in the crystalline ethylene based polymer (CEP); (ii) a crystalline alpha-olefin based polymer (CAOP) having an alpha-olefin content of greater than 90 mol%, based on the total moles of

polymerized monomer units in the crystalline alpha-olefin based copolymer (CAOP); and (iii) a block copolymer comprising a crystalline ethylene block (CEB) and a crystalline alpha-olefin block (CAOB); wherein the CEB of the block copolymer is the same composition as the CEP of component (i) of the crystalline block composite and the CAOB of the block copolymer is the same composition as the CAOP of component (ii) of the crystalline block composite. Additionally, in the crystalline block composite, the compositional split between the amount of CEP and CAOP will be essentially the same as that between the corresponding blocks in the block copolymer. Non-limiting examples of the crystalline block composites of the present disclosure, as well as the processes for preparing the same, are disclosed in US Pat. No. 8,822,598 B2 and WO 2016/01028961 A1, which are incorporated herein by reference in its entirety.

[0036] The term “crystalline” refers to a polymer that possesses a first order transition or crystalline melting point (T_m) as determined by differential scanning calorimetry (DSC) or equivalent techniques. The term may be used interchangeably with the term “semicrystalline.” The term “amorphous” refers to a polymer lacking a crystalline melting point as determined by differential scanning calorimetry (DSC) or equivalent technique.

Chain Transfer Agent

[0037] The chain transfer agent of the present disclosure comprises an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ and an organozinc compound of the formula $Zn(CH_2CH(Y^2)A^2)_2$, wherein: Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond. In certain embodiments, the chain transfer agent comprises a ratio of the organozinc compound of the formula $Zn(CH_2CH(Y^2)A^2)_2$ to the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ of from 1:99 to 80:20, or from 10:90 to 60:40, or from 20:80 to 40:60.

[0038] In certain embodiments, the Y^2 group at each occurrence independently is hydrogen. In further embodiments, the Y^2 group at each occurrence independently is a C_1 to C_{10} alkyl group, or a C_1 to C_6 alkyl group, or a C_1 to C_3 alkyl group.

[0039] In some embodiments, A^2 at each occurrence is a hydrocarbyl group comprising a hindered double bond. In further embodiments, A^2 at each occurrence is a hydrocarbyl group comprising two or more hindered double bonds.

[0040] In some embodiments, A^2 at each occurrence is a hydrocarbyl group comprising a hindered double bond, wherein the hindered double bond is selected from the group

consisting of the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.

[0041] In further embodiments, A^2 at each occurrence is a hydrocarbyl group comprising two or more hindered double bonds, wherein each hindered double bond is independently selected from the group consisting of the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.

[0042] In certain embodiments, A^2 at each occurrence is a hydrocarbyl group comprising a functional group, wherein the functional group is selected from the group consisting of a vinylidene group, a vinylene group, a trisubstituted alkene, and a vinyl group attached to a branched alpha carbon.

[0043] In further embodiments, A^2 at each occurrence is a hydrocarbyl group comprising two or more functional groups, wherein each functional group is independently selected from the group consisting of a vinylidene group, a vinylene group, a trisubstituted alkene, and a vinyl group attached to a branched alpha carbon.

[0044] The A^2 group at each occurrence may be a cyclic or acyclic (linear or branched) hydrocarbyl group. If A^2 is a cyclic hydrocarbyl group, A^2 may comprise one or more rings, wherein each ring may be a monocyclic, bicyclic, or polycyclic ring, and wherein each ring may comprise one or more hindered double bonds.

[0045] Furthermore, if A^2 is a cyclic hydrocarbyl group, each hindered double bond or functional group therein may be an endocyclic double bond, an exocyclic double bond, or an acyclic double bond. For example, A^2 may be a cyclic hydrocarbyl group comprising a vinylene group, wherein the double bond of the vinylene group may be an endocyclic double bond or an acyclic double bond. In further embodiments, A^2 may be a cyclic hydrocarbyl group comprising a vinylidene group, wherein the double bond of the vinylidene group may be an exocyclic double bond or an acyclic double bond. In further embodiments, A^2 may be a cyclic hydrocarbyl group comprising a trisubstituted alkene, wherein the double bond of the trisubstituted alkene may be an endocyclic double bond, an exocyclic double bond, or an acyclic double bond. In further embodiments, A^2 may be a cyclic hydrocarbyl group comprising a vinyl group attached to a branched alpha carbon, wherein the vinyl group attached to a branched alpha carbon is an acyclic double bond.

[0046] In any of the embodiments described herein, A² at each occurrence may comprise from 3 to 30 carbon atoms, or from 3 to 25 carbon atoms, or from 3 to 20 carbon atoms, or from 3 to 15 carbon atoms, or from 3 to 10 carbon atoms, or from 3 to 9 carbon atoms, or from 3 to 8 carbon atoms, or from 3 to 7 carbon atoms, or from 3 to 6 carbon atoms, or from 3 to 5 carbon atoms, or from 3 to 4 carbon atoms, or 3 carbon atoms.

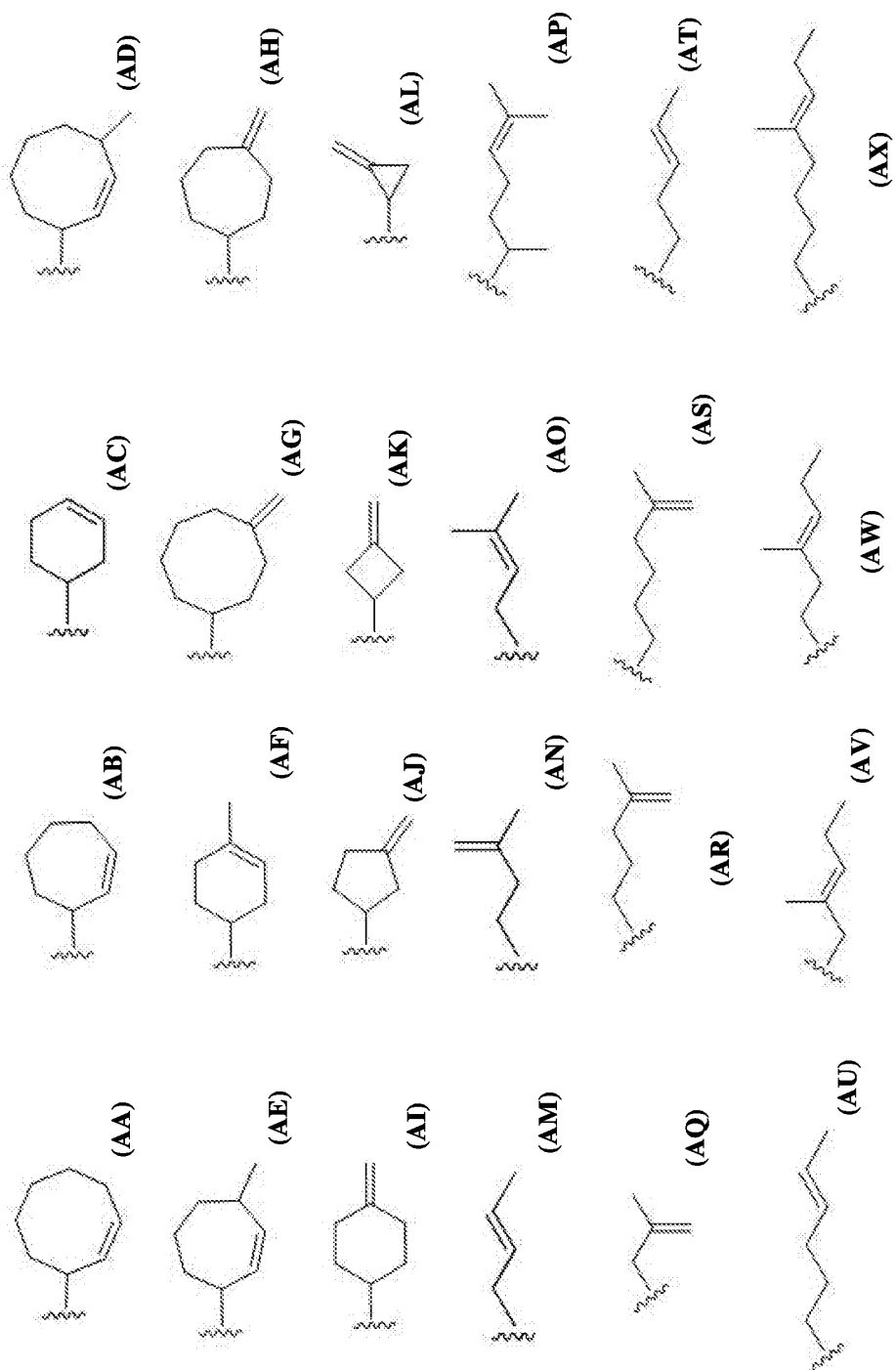
[0047] In certain embodiments, A² at each occurrence is a C₃ to C₃₀ cyclic hydrocarbyl group comprising an alkyl-substituted or unsubstituted cycloalkene. In further embodiments, A² at each occurrence is an alkyl-substituted or unsubstituted cycloalkene comprising from 3 to 30 carbon atoms, or from 3 to 25 carbon atoms, or from 3 to 20 carbon atoms, or from 3 to 15 carbon atoms, or from 3 to 10 carbon atoms, or from 3 to 9 carbon atoms, or from 3 to 8 carbon atoms, or from 3 to 7 carbon atoms, or from 3 to 6 carbon atoms.

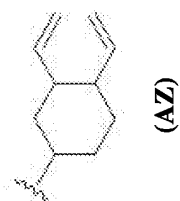
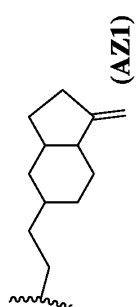
[0048] Exemplary unsubstituted cycloalkenes include but are not limited to cyclohexene, cycloheptene, cyclooctene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1,5-cyclooctadiene. Exemplary alkyl-substituted cycloalkenes include but are not limited to alkyl-substituted cyclohexene, alkyl-substituted cycloheptene, alkyl-substituted cyclooctene, alkyl-substituted 1,3-cyclohexadiene, alkyl-substituted 1,4-cyclohexadiene, and alkyl-substituted 1,5-cyclooctadiene.

[0049] In some embodiments, A² at each occurrence is a methyl-substituted or unsubstituted cycloalkene selected from the group consisting of a methyl-substituted or unsubstituted cyclohexene, a methyl-substituted or unsubstituted cycloheptene, and a methyl-substituted or unsubstituted cyclooctene. In some embodiments, A² at each occurrence is a methyl-substituted or unsubstituted cyclohexene.

[0050] In some embodiments, A² at each occurrence is a C₁ to C₁₀ acyclic alkyl group, or a C₃ to C₁₀ acyclic alkyl group, or a C₄ to C₈ acyclic alkyl group.

[0051] Exemplary A² groups include but are not limited to the following:





[0052] With regard to each of (AA) to (AZ) and (AZ1), the  symbol (squiggly line symbol) denotes the point of connection to the carbon attached to a hydrogen and Y² in the chain transfer agent formulas of Al(CH₂CH(Y²)A²)₃ and Zn(CH₂CH(Y²)A²)₂.

[0053] With regard to each of (AA) to (AF), the endocyclic double bond may be between any two adjacent carbon atoms that are ring members.

[0054] With regard to each of (AD) to (AF), the pendant methyl group may be connected to any carbon atom that is a ring member.

[0055] With regard to each of (AG) to (AL), the exocyclic double bond may be connected to any ring member carbon atom that is not already connected to more than two carbon atoms.

Process for preparing chain transfer agent

[0056] The chain transfer agent is composed of an organoaluminum compound of the formula Al(CH₂CH(Y²)A²)₃, wherein: Y² at each occurrence independently is hydrogen or a C₁ to C₃₀ hydrocarbyl group; and A² at each occurrence independently is a hydrocarbyl group comprising a hindered double bond. In certain embodiments, Y² of the organoaluminum compound of the formula Al(CH₂CH(Y²)A²)₃ may be selected from the group consisting of hydrogen, a methyl group, and an ethyl group. In certain embodiments, A² of the organoaluminum compound of the formula Al(CH₂CH(Y²)A²)₃ may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A² of the organoaluminum compound of the formula Al(CH₂CH(Y²)A²)₃ is selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

[0057] The chain transfer agent is further composed of an organozinc compound of the formula Zn(CH₂CH(Y²)A²)₂, wherein: Y² at each occurrence independently is hydrogen or a C₁ to C₃₀ hydrocarbyl group; and A² at each occurrence independently is a hydrocarbyl group comprising a hindered double bond. In certain embodiments, Y² of the organozinc compound of the formula Zn(CH₂CH(Y²)A²)₂ will be a C₁ to C₃₀ hydrocarbyl group, while A² may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A² of the organozinc compound of the formula Zn(CH₂CH(Y²)A²)₂ is selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

[0058] The chain transfer agent comprising the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and the organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ may be prepared by preparing each of the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and the organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ independently and then mixing the two together at a ratio of the organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ to the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ of from 1:99 to 80:20, or from 10:90 to 60:40, or from 20:80 to 40:60.

[0059] The organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ may be prepared by a thermal process comprising: (a) combining starting materials comprising a hydrocarbon of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$, an aluminum alkyl of the formula $\text{Al}(\text{d})_3$, and an optional solvent to form an organoaluminum solution, (b) heating the organoaluminum solution to a temperature from 60 to 200°C, or from 80 to 180°C, or from 100 to 150°C, or from 110 to 130°C and holding the organo-aluminum solution at the temperature of from 60 to 200°C, or from 80 to 180°C, or from 100 to 150°C, or from 110 to 130°C for a time from 30 minutes to 200 hours, or from 30 minutes to 100 hours, or from 30 minutes to 50 hours, or from 30 minutes to 25 hours, or from 1 hour to 10 hours, or from 1 hour to 5 hours, or from 3 hours to 5 hours, and (c) recovering a product comprising the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$, wherein: d at each occurrence independently is a C_1 to C_{10} alkyl group; Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond. In certain embodiments, the carbon of d that is attached to Al is a carbon that is connected to a tertiary carbon. For example, in certain embodiments, the aluminum alkyl of the formula $\text{Al}(\text{d})_3$ is triisobutylaluminum.

[0060] For the thermal process of preparing the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$, Y^2 and A^2 may be any of the previously described embodiments of Y^2 and A^2 . The optional solvent may be any discussed herein. The starting materials in step (a) may comprise a ratio of the aluminum alkyl of the formula $\text{Al}(\text{d})_3$ to the hydrocarbon of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$ of 1:10, or 1:5, or 1:3. The starting materials in step (a) may comprise one or more hydrocarbons of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$, wherein: Y^2 at each occurrence of each hydrocarbon independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; A^2 at each of occurrence of each hydrocarbon independently is a hydrocarbyl group comprising a hindered double bond; and the starting materials comprise a ratio of the aluminum alkyl of the formula

Al(d)_3 to the one or more hydrocarbons of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$ of 1:10, or 1:5, or 1:3. In certain embodiments, Y^2 may be selected from the group consisting of hydrogen, a methyl group, and an ethyl group, and A^2 may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 may be selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member. In this process of preparing the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$, any excess hydrocarbon of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$ may be removed through the use of vacuum and optional heating.

[0061] Alternatively, the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ may be prepared a catalytic process comprising: (a) combining starting materials comprising a hydrocarbon of the formula $\text{CH}_2=\text{CHA}^2$, an aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$, a catalyst component comprising a procatalyst and an optional co-catalyst, and an optional solvent, and (b) recovering a product comprising the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$, wherein step (a) is conducted at a temperature from 1°C to 50 °C, or from 10°C to 40 °C, or from 20°C to 30°C for a time of 1 to 50 hours, or from 10 to 40 hours, or from 15 to 25 hours, and wherein: Y^2 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

[0062] For the catalytic process of preparing the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$, Y^2 will be a C_1 to C_{30} hydrocarbyl group while A^2 may be any of the previously described embodiments. Each of the procatalyst, the optional co-catalyst, and the optional solvent may be any disclosed herein. The starting materials in step (a) may comprise a ratio of the aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$ to the hydrocarbon of the formula $\text{CH}_2=\text{CHA}^2$ of from 1:10, or 1:5, or 1:3. The starting materials in step (a) may comprise one or more hydrocarbons of the formula $\text{CH}_2=\text{CHA}^2$, wherein: A^2 at each occurrence of each hydrocarbon independently is a hydrocarbyl group comprising a hindered double bond; and the starting materials comprise a ratio of the aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$ to the one or more hydrocarbons of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$ of from 1:10, or 1:5, or 1:3. In certain embodiments, Y^2 may be a C_1 to C_{10} alkyl group, and A^2 may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 may be selected from the group consisting of

(AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

[0063] The organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ may be prepared a catalytic process comprising: (a) combining starting materials comprising a hydrocarbon of the formula $\text{CH}_2=\text{CHA}^2$, a zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$, a catalyst component comprising a procatalyst and an optional co-catalyst, and an optional solvent, and (b) recovering a product comprising the organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$, wherein step (a) is conducted at a temperature from 1°C to 50 °C, or from 10°C to 40 °C, or from 20°C to 30°C for a time of 1 to 50 hours, or from 10 to 40 hours, or from 15 to 25 hours, and wherein: Y^2 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

[0064] For the catalytic process of preparing the organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$, Y^2 will be a C_1 to C_{30} hydrocarbyl group while A^2 may be any of the previously described embodiments. Each of the procatalyst, the optional co-catalyst, and the optional solvent may be any disclosed herein. The starting materials in step (a) may comprise a ratio of the zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$ to the hydrocarbon of the formula $\text{CH}_2=\text{CHA}^2$ of 1:10, or 1:5, or 1:2. The starting materials in step (a) may comprise one or more hydrocarbons of the formula $\text{CH}_2=\text{CHA}^2$, wherein: A^2 at each occurrence of each hydrocarbon independently is a hydrocarbyl group comprising a hindered double bond; and the starting materials comprise a ratio of the zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$ to the one or more hydrocarbons of the formula $\text{CH}_2=\text{C}(\text{Y}^2)\text{A}^2$ of 1:10, or 1:5, or 1:2. In certain embodiments, Y^2 may be a C_1 to C_{10} alkyl group, and A^2 may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 may be selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

[0065] Alternatively, the chain transfer agent comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ may be prepared by a catalytic process, rather than independently preparing the organoaluminum compound and the organozinc compound and mixing them. Specifically, the chain transfer agent comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ may be prepared by a process comprising: (a)

combining starting materials comprising a hydrocarbon of formula $\text{CH}_2=\text{CHA}^2$, an aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$, a zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$, a catalyst component comprising a procatalyst and an optional co-catalyst, and an optional solvent, and (b) recovering a product comprising the (B) chain transfer agent component comprising the organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and the organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$, wherein step (a) is conducted at a temperature of from 1°C to 50°C , or from 10°C to 40°C , or from 20°C to 30°C for a time of 1 to 50 hours, or from 10 to 40 hours, or from 15 to 25 hours, and wherein: Y^2 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

[0066] For the catalytic process of preparing the chain transfer agent comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$, Y^2 will be a C_1 to C_{30} hydrocarbyl group while A^2 may be any of the previously described embodiments. Each of the procatalyst, the optional co-catalyst, and the optional solvent may be any disclosed herein. The starting materials in step (a) may comprise a ratio of the aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$ and the zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$ to the hydrocarbon of formula $\text{CH}_2=\text{CHA}^2$ of 1:1. The starting materials in step (a) may further comprise a ratio of the zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$ to the aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$ from 1:99 to 80:20, or from 10:90 to 60:40, or from 20:80 to 40:60. The starting materials in step (a) may comprise one or more hydrocarbons of the formula $\text{CH}_2=\text{CHA}^2$, wherein: A^2 at each of occurrence of each hydrocarbon independently is a hydrocarbyl group comprising a hindered double bond; and the starting materials comprise a ratio of the aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$ and the zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$ to the one or more hydrocarbons of formula $\text{CH}_2=\text{CHA}^2$ of 1:1 and a ratio of the zinc alkyl of the formula $\text{Zn}(\text{Y}^2)_2$ to the aluminum alkyl of the formula $\text{Al}(\text{Y}^2)_3$ from 1:99 to 80:20, or from 10:90 to 60:40, or from 20:80 to 40:60. In certain embodiments, Y^2 may be a C_1 to C_{10} alkyl group, and A^2 may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 may be selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

[0067] In further embodiments, the (B) chain transfer agent component comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$ may be prepared by a thermal process.

[0068] Suitable procatalysts include but are not limited to those disclosed in WO 2005/090426, WO 2005/090427, WO 2007/035485, WO 2009/012215, WO 2014/105411, WO 2017/173080, U.S. Patent Publication Nos. 2006/0199930, 2007/0167578, 2008/0311812, and U.S. Patent Nos. 7,858,706 B2, 7,355,089 B2, 8,058,373 B2, and 8,785,554 B2. With reference to the paragraphs below, the term “procatalyst” is interchangeable with the terms “catalyst,” “precatalyst,” “catalyst precursor,” “transition metal catalyst,” “transition metal catalyst precursor,” “polymerization catalyst,” “polymerization catalyst precursor,” “transition metal complex,” “transition metal compound,” “metal complex,” “metal compound,” “complex,” and “metal-ligand complex,” and like terms.

[0069] Both heterogeneous and homogeneous catalysts may be employed. Examples of heterogeneous catalysts include the well known Ziegler-Natta compositions, especially Group 4 metal halides supported on Group 2 metal halides or mixed halides and alkoxides and the well known chromium or vanadium based catalysts. Preferably, the catalysts for use herein are homogeneous catalysts comprising a relatively pure organometallic compound or metal complex, especially compounds or complexes based on metals selected from Groups 3-10 or the Lanthanide series of the Periodic Table of the Elements.

[0070] Metal complexes for use herein may be selected from Groups 3 to 15 of the Periodic Table of the Elements containing one or more delocalized, π -bonded ligands or polyvalent Lewis base ligands. Examples include metallocene, half-metallocene, constrained geometry, and polyvalent pyridylamine, or other polychelating base complexes. The complexes are generically depicted by the formula: $\text{MK}_k\text{X}_x\text{Z}_z$, or a dimer thereof, wherein

M is a metal selected from Groups 3-15, preferably 3-10, more preferably 4-10, and most preferably Group 4 of the Periodic Table of the Elements;

K independently at each occurrence is a group containing delocalized π -electrons or one or more electron pairs through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two or more K groups may be joined together forming a bridged structure, and further optionally one or more K groups may be bound to Z, to X or to both Z and X;

X independently at each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X groups may be bonded together thereby forming a divalent or polyvalent anionic group, and, further optionally, one or more X groups and one or more Z groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto; or two X groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π -electrons to M, whereupon M is in the +2 formal oxidation state, and

Z independently at each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3; x is an integer from 1 to 4; z is a number from 0 to 3; and the sum, $k+x$, is equal to the formal oxidation state of M.

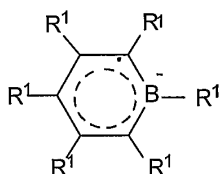
[0071] Suitable metal complexes include those containing from 1 to 3 π -bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized π -bonded anionic ligand groups. Exemplary of such π -bonded groups are conjugated or nonconjugated, cyclic or non-cyclic diene and dienyl groups, allyl groups, boratabenzene groups, phosphole, and arene groups. By the term " π -bonded" is meant that the ligand group is bonded to the transition metal by a sharing of electrons from a partially delocalized π -bond.

[0072] Each atom in the delocalized π -bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted heteroatoms wherein the heteroatom is selected from Group 14-16 of the Periodic Table of the Elements, and such hydrocarbyl-substituted heteroatom radicals further substituted with a Group 15 or 16 hetero atom containing moiety. In addition, two or more such radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems, or they may form a metallocycle with the metal. Included within the term "hydrocarbyl" are C_{1-20} straight, branched and cyclic alkyl radicals, C_{6-20} aromatic radicals, C_{7-20} alkyl-substituted aromatic radicals, and C_{7-20} aryl-substituted alkyl radicals. Suitable hydrocarbyl-substituted heteroatom radicals include mono-, di- and tri-substituted radicals of boron, silicon, germanium, nitrogen, phosphorus or oxygen wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples include N,N-dimethylamino, pyrrolidinyl,

trimethylsilyl, triethylsilyl, t-butyldimethylsilyl, methyldi(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amino, phosphino, alkoxy, or alkylthio moieties or divalent derivatives thereof, for example, amide, phosphide, alkyleneoxy or alkyleneethio groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group, π -bonded group, or hydrocarbyl-substituted heteroatom.

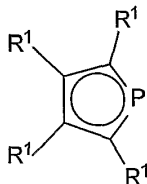
[0073] Examples of suitable anionic, delocalized π -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, phosphole, and boratabenzyl groups, as well as inertly substituted derivatives thereof, especially C_{1-10} hydrocarbyl-substituted or tris(C_{1-10} hydrocarbyl)silyl-substituted derivatives thereof. Preferred anionic delocalized π -bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, 1-indacenyl, 3-pyrrolidinoinden-1-yl, 3,4-(cyclopenta(1)phenanthren-1-yl, and tetrahydroindenyl.

[0074] The boratabenzenyl ligands are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenyl ligands correspond to the formula:



wherein R^1 is an inert substituent, preferably selected from the group consisting of hydrogen, hydrocarbyl, silyl, halo or germyl, said R^1 having up to 20 atoms not counting hydrogen, and optionally two adjacent R^1 groups may be joined together. In complexes involving divalent derivatives of such delocalized π -bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.

[0075] Phospholes are anionic ligands that are phosphorus containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:



wherein R¹ is as previously defined.

[0076] Suitable transition metal complexes for use herein correspond to the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein:

M is a Group 4 metal;

K is a group containing delocalized π -electrons through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two K groups may be joined together forming a bridged structure, and further optionally one K may be bound to X or Z;

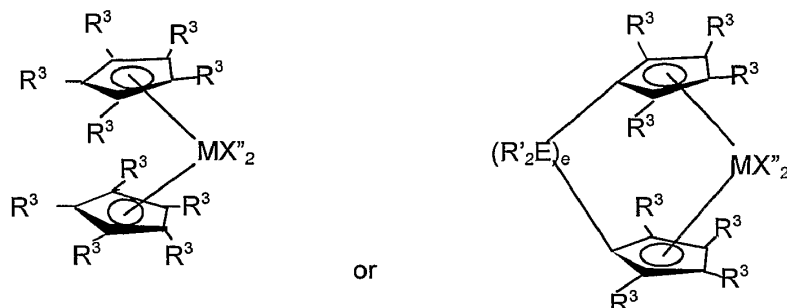
X at each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X and one or more K groups are bonded together to form a metallocycle, and further optionally one or more X and one or more Z groups are bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto;

Z independently at each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3; x is an integer from 1 to 4; z is a number from 0 to 3; and the sum, $k+x$, is equal to the formal oxidation state of M.

[0077] Suitable complexes include those containing either one or two K groups. The latter complexes include those containing a bridging group linking the two K groups. Suitable bridging groups are those corresponding to the formula $(ER'_2)_e$ wherein E is silicon, germanium, tin, or carbon, R' independently at each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms, and e is 1 to 8. Illustratively, R' independently at each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

[0078] Examples of the complexes containing two K groups are compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state; R^3 at each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non-hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

X'' independently at each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X'' groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π -electrons to M, whereupon M is in the +2 formal oxidation state, and R' , E and e are as previously defined.

[0079] Exemplary bridged ligands containing two π -bonded groups are:

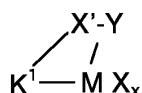
dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane, dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-t-butylcyclopentadien-1-yl)silane, 2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane, dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(fluoren-1-yl)silane, dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)-silane, dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane, dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane, dimethyl(cyclopentadienyl)(tetrahydrofluoren-1-yl)silane, (1,1,2,2-tetramethy)-1,2-bis(cyclopentadienyl)disilane, (1,2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-1-(fluoren-1-yl)methane.

[0080] Suitable X" groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl groups, or two X" groups together form a divalent derivative of a conjugated diene or else together they form a neutral, π -bonded, conjugated diene. Exemplary X" groups are C1-20 hydrocarbyl groups.

[0081] A further class of metal complexes utilized in the present disclosure corresponds to the preceding formula: MKZ_zX_x , or a dimer thereof, wherein M, K, X, x and z are as previously defined, and Z is a substituent of up to 50 non-hydrogen atoms that together with K forms a metallocycle with M.

[0082] Suitable Z substituents include groups containing up to 30 non-hydrogen atoms comprising at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the Elements directly attached to K, and a different atom, selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

[0083] More specifically this class of Group 4 metal complexes used according to the present invention includes "constrained geometry catalysts" corresponding to the formula:



wherein: M is titanium or zirconium, preferably titanium in the +2, +3, or +4 formal oxidation state;

K^1 is a delocalized, π -bonded ligand group optionally substituted with from 1 to 5 R^2 groups,

R^2 at each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^2 having up to 20 non-hydrogen atoms, or adjacent R^2 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

each X is a halo, hydrocarbyl, heterohydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two X groups together form a neutral C5-30 conjugated diene or a divalent derivative thereof;

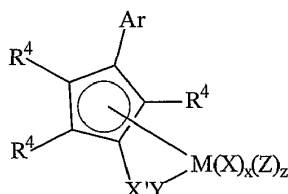
x is 1 or 2;

Y is -O-, -S-, -NR'-, -PR'-;

and X' is SiR'_2 , CR'_2 , $\text{SiR}'_2\text{SiR}'_2$, $\text{CR}'_2\text{CR}'_2$, $\text{CR}'=\text{CR}'$, $\text{CR}'_2\text{SiR}'_2$, or GeR'_2 , wherein

R' independently at each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms.

[0084] Specific examples of the foregoing constrained geometry metal complexes include compounds corresponding to the formula:



wherein,

Ar is an aryl group of from 6 to 30 atoms not counting hydrogen;

R⁴ independently at each occurrence is hydrogen, Ar, or a group other than Ar selected from hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylgermyl, halide, hydrocarbyloxy, trihydrocarbylsiloxy, bis(trihydrocarbylsilyl)amino, di(hydrocarbyl)amino, hydrocarbadiylamino, hydrocarbylimino, di(hydrocarbyl)phosphino, hydrocarbadiylphosphino, hydrocarbylsulfido, halo- substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbylsilyl- substituted hydrocarbyl, trihydrocarbylsiloxy- substituted hydrocarbyl, bis(trihydrocarbylsilyl)amino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino- substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R group having up to 40 atoms not counting hydrogen atoms, and optionally two adjacent R⁴ groups may be joined together forming a polycyclic fused ring group;

M is titanium;

X' is SiR⁶₂, CR⁶₂, SiR⁶₂SiR⁶₂, CR⁶₂CR⁶₂, CR⁶=CR⁶, CR⁶₂SiR⁶₂, BR⁶, BR⁶L", or GeR⁶₂;

Y is -O-, -S-, -NR⁵-, -PR⁵-, -NR⁵₂, or -PR⁵₂;

R⁵, independently at each occurrence is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R⁵ having up to 20 atoms other than hydrogen, and optionally two R⁵ groups or R⁵ together with Y or Z form a ring system;

R⁶, independently at each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, -NR⁵₂, and

combinations thereof, said R^6 having up to 20 non-hydrogen atoms, and optionally, two R^6 groups or R^6 together with Z forms a ring system;

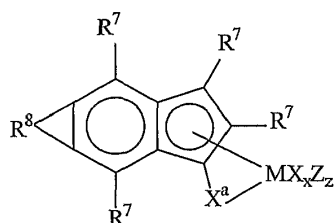
Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to R^5 , R^6 , or X;

X is hydrogen, a monovalent anionic ligand group having up to 60 atoms not counting hydrogen, or two X groups are joined together thereby forming a divalent ligand group;

x is 1 or 2; and

z is 0, 1 or 2.

[0085] Additional examples of suitable metal complexes herein are polycyclic complexes corresponding to the formula:



where M is titanium in the +2, +3 or +4 formal oxidation state;

R^7 independently at each occurrence is hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R^7 group having up to 40 atoms not counting hydrogen, and optionally two or more of the foregoing groups may together form a divalent derivative;

R^8 is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R^8 containing from 1 to 30 atoms not counting hydrogen;

X^a is a divalent moiety, or a moiety comprising one π -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said X^a comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

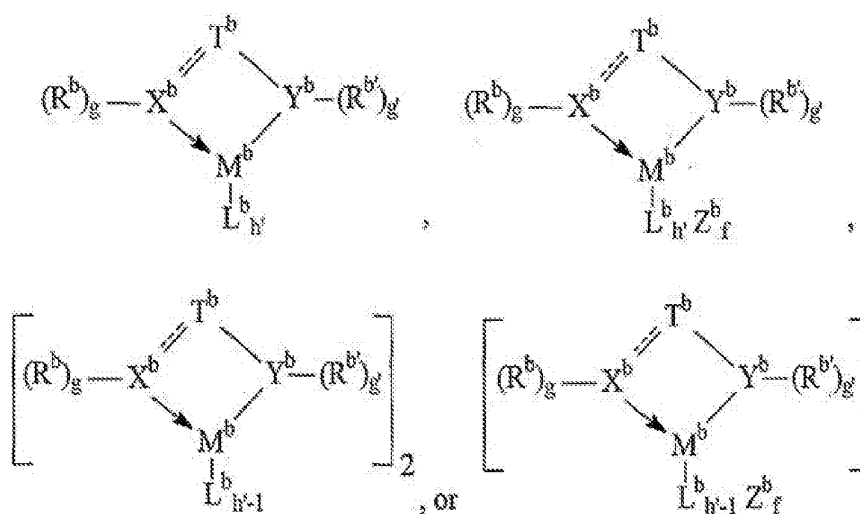
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups and optionally two X groups together form a divalent ligand group;

Z independently at each occurrence is a neutral ligating compound having up to 20 atoms;

x is 0, 1 or 2; and

z is zero or 1.

[0086] Additional examples of metal complexes that are usefully employed as catalysts are complexes of polyvalent Lewis bases, such as compounds corresponding to the formula:



wherein T^b is a bridging group, preferably containing 2 or more atoms other than hydrogen,

X^b and Y^b are each independently selected from the group consisting of nitrogen, sulfur, oxygen and phosphorus; more preferably both X^b and Y^b are nitrogen,

R^b and $R^{b'}$ independently each occurrence are hydrogen or C_{1-50} hydrocarbyl groups optionally containing one or more heteroatoms or inertly substituted derivative thereof. Non-limiting examples of suitable R^b and $R^{b'}$ groups include alkyl, alkenyl, aryl, aralkyl, (poly)alkylaryl and cycloalkyl groups, as well as nitrogen, phosphorus, oxygen and halogen substituted derivatives thereof. Specific examples of suitable R^b and $R^{b'}$ groups include methyl, ethyl, isopropyl, octyl, phenyl, 2,6-dimethylphenyl, 2,6-di(isopropyl)phenyl, 2,4,6-trimethylphenyl, pentafluorophenyl, 3,5-trifluoromethylphenyl, and benzyl;

g and g' are each independently 0 or 1;

M^b is a metallic element selected from Groups 3 to 15, or the Lanthanide series of the Periodic Table of the Elements. Preferably, M^b is a Group 3-13 metal, more preferably M^b is a Group 4-10 metal;

L^b is a monovalent, divalent, or trivalent anionic ligand containing from 1 to 50 atoms, not counting hydrogen. Examples of suitable L^b groups include halide; hydride; hydrocarbyl, hydrocarbyloxy; di(hydrocarbyl)amido, hydrocarbyleneamido, di(hydrocarbyl)phosphido; hydrocarbylsulfido; hydrocarbyloxy, tri(hydrocarbylsilyl)alkyl; and carboxylates. More preferred L^b groups are C_{1-20} alkyl, C_{7-20} aralkyl, and chloride;

h and h' are each independently an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3, and j is 1 or 2, with the value $h \times j$ selected to provide charge balance;

Z^b is a neutral ligand group coordinated to M^b , and containing up to 50 atoms not counting hydrogen. Preferred Z^b groups include aliphatic and aromatic amines, phosphines, and ethers, alkenes, alkadienes, and inertly substituted derivatives thereof. Suitable inert substituents include halogen, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, di(hydrocarbyl)amine, tri(hydrocarbyl)silyl, and nitrile groups. Preferred Z^b groups include triphenylphosphine, tetrahydrofuran, pyridine, and 1,4-diphenylbutadiene;

f is an integer from 1 to 3;

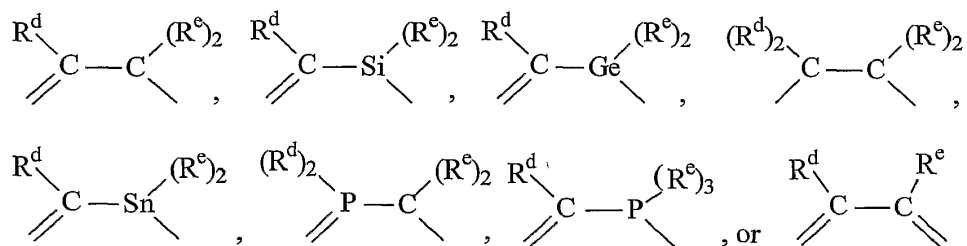
two or three of T^b , R^b and $R^{b'}$ may be joined together to form a single or multiple ring structure;

h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3;

[0087] In one embodiment, it is preferred that R^b have relatively low steric hindrance with respect to X^b . In this embodiment, most preferred R^b groups are straight chain alkyl groups,

straight chain alkenyl groups, branched chain alkyl groups wherein the closest branching point is at least 3 atoms removed from X^b , and halo, dihydrocarbylamino, alkoxy or trihydrocarbysilyl substituted derivatives thereof. Highly preferred R^b groups in this embodiment are C1-8 straight chain alkyl groups.

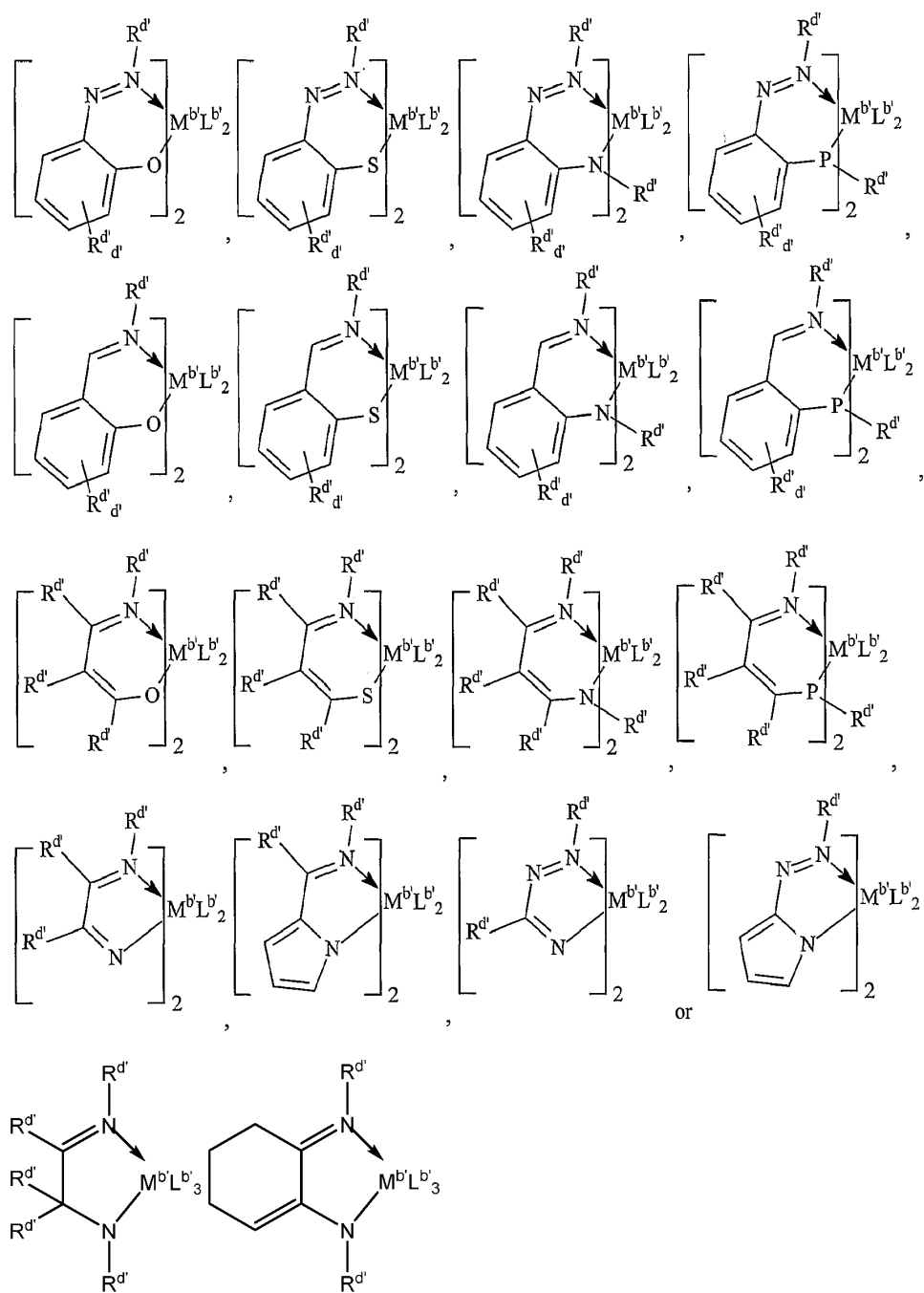
[0088] At the same time, in this embodiment $R^{b'}$ preferably has relatively high steric hindrance with respect to Y^b . Non-limiting examples of suitable $R^{b'}$ groups for this embodiment include alkyl or alkenyl groups containing one or more secondary or tertiary carbon centers, cycloalkyl, aryl, alkaryl, aliphatic or aromatic heterocyclic groups, organic or inorganic oligomeric, polymeric or cyclic groups, and halo, dihydrocarbylamino, alkoxy or trihydrocarbysilyl substituted derivatives thereof. Preferred $R^{b'}$ groups in this embodiment contain from 3 to 40, more preferably from 3 to 30, and most preferably from 4 to 20 atoms not counting hydrogen and are branched or cyclic. Examples of preferred T^b groups are structures corresponding to the following formulas:



wherein

Each R^d is C1-10 hydrocarbyl group, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. Each R^e is C1-10 hydrocarbyl, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. In addition, two or more R^d or R^e groups, or mixtures of R^d and R^e groups may together form a divalent or polyvalent derivative of a hydrocarbyl group, such as, 1,4-butylene, 1,5-pentylene, or a cyclic ring, or a multicyclic fused ring, polyvalent hydrocarbyl- or heterohydrocarbyl- group, such as naphthalene-1,8-diyl.

[0089] Suitable examples of the foregoing polyvalent Lewis base complexes include:



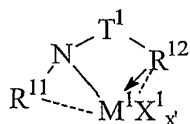
wherein $R^{d'}$ at each occurrence is independently selected from the group consisting of hydrogen and C1-50 hydrocarbyl groups optionally containing one or more heteroatoms, or inertly substituted derivative thereof, or further optionally, two adjacent $R^{d'}$ groups may together form a divalent bridging group;

d' is 4;

$M^{b'}$ is a Group 4 metal, preferably titanium or hafnium, or a Group 10 metal, preferably Ni or Pd;

$L^{b'}$ is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl, or two $L^{b'}$ groups together are a divalent or neutral ligand group, preferably a C₂₋₅₀ hydrocarbylene, hydrocarbadiyl or diene group.

[0090] The polyvalent Lewis base complexes for use in the present invention especially include Group 4 metal derivatives, especially hafnium derivatives of hydrocarbylamine substituted heteroaryl compounds corresponding to the formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

T^1 is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di- C1-20 hydrocarbyl substituted methylene or silane group; and

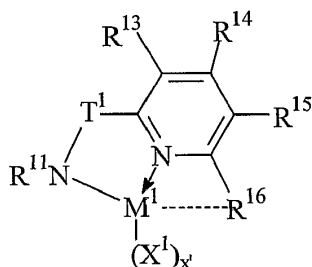
R^{12} is a C₅₋₂₀ heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

M^1 is a Group 4 metal, preferably hafnium;

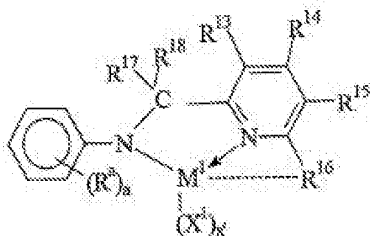
X^1 is an anionic, neutral or dianionic ligand group;

x' is a number from 0 to 5 indicating the number of such X^1 groups; and bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

[0091] Suitable complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from R^{12} . In addition, electron donation from the Lewis base functionality, preferably an electron pair, provides additional stability to the metal center. Suitable metal complexes correspond to the formula:



wherein M^1 , X^1 , x' , R^{11} and T^1 are as previously defined, R^{13} , R^{14} , R^{15} and R^{16} are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent R^{13} , R^{14} , R^{15} or R^{16} groups may be joined together thereby forming fused ring derivatives, and bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively. Suitable examples of the foregoing metal complexes correspond to the formula:



wherein

M^1 , X^1 , and x' are as previously defined,

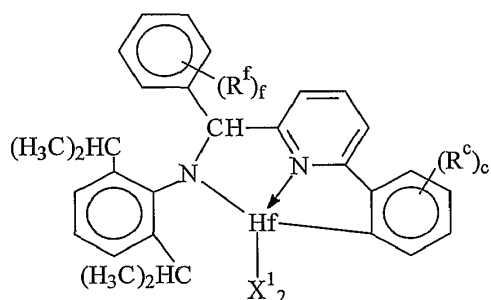
R^{13} , R^{14} , R^{15} and R^{16} are as previously defined, preferably R^{13} , R^{14} , and R^{15} are hydrogen, or C1-4 alkyl, and R^{16} is C₆₋₂₀ aryl, most preferably naphthalenyl;

R^a independently at each occurrence is C₁₋₄ alkyl, and a is 1-5, most preferably R^a in two ortho-positions to the nitrogen is isopropyl or t-butyl;

R^{17} and R^{18} independently at each occurrence are hydrogen, halogen, or a C₁₋₂₀ alkyl or aryl group, most preferably one of R^{17} and R^{18} is hydrogen and the other is a C₆₋₂₀ aryl group,

especially 2-isopropyl, phenyl or a fused polycyclic aryl group, most preferably an anthracenyl group, and bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

[0092] Exemplary metal complexes for use herein as catalysts correspond to the formula:

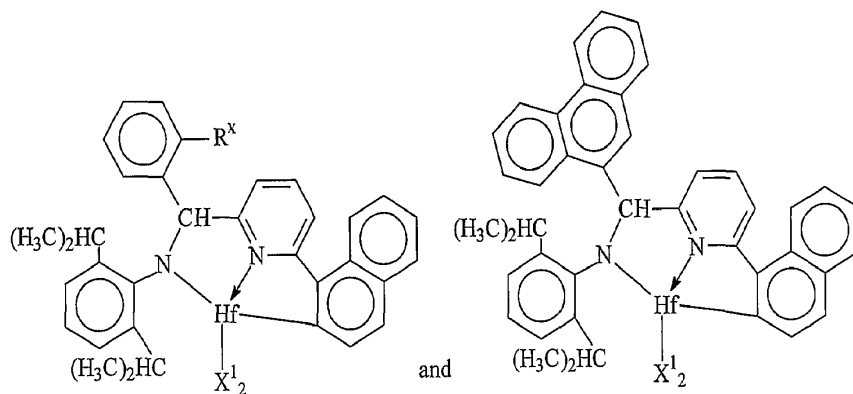


wherein X^1 at each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, and preferably at each occurrence X^1 is methyl;

R^f independently at each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^f groups are joined together thereby forming a ring, and f is 1-5; and

R^c independently at each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^c groups are joined together thereby forming a ring, and c is 1-5.

[0093] Suitable examples of metal complexes for use as catalysts according to the present invention are complexes of the following formulas:



wherein R^x is C_{1-4} alkyl or cycloalkyl, preferably methyl, isopropyl, t-butyl or cyclohexyl; and X^1 at each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, preferably methyl.

[0094] Examples of metal complexes usefully employed as catalysts according to the present invention include:

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

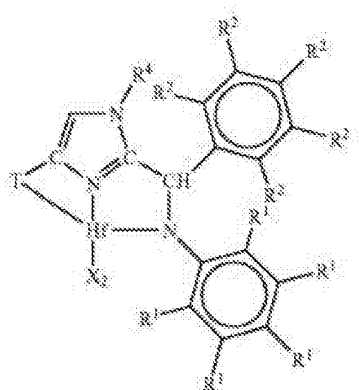
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido); and

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

[0095] Under the reaction conditions used to prepare the metal complexes used in the present disclosure, the hydrogen of the 2-position of the α -naphthalene group substituted at the 6-position of the pyridin-2-yl group is subject to elimination, thereby uniquely forming metal complexes wherein the metal is covalently bonded to both the resulting amide group and to the 2-position of the α -naphthalenyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair of the nitrogen atom.

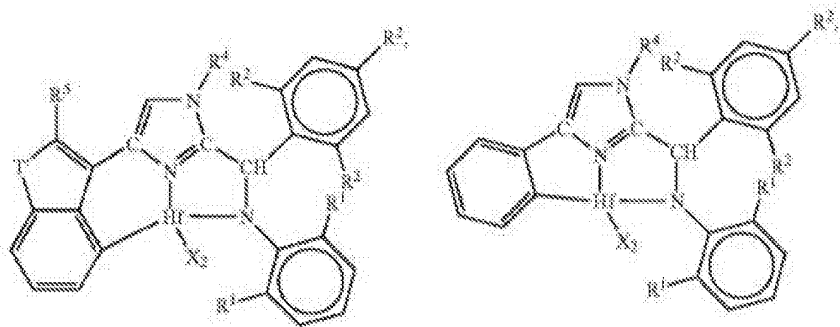
[0096] Further procatalysts that are suitable include imidazole-amine compounds corresponding to those disclosed in WO 2007/130307A2, WO 2007/130306A2, and U.S. Patent Application Publication No. 20090306318A1, which are incorporated herein by reference in their entirety. Such imidazole-amine compounds include those corresponding to the formula:

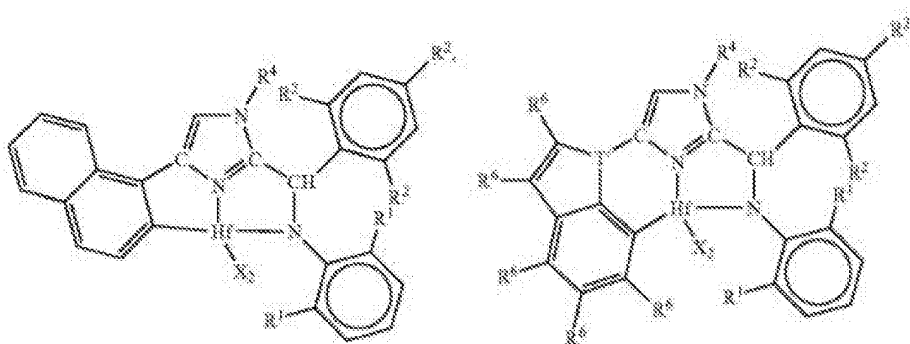


, wherein

X independently each occurrence is an anionic ligand, or two X groups together form a dianionic ligand group, or a neutral diene; T is a cycloaliphatic or aromatic group containing one or more rings; R¹ independently each occurrence is hydrogen, halogen, or a univalent, polyatomic anionic ligand, or two or more R¹ groups are joined together thereby forming a polyvalent fused ring system; R² independently each occurrence is hydrogen, halogen, or a univalent, polyatomic anionic ligand, or two or more R² groups are joined together thereby forming a polyvalent fused ring system; and R⁴ is hydrogen, alkyl, aryl, aralkyl, trihydrocarbylsilyl, or trihydrocarbylsilylmethyl of from 1 to 20 carbons.

[0097] Further examples of such imidazole-amine compounds include but are not limited to the following:

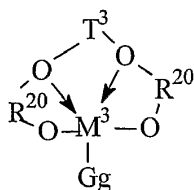




, wherein:

R^1 independently each occurrence is a C_{3-12} alkyl group wherein the carbon attached to the phenyl ring is secondary or tertiary substituted; R^2 independently each occurrence is hydrogen or a C_{1-2} alkyl group; R^4 is methyl or isopropyl; R^5 is hydrogen or C_{1-6} alkyl; R^6 is hydrogen, C_{1-6} alkyl or cycloalkyl, or two adjacent R^6 groups together form a fused aromatic ring; T' is oxygen, sulfur, or a C_{1-20} hydrocarbyl-substituted nitrogen or phosphorus group; T'' is nitrogen or phosphorus; and X is methyl or benzyl.

[0098] Additional suitable metal complexes of polyvalent Lewis bases for use herein include compounds corresponding to the formula:



, wherein:

R^{20} is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

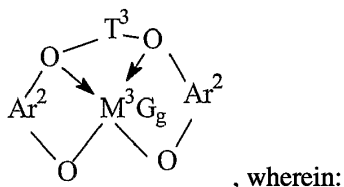
T^3 is a hydrocarbylene or hydrocarbyl silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

M^3 is a Group 4 metal, preferably zirconium or hafnium;

G is an anionic, neutral or dianionic ligand group; preferably a halide, hydrocarbyl, silane, trihydrocarbylsilylhydrocarbyl, trihydrocarbylsilyl, or dihydrocarbylamide group having up to 20 atoms not counting hydrogen;

g is a number from 1 to 5 indicating the number of such G groups; and bonds and electron donative interactions are represented by lines and arrows respectively.

[0099] Illustratively, such complexes correspond to the formula:



T³ is a divalent bridging group of from 2 to 20 atoms not counting hydrogen, preferably a substituted or unsubstituted, C3-6 alkylene group;

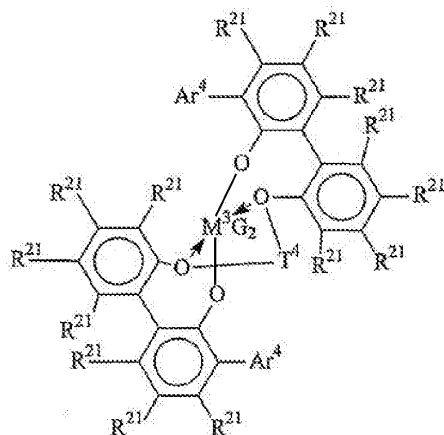
and Ar² independently at each occurrence is an arylene or an alkyl- or aryl-substituted arylene group of from 6 to 20 atoms not counting hydrogen;

M³ is a Group 4 metal, preferably hafnium or zirconium;

G independently at each occurrence is an anionic, neutral or dianionic ligand group;

g is a number from 1 to 5 indicating the number of such X groups; and electron donative interactions are represented by arrows.

[0100] Suitable examples of metal complexes of foregoing formula include the following compounds



where M³ is Hf or Zr;

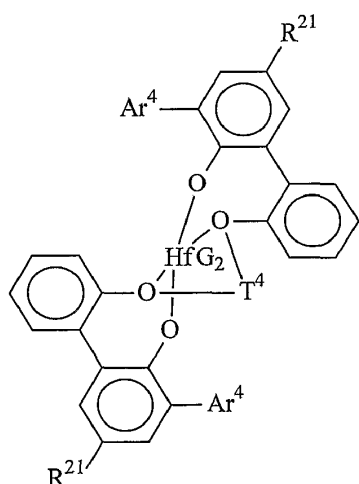
Ar⁴ is C₆₋₂₀ aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl, and

T⁴ independently at each occurrence comprises a C₃₋₆ alkylene group, a C₃₋₆ cycloalkylene group, or an inertly substituted derivative thereof;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl of up to 50 atoms not counting hydrogen; and

G, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 G groups together are a divalent derivative of the foregoing hydrocarbyl or trihydrocarbylsilyl groups.

[0101] Suitable compounds are compounds of the formulas:



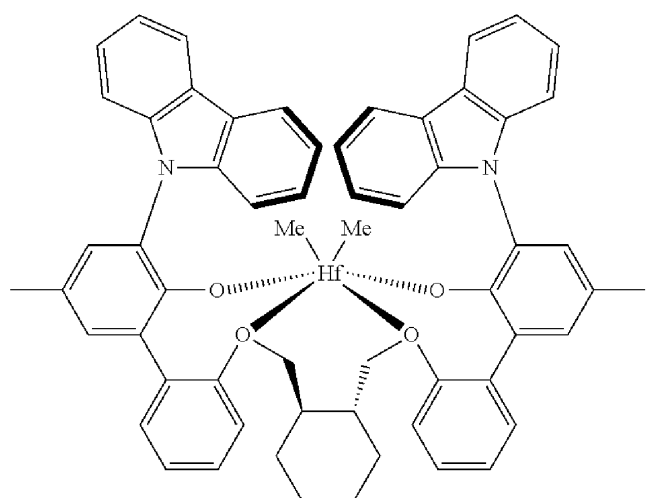
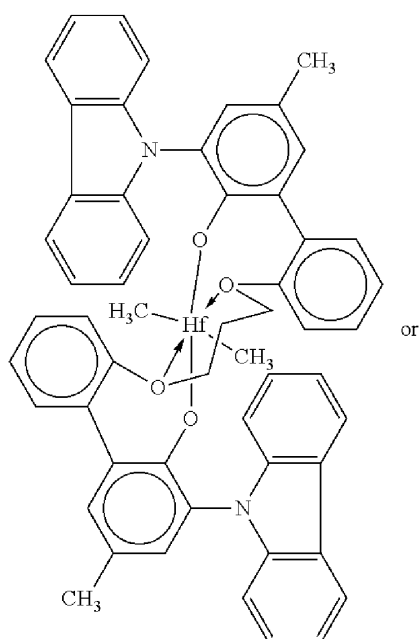
wherein Ar^4 is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R^{21} is hydrogen, halo, or C1-4 alkyl, especially methyl

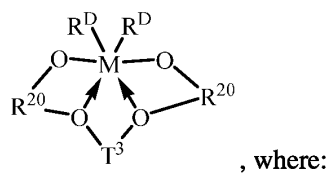
T^4 is propan-1,3-diyl or butan-1,4-diyl, and

G is chloro, methyl or benzyl.

[0102] Exemplary metal complexes of the foregoing formula are:



[0103] Suitable metal complexes for use according to the present disclosure further include compounds corresponding to the formula:



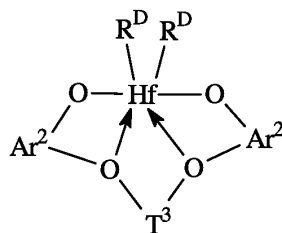
M is zirconium or hafnium;

R²⁰ independently at each occurrence is a divalent aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen;

T³ is a divalent hydrocarbon or silane group having from 3 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof; and

R^D independently at each occurrence is a monovalent ligand group of from 1 to 20 atoms, not counting hydrogen, or two R^D groups together are a divalent ligand group of from 1 to 20 atoms, not counting hydrogen.

[0104] Such complexes may correspond to the formula:



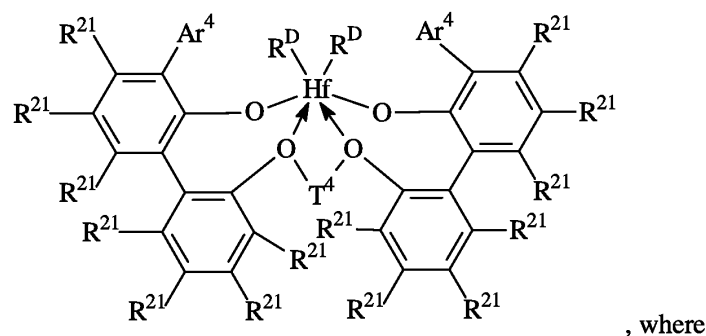
, wherein:

Ar² independently at each occurrence is an arylene or an alkyl-, aryl-, alkoxy- or amino-substituted arylene group of from 6 to 20 atoms not counting hydrogen or any atoms of any substituent;

T³ is a divalent hydrocarbon bridging group of from 3 to 20 atoms not counting hydrogen, preferably a divalent substituted or unsubstituted C₃₋₆ aliphatic, cycloaliphatic, or bis(alkylene)-substituted cycloaliphatic group having at least 3 carbon atoms separating oxygen atoms; and

R^D independently at each occurrence is a monovalent ligand group of from 1 to 20 atoms, not counting hydrogen, or two R^D groups together are a divalent ligand group of from 1 to 40 atoms, not counting hydrogen.

[0105] Further examples of metal complexes suitable for use herein include compounds of the formula:

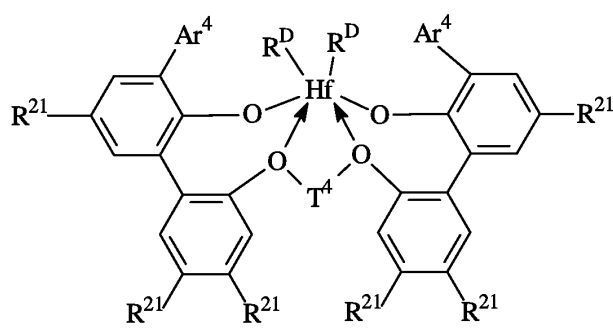


Ar^4 independently at each occurrence is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, naphthyl, anthracen-5-yl, 1,2,3,4,6,7,8,9-octahydroanthracen-5-yl;

T^4 independently at each occurrence is a propylene-1,3-diyl group, a bis(alkylene)cyclohexan-1,2-diyl group, or an inertly substituted derivative thereof substituted with from 1 to 5 alkyl, aryl or aralkyl substituents having up to 20 carbons each;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen; and R^D , independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group of up to 40 atoms not counting hydrogen.

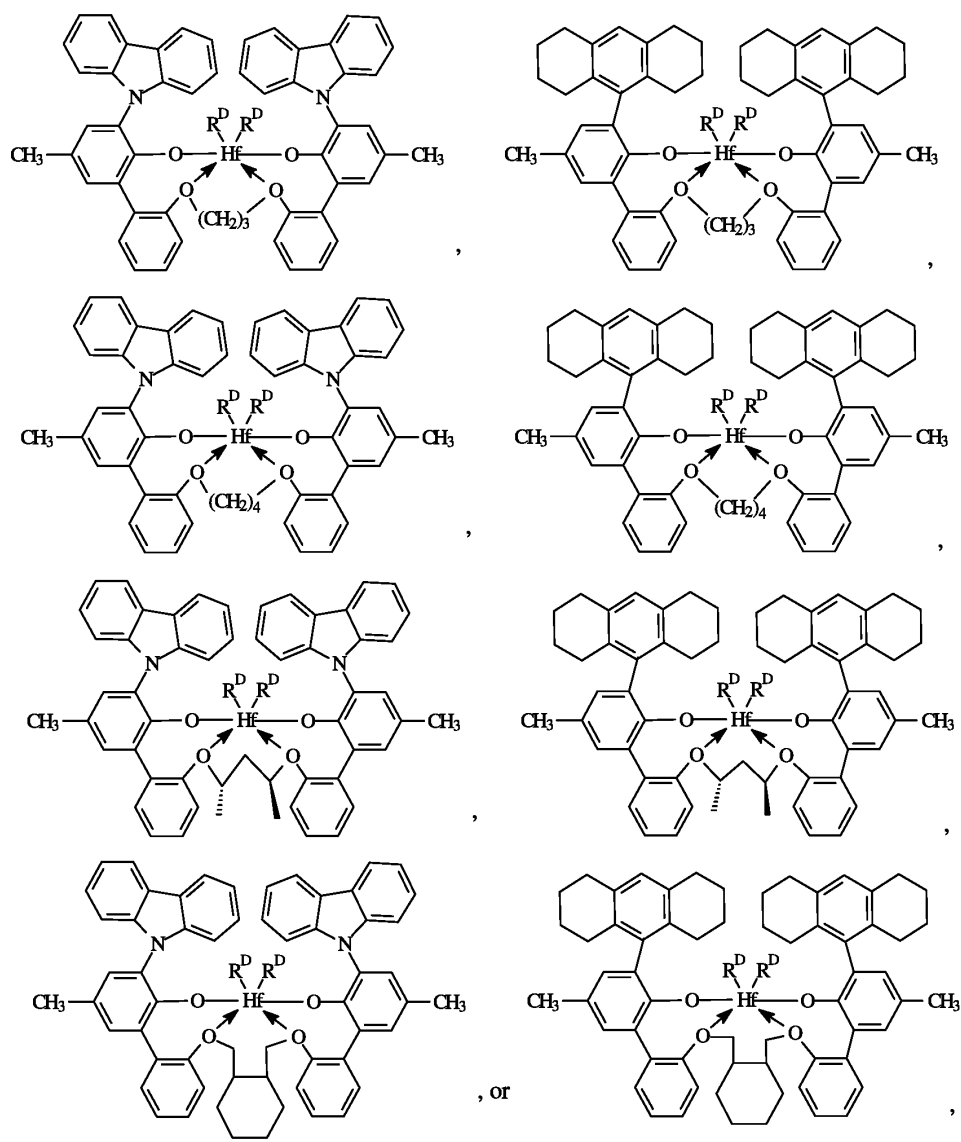
[0106] Exemplary metal complexes are compounds of the formula:



where, Ar^4 , independently at each occurrence, is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R²¹ independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen; T⁴ is propan-1,3-diyl or bis(methylene)cyclohexan-1,2-diyl; and R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl or hydrocarbylsilanediy group of up to 40 atoms not counting hydrogen.

[0107] Suitable metal complexes according to the present disclosure correspond to the formulas:



wherein, R^D independently at each occurrence is chloro, methyl or benzyl.

[0108] Specific examples of suitable metal complexes are the following compounds:

A) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dimethyl,

bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dichloride,

bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dibenzyl,

B) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-1,4-butanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-1,4-butanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-1,4-butanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-1,4-butanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-1,4-butanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-1,4-butanediylhafnium (IV) dibenzyl,

C) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediyhlhafnium (IV) dimethyl,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediyhlhafnium (IV) dichloride,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediyhlhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediyhlhafnium (IV) dimethyl,

bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediyldhafnium (IV) dichloride,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediyldhafnium (IV) dibenzyl,

D) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dichloride, and
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy-methyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dibenzyl.

[0109] The foregoing metal complexes may be conveniently prepared by standard metallation and ligand exchange procedures involving a source of the transition metal and a neutral polyfunctional ligand source. The techniques employed are the same as or analogous to those disclosed in USP 6,827,976 and US2004/0010103, and elsewhere.

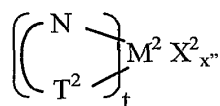
[0110] The foregoing polyvalent Lewis base complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the Group 4 metal and the neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. Other techniques may be used as well. These complexes are known from the disclosures of, among others, US patents 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, and US 04/0220050.

[0111] Catalysts having high comonomer incorporation properties are also known to reincorporate in situ prepared long chain olefins resulting incidentally during the polymerization

through β -hydride elimination and chain termination of growing polymer, or other process. The concentration of such long chain olefins is particularly enhanced by use of continuous solution polymerization conditions at high conversions, especially ethylene conversions of 95 percent or greater, more preferably at ethylene conversions of 97 percent or greater. Under such conditions a small but detectable quantity of olefin terminated polymer may be reincorporated into a growing polymer chain, resulting in the formation of long chain branches, that is, branches of a carbon length greater than would result from other deliberately added comonomer. Moreover, such chains reflect the presence of other comonomers present in the reaction mixture. That is, the chains may include short chain or long chain branching as well, depending on the comonomer composition of the reaction mixture. Long chain branching of olefin polymers is further described in USP's 5,272,236, 5,278,272, and 5,665,800.

[0112] Alternatively, branching, including hyper-branching, may be induced in a particular segment of the present multi-block copolymers by the use of specific catalysts known to result in "chain-walking" in the resulting polymer. For example, certain homogeneous bridged bis indenyl- or partially hydrogenated bis indenyl- zirconium catalysts, disclosed by Kaminski, et al., *J. Mol. Catal. A: Chemical*, 102 (1995) 59-65; Zambelli, et al., *Macromolecules*, 1988, 21, 617-622; or Dias, et al., *J. Mol. Catal. A: Chemical*, 185 (2002) 57-64 may be used to prepare branched copolymers from single monomers, including ethylene.

[0113] Additional complexes suitable for use include Group 4-10 derivatives corresponding to the formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements, preferably Group 4 metals,

Ni(II) or Pd(II), most preferably zirconium;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

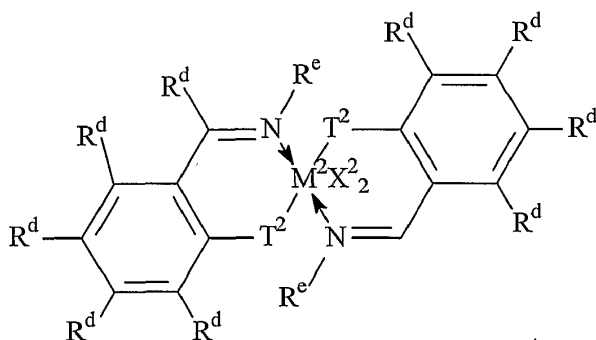
t is one or two;

x'' is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

Such catalysts have been previously disclosed in J. Am. Chem. Soc., 118, 267-268 (1996), J. Am. Chem. Soc., 117, 6414 -6415 (1995), and Organometallics, 16, 1514-1516, (1997), among other disclosures.

[0114] Suitable examples of the foregoing metal complexes for use as catalysts are aromatic diimine or aromatic dioximine complexes of Group 4 metals, especially zirconium, corresponding to the formula:



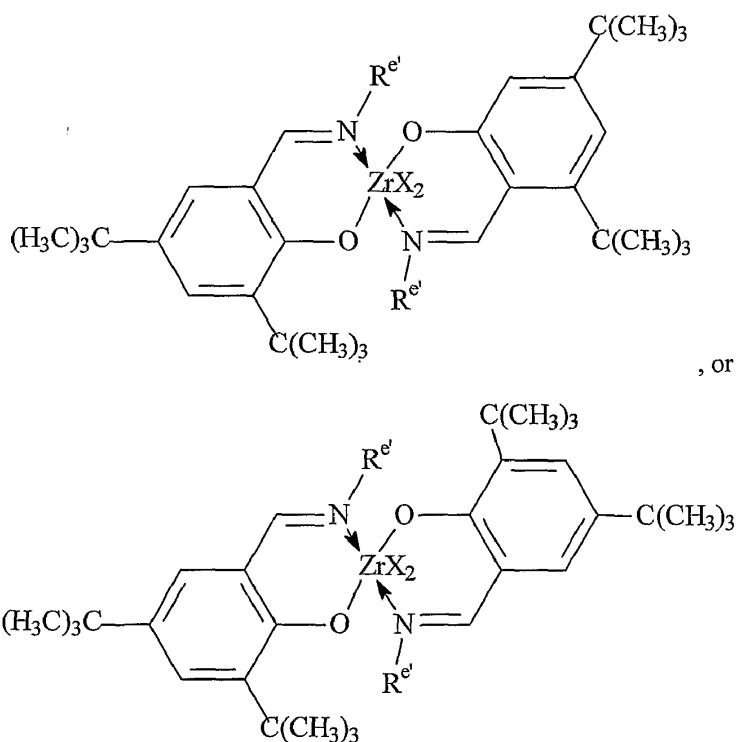
wherein;

M^2 , X^2 and T^2 are as previously defined;

R^d independently in each occurrence is hydrogen, halogen, or R^e ; and

R^e independently in each occurrence is C1-20 hydrocarbyl or a heteroatom-, especially a F, N, S or P- substituted derivative thereof, more preferably C1-20 hydrocarbyl or a F or N substituted derivative thereof, most preferably alkyl, dialkylaminoalkyl, pyrrolyl, piperidenyl, perfluorophenyl, cycloalkyl, (poly)alkylaryl, or aralkyl.

[0115] Suitable examples of the foregoing metal complexes for use as catalysts are aromatic dioximine complexes of zirconium, corresponding to the formula:



wherein;

X^2 is as previously defined, preferably C1-10 hydrocarbyl, most preferably methyl or benzyl;

and

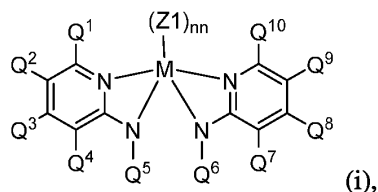
$R^{e'}$ is methyl, isopropyl, t-butyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, 2,4-dimethylcyclohexyl, 2-pyrrolyl, N-methyl-2-pyrrolyl, 2-piperidenyl, N-methyl-2-piperidenyl, benzyl, o-tolyl, 2,6-dimethylphenyl, perfluorophenyl, 2,6-di(isopropyl)phenyl, or 2,4,6-trimethylphenyl.

[0116] The foregoing complexes for use as also include certain phosphinimine complexes are disclosed in EP-A-890581. These complexes correspond to the formula: $[(R^f)_3-P=N]_f M(K^2)(R^f)_{3-f}$, wherein: R^f is a monovalent ligand or two R^f groups together are a divalent ligand, preferably R^f is hydrogen or C1-4 alkyl;

M is a Group 4 metal,

K^2 is a group containing delocalized π -electrons through which K^2 is bound to M , said K^2 group containing up to 50 atoms not counting hydrogen atoms, and f is 1 or 2.

[0117] Further suitable procatalysts include a those disclosed in WO 2017/173080 A1, which is incorporated by reference in its entirety. Such procatalysts include the metal-ligand complex of Formula (i):



wherein M is titanium, zirconium, or hafnium;

wherein each Z1 is independently a monodentate or polydentate ligand that is neutral, monoanionic, or dianionic, wherein nn is an integer, and wherein Z1 and nn are chosen in such a way that the metal-ligand complex of Formula (i) is overall neutral;

wherein each Q¹ and Q¹⁰ independently is selected from the group consisting of (C₆-C₄₀)aryl, substituted (C₆-C₄₀)aryl, (C₃-C₄₀)heteroaryl, and substituted (C₃-C₄₀)heteroaryl;

wherein each Q², Q³, Q⁴, Q⁷, Q⁸, and Q⁹ independently is selected from a group consisting of hydrogen, (C₁-C₄₀)hydrocarbyl, substituted (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, substituted (C₁-C₄₀)heterohydrocarbyl, halogen, and nitro (NO₂);

wherein each Q⁵ and Q⁶ independently is selected from the group consisting of a (C₁-C₄₀)alkyl, substituted (C₁-C₄₀)alkyl, and [(Si)₁-(C+Si)₄₀] substituted organosilyl;

wherein each N independently is nitrogen;

optionally, two or more of the Q¹⁻⁵ groups can combine together to form a ring structure, with such ring structure having from 5 to 16 atoms in the ring excluding any hydrogen atoms; and

optionally, two or more of the Q⁶⁻¹⁰ groups can combine together to form a ring structure, with such ring structure having from 5 to 16 atoms in the ring excluding any hydrogen atoms.

[0118] The metal ligand complex of Formula (i) above, and all specific embodiments thereof herein, is intended to include every possible stereoisomer, including coordination isomers, thereof.

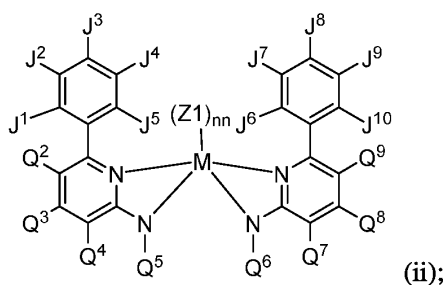
[0119] The metal ligand complex of Formula (i) above provides for homoleptic as well as heteroleptic procatalyst components.

[0120] In an alternative embodiment, each of the (C₁-C₄₀) hydrocarbyl and (C₁-C₄₀) heterohydrocarbyl of any one or more of Q¹, Q², Q³, Q⁴, Q⁵, Q⁶, Q⁷, Q⁸, Q⁹ and Q¹⁰ each independently is unsubstituted or substituted with one or more R^S substituents, and wherein each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C₁-C₁₈)alkyl, (C₆-C₁₈)aryl, F₃C, FCH₂O, F₂HCO, F₃CO, (R^{C1})₃Si, (R^{C1})₃Ge, (R^{C1})O, (R^{C1})S, (R^{C1})S(O), (R^{C1})S(O)₂, (R^{C1})₂P, (R^{C1})₂N, (R^{C1})₂C=N, NC, NO₂, (R^{C1})C(O)O, (R^{C1})OC(O), (R^{C1})C(O)N(R^{C1}), or (R^{C1})₂NC(O), or two of the R^S are taken together to form an unsubstituted (C₁-C₁₈)alkylene where each R^S independently is an unsubstituted (C₁-C₁₈)alkyl, and wherein independently each R^{C1} is hydrogen, unsubstituted (C₁-C₁₈)hydrocarbyl or an unsubstituted (C₁-C₁₈)heterohydrocarbyl, or absent (e.g., absent when N comprises -N=). In particular embodiments, Q⁵ and Q⁶ are each independently (C₁-C₄₀) primary or secondary alkyl groups with respect to their connection to the amine nitrogen of the parent ligand structure. The terms primary and secondary alkyl groups are given their usual and customary meaning herein; i.e., primary indicating that the carbon atom directly linked to the ligand nitrogen bears at least two hydrogen atoms and secondary indicates that the carbon atom directly linked to the ligand nitrogen bears only one hydrogen atom.

[0121] Optionally, two or more Q¹⁻⁵ groups or two or more Q⁶⁻¹⁰ groups each independently can combine together to form ring structures, with such ring structures having from 5 to 16 atoms in the ring excluding any hydrogen atoms.

[0122] In preferred embodiments, Q⁵ and Q⁶ are each independently (C₁-C₄₀) primary or secondary alkyl groups and most preferably, Q⁵ and Q⁶ are each independently propyl, isopropyl, neopentyl, hexyl, isobutyl and benzyl.

[0123] In particular embodiments, Q¹ and Q¹⁰ of the olefin polymerization procatalyst of Formula (i) are substituted phenyl groups; as shown in Formula (ii),



wherein J^1 - J^{10} are each independently selected from the group consisting of R^S substituents and hydrogen; and wherein each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C_1-C_{18}) alkyl, (C_6-C_{18}) aryl, F_3C , FCH_2O , F_2HCO , F_3CO , $(R^{C1})_3Si$, $(R^{C1})_3Ge$, $(R^{C1})O$, $(R^{C1})S$, $(R^{C1})S(O)$, $(R^{C1})S(O)_2$, $(R^{C1})_2P$, $(R^{C1})_2N$, $(R^{C1})_2C=N$, NC , NO_2 , $(R^{C1})C(O)O$, $(R^{C1})OC(O)$, $(R^{C1})C(O)N(R^{C1})$, or $(R^{C1})_2NC(O)$, or two of the R^S are taken together to form an unsubstituted (C_1-C_{18}) alkylene where each R^S independently is an unsubstituted (C_1-C_{18}) alkyl, and wherein independently each R^{C1} is hydrogen, unsubstituted (C_1-C_{18}) hydrocarbyl or an unsubstituted (C_1-C_{18}) heterohydrocarbyl, or absent (e.g., absent when N comprises $-N=$). More preferably, J^1 , J^5 , J^6 and J^{10} of Formula (ii) are each independently selected from the group consisting of halogen atoms, (C_1-C_8) alkyl groups, and (C_1-C_8) alkoxy groups. Most preferably, J^1 , J^5 , J^6 and J^{10} of Formula (ii) are each independently methyl; ethyl or isopropyl.

[0124] The term “[$(Si)_1-(C+Si)_{40}$] substituted organosilyl” means a substituted silyl radical with 1 to 40 silicon atoms and 0 to 39 carbon atoms such that the total number of carbon plus silicon atoms is between 1 and 40. Examples of [$(Si)_1-(C+Si)_{40}$] substituted organosilyl include trimethylsilyl, triisopropylsilyl, dimethylphenylsilyl, diphenylmethylsilyl, triphenylsilyl, and triethylsilyl.

[0125] Preferably, there are no O-O, S-S, or O-S bonds, other than O-S bonds in an $S(O)$ or $S(O)_2$ diradical functional group, in the metal-ligand complex of Formula (i). More preferably, there are no O-O, P-P, S-S, or O-S bonds, other than O-S bonds in an $S(O)$ or $S(O)_2$ diradical functional group, in the metal-ligand complex of Formula (i).

[0126] M is titanium, zirconium, or hafnium. In one embodiment, M is titanium. In another embodiment, M is zirconium. In another embodiment, M is hafnium. In some embodiments, M is in a formal oxidation state of +2, +3, or +4. Each Z1 independently is a monodentate or polydentate ligand that is neutral, monoanionic, or dianionic. Z1 and nn are chosen in such a way that the metal-ligand complex of Formula (i) is, overall, neutral. In some embodiments each Z1 independently is the monodentate ligand. In one embodiment when there are two or more Z1 monodentate ligands, each Z1 is the same. In some embodiments the monodentate ligand is the monoanionic ligand. The monoanionic ligand has a net formal oxidation state of -1. Each monoanionic ligand may independently be hydride, (C_1-C_{40}) hydrocarbyl carbanion,

(C₁-C₄₀)heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, borate, borohydride, sulfate, HC(O)O⁻, alkoxide or aryloxide (RO⁻), (C₁-C₄₀)hydrocarbylC(O)O⁻, HC(O)N(H)⁻, (C₁-C₄₀)hydrocarbylC(O)N(H)⁻, (C₁-C₄₀)hydrocarbylC(O)N((C₁-C₂₀)hydrocarbyl)⁻, R^KR^LB⁻, R^KR^LN⁻, R^KO⁻, R^KS⁻, R^KR^LP⁻, or R^MR^KR^LSi⁻, wherein each R^K, R^L, and R^M independently is hydrogen, (C₁-C₄₀)hydrocarbyl, or (C₁-C₄₀)heterohydrocarbyl, or R^K and R^L are taken together to form a (C₂-C₄₀)hydrocarbylene or (C₁-C₄₀)heterohydrocarbylene and R^M is as defined above.

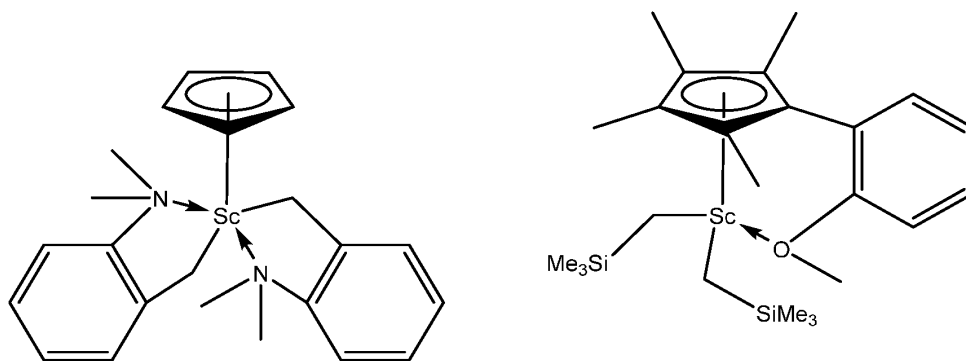
[0127] In some embodiments at least one monodentate ligand of Z1 independently is the neutral ligand. In one embodiment, the neutral ligand is a neutral Lewis base group that is R^{X1}NR^KR^L, R^KOR^L, R^KSR^L, or R^{X1}PR^KR^L, wherein each R^{X1} independently is hydrogen, (C₁-C₄₀)hydrocarbyl, [(C₁-C₁₀)hydrocarbyl]₃Si, [(C₁-C₁₀)hydrocarbyl]₃Si(C₁-C₁₀)hydrocarbyl, or (C₁-C₄₀)heterohydrocarbyl and each R^K and R^L independently is as defined above.

[0128] In some embodiments, each Z1 is a monodentate ligand that independently is a halogen atom, unsubstituted (C₁-C₂₀)hydrocarbyl, unsubstituted (C₁-C₂₀)hydrocarbylC(O)O⁻, or R^KR^LN⁻ wherein each of R^K and R^L independently is an unsubstituted (C₁-C₂₀)hydrocarbyl. In some embodiments each monodentate ligand Z1 is a chlorine atom, (C₁-C₁₀)hydrocarbyl (e.g., (C₁-C₆)alkyl or benzyl), unsubstituted (C₁-C₁₀)hydrocarbylC(O)O⁻, or R^KR^LN⁻ wherein each of R^K and R^L independently is an unsubstituted (C₁-C₁₀)hydrocarbyl.

[0129] In some embodiments there are at least two Z1s and the two Z1s are taken together to form the bidentate ligand. In some embodiments the bidentate ligand is a neutral bidentate ligand. In one embodiment, the neutral bidentate ligand is a diene of Formula (R^{D1})₂C=C(R^{D1})-C(R^{D1})=C(R^{D1})₂, wherein each R^{D1} independently is H, unsubstituted (C₁-C₆)alkyl, phenyl, or naphthyl. In some embodiments the bidentate ligand is a monoanionic-mono(Lewis base) ligand.

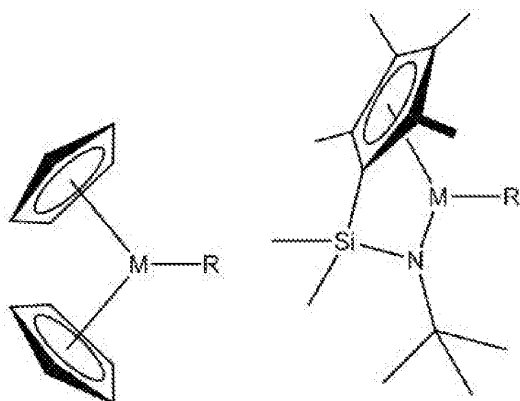
The monoanionic-mono(Lewis base) ligand may be a 1,3-dionate of Formula (D): R^{E1}-C(O⁻)=CH-C(=O)-R^{E1} (D), wherein each R^{E1} independently is H, unsubstituted (C₁-C₆)alkyl, phenyl, or naphthyl. In some embodiments the bidentate ligand is a dianionic ligand. The dianionic ligand has a net formal oxidation state of -2. In one embodiment, each dianionic ligand independently is carbonate, oxalate (i.e., ⁻O₂CC(O)O⁻), (C₂-C₄₀)hydrocarbylene dicarbanion, (C₁-C₄₀)heterohydrocarbylene dicarbanion, phosphate, or sulfate.

[0134] Further suitable procatalysts include those disclosed in *Acc. Chem. Res.*, **2015**, 48 (8), pp 2209–2220, including but not limited to those of the following structures:



[0135] Suitable procatalyst further include “single-component catalysts” that can catalyze olefin polymerization without the use of a co-catalyst. Such simple-component catalysts include those disclosed in Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337–339; Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53–101; Ihara, E.; Nodono, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; and Kai, Y. *Organometallics* **1998**, *17*, 3945–3956; Long, D. P.; Bianconi, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 12453–12454; Gilchrist, J. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 12021–12028; Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045–1053; Evans, W. J.; DeCoster, D. M.; Greaves, J. *Organometallics* **1996**, *15*, 3210–3221; Evans, W. J.; DeCoster, D. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929–7936; Shapiro, P. J.;

Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623–4640; Schaverien, C. J. *Organometallics* **1994**, *13*, 69–82; Coughlin, E. B. *J. Am. Chem. Soc.* **1992**, *114*, 7606–7607; Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406–9407; Burger, B. J.; Thompson, M. E., Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577; Shapiro, P. J.; Bunel, E.; Schaefer, W. P. *Organometallics* **1990**, *9*, 867–869; Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103; Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110; and *Organometallics*, **2001**, *20* (9), pp 1752–1761. Exemplary, non-limiting formulas of such simple-component catalysts include:

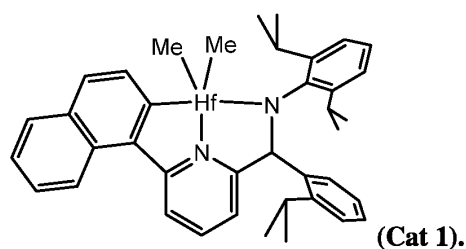


, wherein:

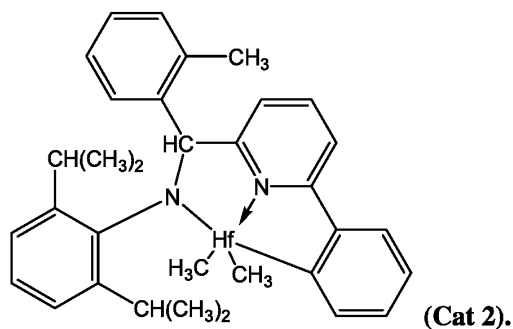
M is Sm or Y; and R is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl.

[0136] Suitable procatalysts include but are not limited to the following named as (Cat 1) to (Cat 17).

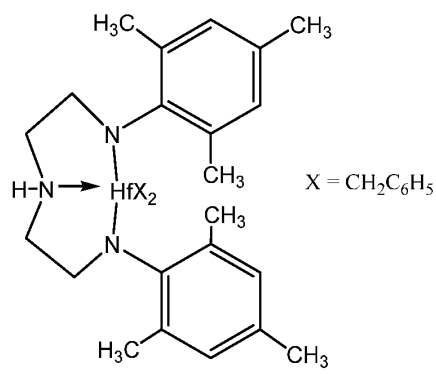
[0137] (Cat 1) may be prepared according to the teachings of WO 03/40195 and U.S. Patent No. 6,953,764 B2 and has the following structure:



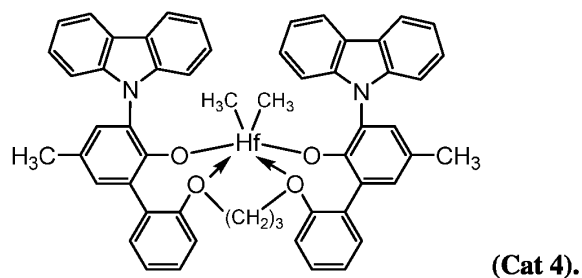
[0138] (Cat 2) may be prepared according to the teachings of WO 03/40195 and WO 04/24740 and has the following structure:



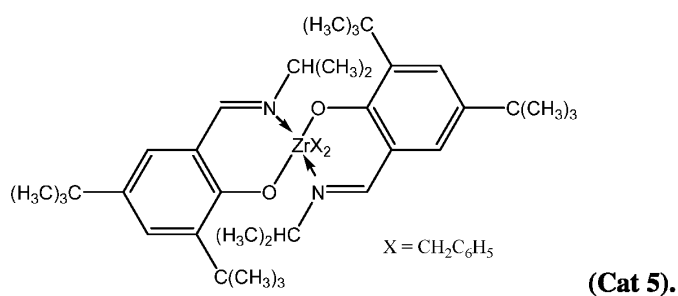
[0139] (Cat 3) may be prepared according to methods known in the art and has the following structure:



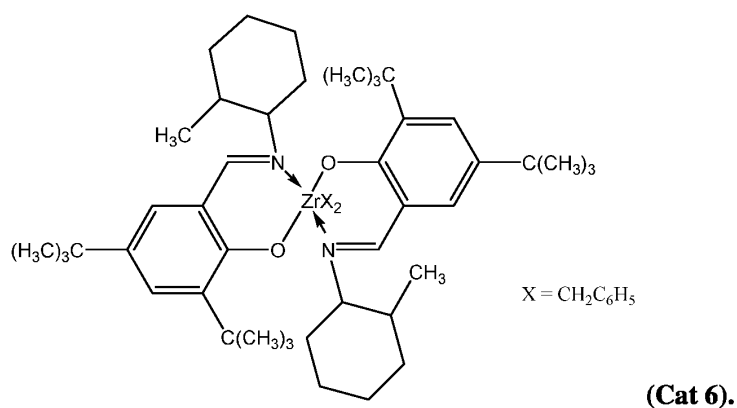
[0140] (Cat 4) may be prepared according to the teachings of U.S. Patent Application Publication No. 2004/0010103 and has the following structure:



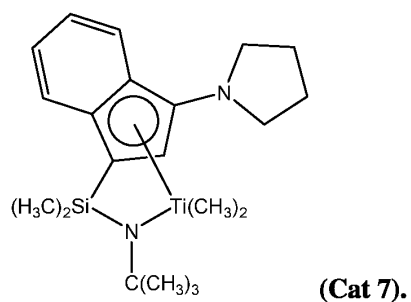
[0141] (Cat 5) may be prepared according to the teachings of U.S. Patent No. 7,858,706 B2 and has the following structure:



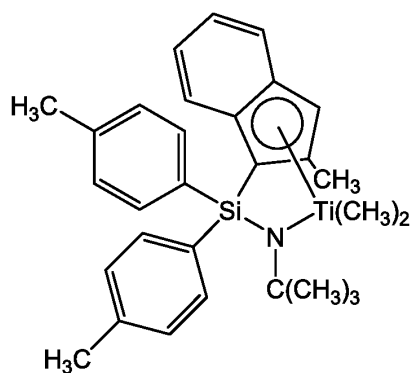
[0142] (Cat 6) may be prepared according to the teachings of U.S. Patent No. 7,858,706 B2 and has the following structure:



[0143] (Cat 7) may be prepared by the teachings of U.S. Pat. No. 6,268,444 and has the following structure:

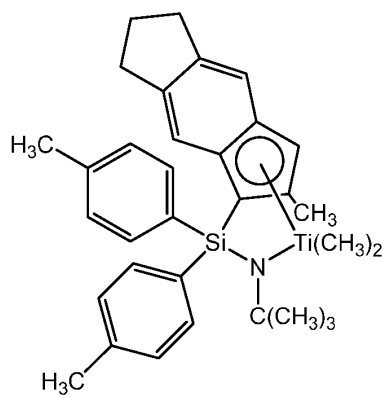


[0144] (Cat 8) may be prepared according to the teachings of U.S. Pat. Pub. No. 2003/004286 and has the following structure:



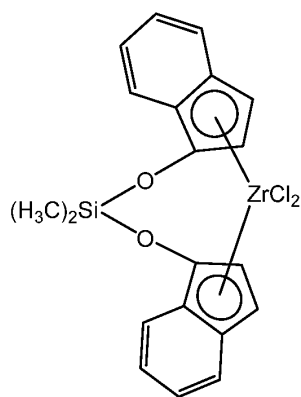
(Cat 8).

[0145] (Cat 9) may be prepared according to the teachings of U.S. Pat. Pub. No. 2003/004286 and has the following structure:



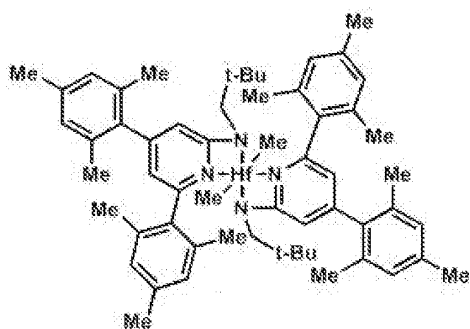
(Cat 9).

[0146] (Cat 10) is commercially available from Sigma-Aldrich and has the following structure:



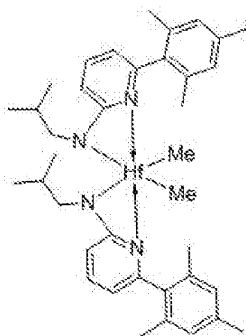
(Cat 10).

[0147] (Cat 11) may be prepared according to the teachings of WO 2017/173080 A1 and has the following structure:



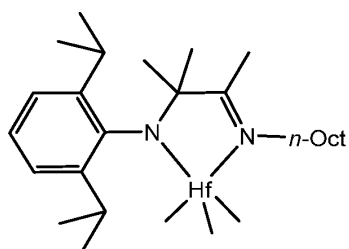
(Cat 11).

[0148] (Cat 12) may be prepared according to the teachings of WO 2017/173080 A1 and has the following structure:



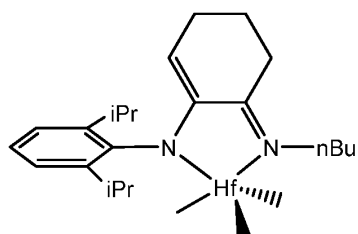
(Cat 12).

[0149] (Cat 13) may be prepared according to the teachings of Macromolecules (Washington, DC, United States), 43(19), 7903-7904 (2010) and has the following structure:



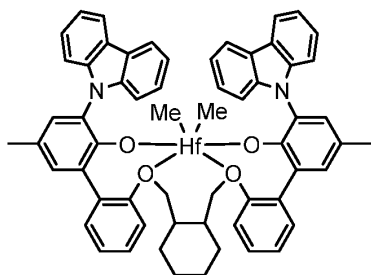
(Cat 13).

[0150] (Cat 14) may be prepared according to the teachings of WO 2011/102989 A1 and has the following structure:



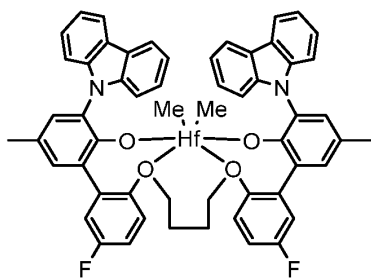
(Cat 14).

[0151] (Cat 15) may be prepared according to the teachings of U.S. Pat. No. 8,101,696 B2 and has the following structure:



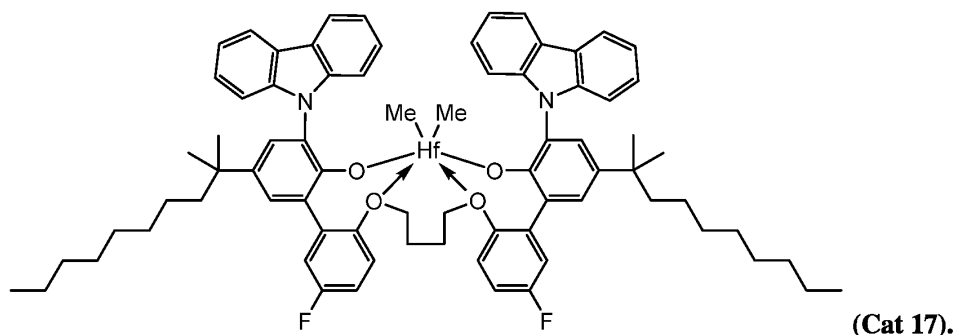
(Cat 15).

[0152] (Cat 16) may be prepared according to the teachings of WO 2018/170138 A1 and has the following structure:



(Cat 16).

[0153] (Cat 17) may be prepared according to the teachings of WO 2018/170138 A1 and has the following structure:



[0154] In certain embodiments, the (c1) catalyst component comprises a procatalyst and a co-catalyst. In these embodiments, the procatalyst may be activated to form an active catalyst by combination with a co-catalyst (activator), preferably a cation forming co-catalyst, a strong Lewis acid, or a combination thereof.

[0155] Suitable cation forming co-catalysts include those previously known in the art for metal olefin polymerization complexes. Examples include neutral Lewis acids, such as C_{1-30} hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium-salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating co-catalysts and activating techniques have been previously taught with respect to different metal complexes for olefin polymerizations in the following references: EP-A-277,003; U.S. Pat. Nos. 5,153,157; 5,064,802; 5,321,106; 5,721,185; 5,350,723; 5,425,872; 5,625,087; 5,883,204; 5,919,983; 5,783,512; WO 99/15534, and WO99/42467.

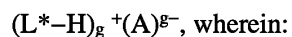
[0156] Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbons in each hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis

acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane may be used as activating cocatalysts. Exemplary molar ratios of metal complex:tris(pentafluorophenyl)borane:alumoxane are from 1:1:1 to 1:5:20, such as from 1:1:1.5 to 1:5:10.

[0157] Suitable ion forming compounds useful as co-catalysts in one embodiment of the present disclosure comprise a cation which is a Brønsted acid capable of donating a proton, and a compatible, noncoordinating anion, A^- . As used herein, the term “noncoordinating” refers to an anion or substance which either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived there from, or which is only weakly coordinated to such complexes thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion which when functioning as a charge balancing anion in a cationic metal complex does not transfer an anionic substituent or fragment thereof to said cation thereby forming neutral complexes. “Compatible anions” are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

[0158] Suitable anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

[0159] In one aspect, suitable cocatalysts may be represented by the following general formula:



L^* is a neutral Lewis base;

$(L^*-H)^+$ is a conjugate Brønsted acid of L^* ;

A^{g-} is a noncoordinating, compatible anion having a charge of $g-$, and g is an integer from 1 to 3.

[0160] More particularly, A^{g-} corresponds to the formula: $[M'Q_4]^{g-}$; wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

Q independently in each occurrence is selected from hydride, dialkyl-amido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo-substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl-perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), each Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxy Q groups are disclosed in U.S. Pat. No. 5,296,433.

[0161] In an exemplary embodiment, g is one, that is, the counter ion has a single negative charge and is A⁻. Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this disclosure may be represented by the following general formula: (L*–H)⁺(BQ₄)⁻; wherein:

L* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl-group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

[0162] Especially useful Lewis base salts are ammonium salts, more preferably trialkyl-ammonium salts containing one or more C₁₂₋₄₀ alkyl groups. In this aspect, for example, Q in each occurrence can be a fluorinated aryl group, especially, a pentafluorophenyl group.

[0163] Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this disclosure include the tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl)borate,
triethylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(pentafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium n-butyltris(pentafluorophenyl)borate,
N,N-dimethylanilinium benzyltris(pentafluorophenyl)borate,

N,N-dimethylanilinium tetrakis(4-(t-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl)borate,
 N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2,3,5,6-tetrafluorophenyl)borate,
 N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl)borate,
 N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
 N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl)borate,
 dimethyloctadecylammonium tetrakis(pentafluorophenyl)borate,
 methyldioctadecylammonium tetrakis(pentafluorophenyl)borate;
 a number of dialkyl ammonium salts such as:
 di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
 methyloctadecylammonium tetrakis(pentafluorophenyl)borate,
 methyloctadodecylammonium tetrakis(pentafluorophenyl)borate, and
 dioctadecylammonium tetrakis(pentafluorophenyl)borate;
 various tri-substituted phosphonium salts such as:
 triphenylphosphonium tetrakis(pentafluorophenyl)borate,
 methyldioctadecylphosphonium tetrakis(pentafluorophenyl)borate, and
 tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate;
 di-substituted oxonium salts such as:
 diphenyloxonium tetrakis(pentafluorophenyl)borate,
 di(o-tolyl)oxonium tetrakis(pentafluorophenyl)borate, and
 di(octadecyl)oxonium tetrakis(pentafluorophenyl)borate; and
 di-substituted sulfonium salts such as:
 di(o-tolyl)sulfonium tetrakis(pentafluorophenyl)borate, and
 methylcotadecylsulfonium tetrakis(pentafluorophenyl)borate.

[0164] Further to this aspect of the disclosure, examples of useful $(L^*-H)^+$ cations include, but are not limited to, methyldioctadecylammonium cations, dimethyloctadecylammonium cations, and ammonium cations derived from mixtures of trialkyl amines containing one or two C_{14-18} alkyl groups.

[0165] Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:
 $(Ox^{h+})_g(A^{g-})_h$, wherein:

Ox^{h+} is a cationic oxidizing agent having a charge of $h+$;

h is an integer from 1 to 3; and

A^{g-} and g are as previously defined.

[0166] Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ , or Pb^{+2} . Particularly useful examples of A^{g-} are those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate.

[0167] Another suitable ion forming, activating cocatalyst can be a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the following formula:
 $[C]^+A^-$

wherein:

$[C]^+$ is a C_{1-20} carbenium ion; and

A^- is a noncoordinating, compatible anion having a charge of -1 . For example, one carbenium ion that works well is the trityl cation, that is triphenylmethyl.

[0168] A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:
 $(Q^1)_3Si^+A^-$

wherein:

Q^1 is C_{1-10} hydrocarbyl, and A^- is as previously defined.

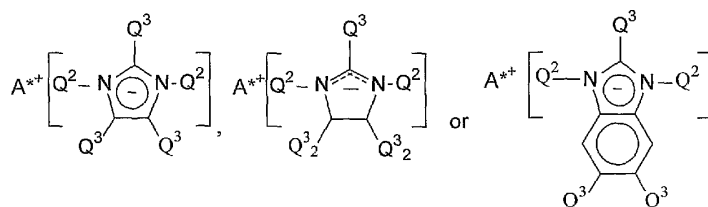
[0169] Suitable silylium salt activating cocatalysts include trimethylsilylium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate, and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in *J. Chem. Soc. Chem. Comm.* 1993, 383-384, as well as in Lambert, J. B., et al., *Organometallics* 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is also described in U.S. Pat. No. 5,625,087.

[0170] Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present disclosure. Such cocatalysts are disclosed in U.S. Pat. No. 5,296,433.

[0171] Suitable activating cocatalysts for use herein also include polymeric or oligomeric alumoxanes (also called aluminoxanes), especially methylalumoxane (MAO), triisobutyl aluminum modified methylalumoxane (MMAO), or isobutylalumoxane; Lewis acid modified

alumoxanes, especially perhalogenated tri(hydrocarbyl)aluminum- or perhalogenated tri(hydrocarbyl)boron modified alumoxanes, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, and most especially tris(pentafluorophenyl)borane modified alumoxanes. Such co-catalysts are previously disclosed in U.S. Pat. Nos. 6,214,760, 6,160,146, 6,140,521, and 6,696,379.

[0172] A class of co-catalysts comprising non-coordinating anions generically referred to as expanded anions, further disclosed in U.S. Pat. No. 6,395,671, may be suitably employed to activate the metal complexes of the present disclosure for olefin polymerization. Generally, these co-catalysts (illustrated by those having imidazolidine, substituted imidazolidine, imidazolinide, substituted imidazolinide, benzimidazolidine, or substituted benzimidazolidine anions) may be depicted as follows:



wherein:

A^{*+} is a cation, especially a proton containing cation, and can be trihydrocarbyl ammonium cation containing one or two C_{10-40} alkyl groups, especially a methyl-di(C_{14-20} alkyl)ammonium cation,

Q^3 , independently in each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including for example mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, such as C_{1-20} alkyl, and

Q^2 is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)alumane).

[0173] Examples of these catalyst activators include trihydrocarbylammonium-salts, especially, methyl-di(C_{14-20} alkyl)ammonium-salts of:

- bis(tris(pentafluorophenyl)borane)imidazolidine,
- bis(tris(pentafluorophenyl)borane)-2-undecylimidazolidine,
- bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolidine,
- bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolidine,

bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolidide,
 bis(tris(pentafluorophenyl)borane)imidazolinide,
 bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide,
 bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide,
 bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide,
 bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide,
 bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolidide,
 bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolidide,
 bis(tris(pentafluorophenyl)alumane)imidazolidide,
 bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolidide,
 bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolidide,
 bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolidide,
 bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolidide,
 bis(tris(pentafluorophenyl)alumane)imidazolinide,
 bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide,
 bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide,
 bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,
 bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,
 bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolidide, and
 bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolidide.

[0174] Other activators include those described in the PCT publication WO 98/07515, such as tris(2,2',2''-nonafluorobiphenyl)fluoroaluminate. Combinations of activators are also contemplated by the disclosure, for example, alumoxanes and ionizing activators in combinations, see for example, EP-A-0 573 120, PCT publications WO 94/07928 and WO 95/14044, and U.S. Pat. Nos. 5,153,157 and 5,453,410. For example, and in general terms, WO 98/09996 describes activating catalyst compounds with perchlorates, periodates and iodates, including their hydrates. WO 99/18135 describes the use of organoboroaluminum activators. WO 03/10171 discloses catalyst activators that are adducts of Brønsted acids with Lewis acids. Other activators or methods for activating a catalyst compound are described in, for example, U.S. Pat. Nos. 5,849,852, 5,859,653, and 5,869,723, in EP-A-615981, and in PCT publication WO 98/32775. All of the foregoing catalyst activators as well as any other known activator for

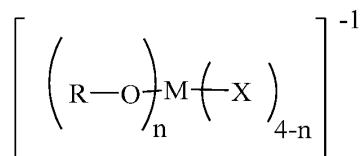
transition metal complex catalysts may be employed alone or in combination according to the present disclosure. In one aspect, however, the co-catalyst can be alumoxane-free. In another aspect, for example, the co-catalyst can be free of any specifically-named activator or class of activators as disclosed herein.

[0175] In a further aspect, the molar ratio of procatalyst/co-catalyst employed generally ranges from 1:10,000 to 100:1, for example, from 1:5000 to 10:1, or from 1:1000 to 1:1. Alumoxane, when used by itself as an activating co-catalyst, can be employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis.

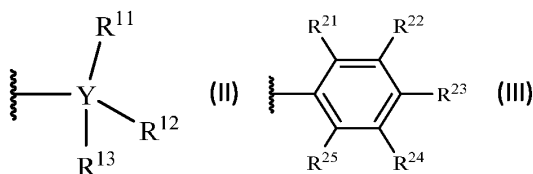
[0176] Tris(pentafluorophenyl)borane, where used as an activating co-catalyst can be employed generally in a molar ratio to the metal complex of from 0.5:1 to 10:1, such as from 1:1 to 6:1 and from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately equimolar quantity with the metal complex.

[0177] In exemplary embodiments of the present disclosure, the co-catalyst is $[(C_{16-18}H_{33-37})_2CH_3NH]$ tetrakis(pentafluorophenyl)borate salt.

[0178] Suitable co-catalysts also include those disclosed in U.S. Provisional Pat. App. Nos. 62650423, 62650412, and 62650453, which are incorporated herein by reference in their entirety. Such co-catalysts include those of the ionic complex comprising an anion and a counteranion, the anion having the structure:



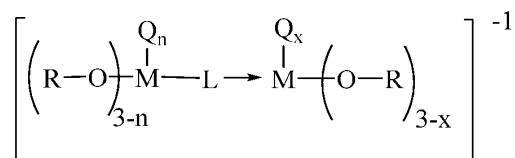
wherein: M is aluminum, boron, or gallium; n is 2, 3, or 4; each R is independently selected from the group consisting of: radical (II) and radical (III):



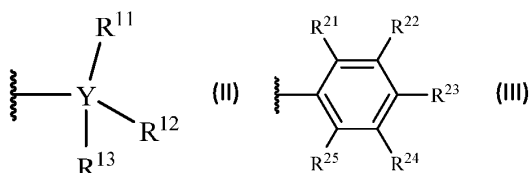
each Y is independently carbon or silicon; each R^{11} , R^{12} , R^{13} , R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from (C_1-C_{40}) alkyl, (C_6-C_{40}) aryl, $-OR^C$, $-O-$, $-SR^C$, $-H$, or $-F$, wherein

when R is a radical according to radical (III), at least one of R²¹⁻²⁵ is a halogen-substituted (C₁–C₄₀)alkyl, a halogen-substituted (C₆–C₄₀)aryl, or –F; and provided that: when each R is a radical (II) and Y is carbon, at least one of R¹¹⁻¹³ is a halogen-substituted (C₁–C₄₀)alkyl, a halogen-substituted (C₆–C₄₀)aryl, or –F; or when M is aluminum and n is 4 and each R is a radical (II), and each Y is carbon: each R¹¹, R¹², and R¹³ of each R is a halogen-substituted (C₁–C₄₀)alkyl, a halogen-substituted (C₆–C₄₀)aryl, or –F; or a total number of halogen atoms in R¹¹, R¹², and R¹³ of each R is at least six; each X is a monodentate ligand independently chosen from halogen-substituted (C₁–C₂₀)alkyl, (C₁–C₂₀)alkyl, halogen-substituted (C₆–C₄₀)aryl, (C₆–C₄₀)aryl, triflate, or –S(O)₃; optionally, two groups R are covalently connected; each R^N and R^C is independently (C₁–C₃₀)hydrocarbyl or –H.

[0179] Such co-catalysts further include the bimetallic activator complex comprising an anion and a counteranion, the anion having a structure:

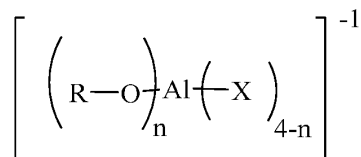


where: each M is independently aluminum, boron, or gallium; L is chosen from a species having at least two Lewis basic sites; each Q is independently a monodentate ligand; n is 0, 1, or 2, wherein when n is 0, Q is not present; x is 0, 1, or 2, wherein when x is 0, Q is not present; each R is independently selected from the group consisting of radical (II) and radical (III):

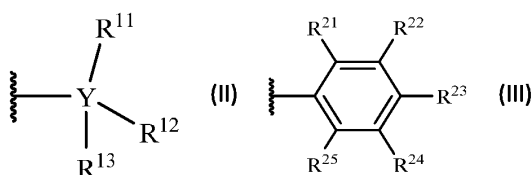


each Y is independently carbon or silicon; each R¹¹, R¹², R¹³, R²¹, R²², R²³, R²⁴, and R²⁵, is independently chosen from (C₁–C₄₀)alkyl, (C₆–C₄₀)aryl, –H, –NR^N₂, –OR^C, –SR^C, or halogen, wherein when R is radical (II), at least one of R¹¹⁻¹³ is perhalogenated (C₁–C₄₀)alkyl, perhalogenated (C₆–C₄₀)aryl, or –F; and when R is radical (III), at least one of R²¹⁻²⁵ is perhalogenated (C₁–C₄₀)alkyl, perhalogenated (C₆–C₄₀)aryl, or –F; optionally, when n is 0 or 1, two R groups are covalently connected; and each R^N or R^C is independently (C₁–C₃₀)hydrocarbyl or –H.

[0180] Such co-catalysts further include the metallic activator comprising an anion and a counteranion, the anion having a structure:



where: n is 0 or 1; each R is independently selected from the group consisting of radical (II) and radical (III):



each Y is independently carbon or silicon; each R^{11} , R^{12} , R^{13} , R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from $(\text{C}_1\text{--}\text{C}_{40})$ alkyl, halogen-substituted $(\text{C}_1\text{--}\text{C}_{40})$ alkyl, $(\text{C}_6\text{--}\text{C}_{40})$ aryl, halogen-substituted $(\text{C}_6\text{--}\text{C}_{40})$ aryl, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{H}$, $-\text{F}$ or Cl , wherein at least one of $\text{R}^{11\text{--}13}$ and one of $\text{R}^{21\text{--}25}$ is a halogen-substituted $(\text{C}_1\text{--}\text{C}_{40})$ alkyl, a halogen-substituted $(\text{C}_6\text{--}\text{C}_{40})$ aryl, or $-\text{F}$; and each X is a monodentate ligand independently chosen from halogen-substituted $(\text{C}_1\text{--}\text{C}_{20})$ alkyl or halogen-substituted $(\text{C}_6\text{--}\text{C}_{40})$ aryl; optionally, two X groups are covalently connected; each R^{C} is independently halogen-substituted $(\text{C}_1\text{--}\text{C}_{30})$ hydrocarbyl; provided that when the counteranion is $(\text{Ph})_3\text{C}^+$, and the anion is $\text{Al}(\text{C}_6\text{F}_5)_4$.

Applications and End Uses

[0181] The chain transfer agent of the present disclosure can be used for polymerizing polyolefins. In certain embodiments, the chain transfer agent may be used during a process to prepare a novel telechelic polyolefin of the formula (I): $\text{A}^1\text{L}^1\text{L}^2\text{A}^2$ (I), wherein:

L^1 is a polyolefin;

A^1 is selected from the group consisting of a vinyl group, a vinylidene group of the formula $\text{CH}_2=\text{C}(\text{Y}^1)-$, a vinylene group of the formula $\text{Y}^1\text{CH}=\text{CH}-$, a mixture of a vinyl group and a vinylene group of the formula $\text{Y}^1\text{CH}=\text{CH}-$, a mixture of a vinyl group and a vinylidene group of the formula $\text{CH}_2=\text{C}(\text{Y}^1)-$, a mixture of a vinylidene group of the formula $\text{CH}_2=\text{C}(\text{Y}^1)-$

and a vinylene group of the formula $Y^1CH=CH-$, and a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)-$, and a vinylene group of the formula $Y^1CH=CH-$;

Y^1 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group;

L^2 is a C_1 to C_{32} hydrocarbylene group; and

A^2 is a hydrocarbyl group comprising a hindered double bond.

[0182] In certain embodiments, L^2 is $-CH_2CH(Y^2)-$, such that the telechelic polyolefin of the formula (I) is $A^1L^1CH_2CH(Y^2)A^2$, wherein Y^2 is hydrogen or a C_1 to C_{30} hydrocarbyl group. In certain embodiments, the Y^2 group is hydrogen. In further embodiments, the Y^2 group is a C_1 to C_{10} alkyl group, or a C_1 to C_6 alkyl group, or a C_1 to C_3 alkyl group. In further embodiments, the Y^2 group is an ethyl group.

[0183] As one of ordinary skill in the art would understand in view of the formula $A^1L^1L^2A^2$, A^1 is covalently bonded to L^1 through a carbon-carbon single bond, L^1 is covalently bonded to L^2 through a carbon-carbon single bond, and L^2 is covalently bonded to A^2 through a carbon-carbon single bond. Accordingly, when it is stated herein that L^1 of the formula $A^1L^1L^2A^2$ is a polyolefin, it is understood that L^1 is a divalent polyolefinyl group (a polyolefin missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds. Likewise, when it is stated that L^1 of the formula $A^1L^1L^2A^2$ is a polymer, it is understood that L^1 is a divalent polymeryl group (a polymer missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds. For example, when it is stated that L^1 is an ethylene homopolymer, it is understood that L^1 is a divalent ethylene homopolymeryl group (an ethylene homopolymer missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds. As a further example, when it is stated that L^1 is an ethylene/alpha-olefin copolymer, it is understood that L^1 is a divalent ethylene/alpha-olefin copolymeryl group (an ethylene/alpha-olefin copolymer missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds.

[0184] In some embodiments, L^1 of the formula (I) is a polyolefin resulting from the coordination polymerization of unsaturated monomers (and comonomers). Examples of suitable monomers (and comonomers) include but are not limited to ethylene and alpha-olefins of 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene,

1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 5-ethyl-1-nonene, 1-octadecene and 1-eicosene; conjugated or nonconjugated dienes, such as butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,5-heptadiene, 1,6-heptadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, 1,9-decadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene, 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene, and mixed isomers of dihydromyrcene and dihydroocimene; norbornene and alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, 5-methylene-2-norbornene, 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, and norbornadiene; and aromatic vinyl compounds such as styrenes, mono or poly alkylstyrenes (including styrene, o-methylstyrene, t-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene and p-ethylstyrene).

[0185] The polyolefin that is L^1 may be linear (unbranched), branched, or cyclic. The presence or absence of branching in L^1 , and the amount of branching (if branching is present), can vary widely and may depend on the desired processing conditions and the desired polymer properties. If branching is present in L^1 , the branching may be short chain branching or long chain branching. Exemplary types of long chain branching that may be present in L^1 include but are not limited to T-type branching and H-type branching. Accordingly, in some embodiments, L^1 may comprise long chain branching. In other words, in some embodiments, L^1 may comprise one or more long chain branches, wherein each long chain branch optionally comprises an A^2 group as defined herein for the formula (I).

[0186] In some embodiments, the A^1 group of the formula (I) correlates to the last inserted monomer or comonomer based on the coordination polymerization of monomers and comonomers to form L^1 . Accordingly, the selection of the monomers and comonomers for the coordination polymerization of L^1 will indicate what the A^1 group and the Y^1 group may be. In some embodiments, the A^1 group is a vinyl group. In some embodiments, the A^1 group is a vinylidene group of the formula $CH_2=C(Y^1)-$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a vinylene group of the formula $Y^1CH=CH-$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinyl group

and a vinylene group of the formula $Y^1CH=CH-$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)-$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinylidene group of the formula $CH_2=C(Y^1)-$ and a vinylene group of the formula $Y^1CH=CH-$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)-$, and a vinylene group of the formula $Y^1CH=CH-$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0187] In further embodiments, the A^1 group is a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH-$, wherein A^1 comprises a ratio of the vinyl group to the vinylene group of the formula $Y^1CH=CH-$ of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0188] In further embodiments, the A^1 group is a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)-$, wherein A^1 comprises a ratio of the vinyl group to the vinylidene group of the formula $CH_2=C(Y^1)-$ of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0189] In further embodiments, the A^1 group is a mixture of a vinylidene group of the formula $CH_2=C(Y^1)-$ and a vinylene group of the formula $Y^1CH=CH-$, wherein A^1 comprises a ratio of the vinylidene group of the formula $CH_2=C(Y^1)-$ to the vinylene group of the formula $Y^1CH=CH-$ of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0190] In further embodiments, the A^1 group is a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)-$, and a vinylene group of the formula $Y^1CH=CH-$, wherein A^1 comprises a ratio of the vinyl group to the sum of the vinylene group of the formula $Y^1CH=CH-$, the vinylidene group of the formula $CH_2=C(Y^1)-$, and the vinyl group of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0191] In certain embodiments, L^1 is a homopolymer comprising units derived from one monomer. The monomer may be selected from any of the suitable monomers discussed previously. In further embodiments, L^1 is an ethylene homopolymer comprising units derived from ethylene. In further embodiments, L^1 is a propylene homopolymer comprising units derived from propylene.

[0192] In some embodiments, L^1 is an interpolpolymer comprising units derived from at least two different types of monomers, such as a monomer and a comonomer. Accordingly, in certain

embodiments, L^1 is an interpolymer comprising units derived from a monomer and at least one comonomer that is different from the monomer. Each of the monomer and the at least one comonomer that is different from the monomer may be selected from any of the suitable monomers discussed previously.

[0193] In further embodiments, L^1 is a copolymer comprising units derived from two different types of monomers, such as a monomer and a comonomer. Accordingly, in certain embodiments, L^1 is a copolymer comprising units derived from a monomer and a comonomer that is different from the monomer. Each of the monomer and the comonomer may be selected from any of the suitable monomers discussed previously.

[0194] In certain embodiments, L^1 is an ethylene/alpha-olefin copolymer. In some embodiments, L^1 is an ethylene/alpha-olefin copolymer comprising units derived from ethylene and a C_3 to C_{30} alpha-olefin, wherein the telechelic polyolefin of the formula (I) comprises an amount of ethylene that is greater than or equal to 50 wt%, or greater than or equal to 60 wt%, or greater than or equal to 70 wt%, or greater than or equal to 75 wt%, or greater than or equal to 80 wt%, or greater than or equal to 85 wt%, or greater than or equal to 88 wt%, or greater than or equal to 89 wt%, or greater than or equal to 90 wt%, based on the total weight of the telechelic polyolefin of the formula (I). The C_3 to C_{30} alpha-olefin may be selected from any of the suitable alpha-olefins discussed previously. In certain embodiments, the C_3 to C_{30} alpha-olefin may be propylene, isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, or the like. In some embodiments, L^1 is an ethylene/alpha-olefin copolymer comprising units derived from ethylene and a C_3 to C_{30} alpha-olefin, wherein the C_3 to C_{30} alpha-olefin is selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene.

[0195] In further embodiments, L^1 is a propylene/alpha-olefin copolymer. L^1 may be a propylene/alpha-olefin copolymer comprising units derived from propylene and either ethylene or a C_4 to C_{30} alpha-olefin, wherein the telechelic polyolefin of the formula (I) comprises an amount of propylene that is greater than or equal to 50 wt%, or greater than or equal to 60 wt%, or greater than or equal to 70 wt%, or greater than or equal to 75 wt%, or greater than or equal to 80 wt%, or greater than or equal to 85 wt%, or greater than or equal to 88 wt%, or greater than or equal to 89 wt%, or greater than or equal to 90 wt%, based on the total weight of the telechelic polyolefin of the formula (I). The C_4 to C_{30} alpha-olefin may be any of the suitable alpha-olefins

discussed above. In certain embodiments, the C₄ to C₃₀ alpha-olefin may be isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, or the like. In certain embodiments, L¹ may be a propylene/alpha-olefin copolymer comprising units derived from propylene and either ethylene or a C₄ to C₃₀ alpha-olefin, wherein the C₄ to C₃₀ alpha-olefin is selected from the group consisting of 1-butene, 1-hexene, and 1-octene.

[0196] In certain embodiments, L¹ is a terpolymer comprising units derived from three different types of monomers, each of which may be selected from any of the suitable monomers discussed above. In further embodiments, L¹ is a terpolymer comprising ethylene or propylene as a first monomer, a C₃ to C₃₀ alpha-olefin or styrene as a second monomer, and a diene or polar monomer as a third monomer.

[0197] In some embodiments, L¹ comprises from 0 to 10 wt% of units derived from diene monomers, based on the total weight of the telechelic polyolefin of the formula (I). For example, L¹ may comprise from 1 to 8 wt%, or from 1 to 5 wt%, or from 1 to 3 wt% of units derived from diene monomers, based on the total weight of the telechelic polyolefin of the formula (I). In further embodiments, L¹ may be substantially free of units derived from diene monomers. For example, in certain embodiments, L¹ may comprise from 0 to 1 wt%, or from 0 to 0.2 wt%, or from 0 to 0.01 wt%, or from 0 to 0.001 wt%, or from 0 to 0.0001 wt% of units derived from diene monomers, based on the total weight of the telechelic polyolefin of the formula (I).

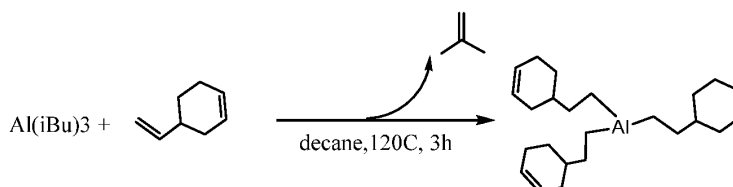
[0198] In certain embodiments, L¹ is an olefin block copolymer as defined herein. In further embodiments, L¹ is a block composite, a specified block composite, or a crystalline block composite as defined herein.

EXAMPLES

Preparation of Materials

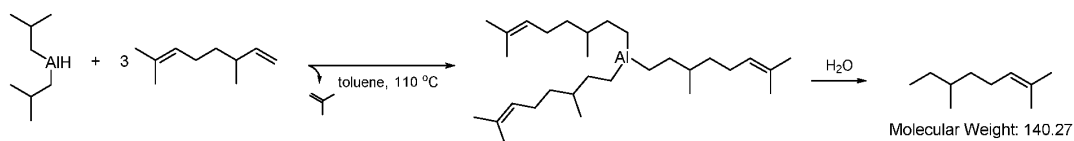
[0199] Unless otherwise noted, all starting reagents and materials were obtained from Sigma-Aldrich. The procatalysts (Cat 1), (Cat 13), (Cat 14), and (Cat 17), as well as any others, used in the examples below are the same as those discussed previously and prepared according to the methods discussed previously. Procatalyst (Cat 1) may also be identified as [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl. "Cocat A" is the co-catalyst used in the examples below and is bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl) borate(1-) amine.

[0200] Synthesis of tris(2-(cyclohex-3-en-1-yl)ethyl)aluminum (“CTA 1”). An exemplary chain transfer agent of the present disclosure was prepared as follows. In a drybox, 4-vinyl-1-cyclohexene (3.2 mL, 24.6 mmol) and triisobutylaluminum (2.0 mL, 7.92 mmol) were added to 5 mL of decane in a vial equipped with a stirbar and a venting needle on the cap. This mixture was heated at 120° C with stirring for 3 hours. After 3 hours, a sample was dissolved in benzene- d_6 for ^1H NMR analysis, and another aliquot was hydrolyzed with water and analyzed by GC/MS. ^1H NMR showed all vinyl groups reacted and the internal double bond remained (FIG. 1A). GC/MS showed a clean peak at m/z of 110, consistent to the molecular weight of ethylcyclohexene (FIG. 1B). Accordingly, ^1H NMR and GC/MS confirmed the synthesis of tris(2-(cyclohex-3-en-1-yl)ethyl)aluminum (“CTA 1”) via non-limiting Scheme 1.



Scheme 1.

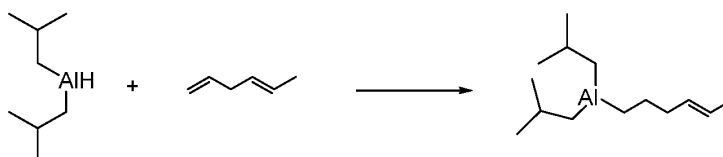
[0201] Synthesis of tris(3,7-dimethyloct-6-en-1-yl)aluminum (“CTA 2”). In a nitrogen-filled drybox, a 40 mL vial was equipped with a stirbar and charged with DIBAL-H (8.10 mL, 9.64 mmol; 20 wt% solution in toluene) and citronellene (4.00 g, 28.93 mmol; mixture of isomers). The vial was placed in a heating block and a vent needle was inserted into the headspace. The solution was heated at 110 – 112 °C for 9 hours giving a colorless transparent solution ($[\text{Al}] = 0.88 \text{ M}$). The material was determined to be the desired product via ^1H NMR (FIG. 2) of an aliquot dissolved in C_6D_6 as well as the GC/MS of a hydrolyzed aliquot ($m/z = 140$). Accordingly, ^1H NMR and GC/MS confirmed the synthesis of tris(3,7-dimethyloct-6-en-1-yl)aluminum (“CTA 2”) via non-limiting Scheme 2.



Scheme 2.

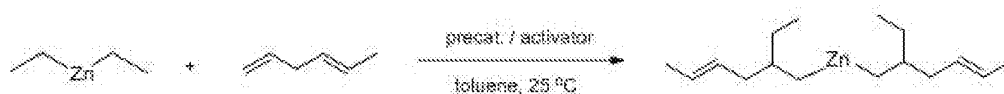
[0202] Synthesis of hex-4-en-1-yl-diisobutylaluminum (“CTA 3”). An exemplary chain transfer agent of the present disclosure was prepared as follows. In a nitrogen-filled drybox, DIBAL-H

(0.800 g, 5.63 mmol) and 1,4-hexadiene (0.65 mL, 5.63 mmol, d 0.710; mixture of *cis* and *trans* isomers) were added to 3 mL of dry, degassed toluene. The reaction mixture was stirred at 25 °C for 14 hours. ¹H NMR analysis of a hydrolyzed sample (see hydrolysis procedure below) showed no reaction. The solution was heated at 60 °C with stirring for 22 hours. After the vial was allowed to cool to 25 °C an aliquot was hydrolyzed and analyzed. Complete reaction was observed by ¹H NMR indicated by the disappearance of the starting diene and appearance of signals consistent with the hydrolysis products: isobutane and 2-hexene. Hydrolysis for analysis was carried out by diluting ca 0.1 mL of the sample to ca 2 mL with C₆D₆ in a vial, removing the sample from the glove box, and adding ca 0.1 mL of nitrogen-purged water via syringe. After shaking the vial the mixture was passed through a 0.45 μm syringe filter. The organic phase passes through more easily than the aqueous phase, allowing for quick isolation of the organic phase for analysis. The sample was then mixed with a small amount of silica gel and filtered again. This helps remove residual Al species that can cause gelation. Accordingly, ¹H NMR confirmed the synthesis of hex-4-en-1-yl-diisobutylaluminum (“CTA 3”) via non-limiting Scheme 3.



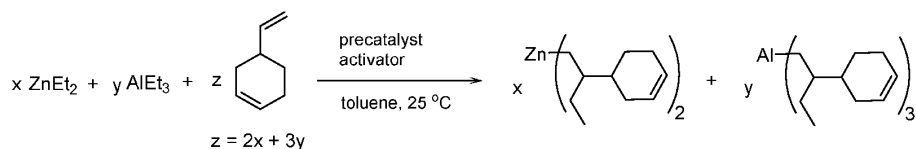
Scheme 3.

[0203] Synthesis of bis(-2-ethylhex-4-en-1-yl)zinc (“CTA 4”): In a nitrogen-filled drybox, diethylzinc (3.40 mL, 5.00 mmol, 20 wt% in toluene), 1,4-hexadiene (1.16 mL, 10.00 mmol, d 0.710; mixture of *cis* and *trans* isomers), and the activator [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄] (1.40 mL, 0.09 mmol, 0.064 M in methylcyclohexane) were mixed in a vial. (Cat 13) (0.045 g, 0.08 mmol) was added as a solid and the reaction mixture was stirred at 25 °C for 20 hours. ¹H NMR and GC/MS analysis of a hydrolyzed sample (see hydrolysis procedure below) showed complete reaction. ¹H NMR indicated by the disappearance of the starting diene and appearance of signals consistent with the hydrolysis product 5-methylhept-2-ene. GC/MS showed the same expected hydrolysis product. Accordingly, ¹H NMR and GC/MS confirmed the synthesis of bis(-2-ethylhex-4-en-1-yl)zinc (“CTA 4”) via non-limiting Scheme 4.



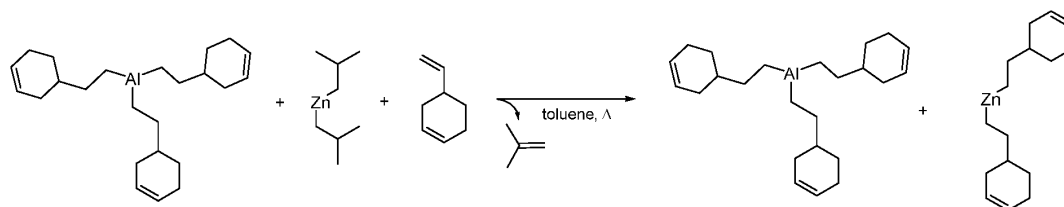
Scheme 4.

[0204] **Synthesis of “CTA 5”:** Diethylzinc (0.66 mL, 0.97 mmol; 1.47 M solution in toluene), 4-vinylcyclohexene (1.77 mL, 13.58 mmol; d 0.832), the activator ([HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄]) solution in methylcyclohexane (0.60 mL, 0.039 mmol; 0.0644M) and triethylaluminum (0.53 mL, 3.88 mmol; neat, 93%) were dissolved in toluene (~10 mL). (Cat 13) (0.023 g, 0.039 mmol) was added as a solid and the reaction mixture was stirred at 25 °C for 14 hours. An aliquot was dissolved in C₆D₆ and quenched with water. GC/MS and ¹H NMR confirmed the consumption of 4-vinylcyclohexene and the formation of the desired product (m/z = 138). Accordingly, this confirms that CTA 5 was prepared via non-limiting Scheme 5.



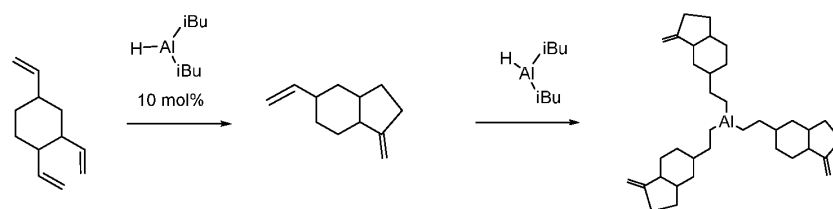
Scheme 5.

[0205] **Synthesis of “CTA 6”:** The toluene solution of tris(2-(cyclohex-3-en-1-yl)ethyl)aluminum (10 mL, [Al] = 0.424 M) was mixed with diisobutylzinc (0.286 g, 1.59 mmol) and 4-vinylcyclohexene (0.416 mL, 3.19 mmol; d 0.830). The solution was heated for 4 hours at 110 °C with a vent needle inserted through the septum cap of the vial to allow isobutylene to escape. During this treatment ⁱBu groups from DIBZ transferred to Al and thermal elimination of isobutylene followed by 4-vinylcyclohexene insertions ensured that all alkyl groups on Al and Zn were cyclohexenylethyl groups. An aliquot (0.1 mL) of this mixture was diluted with C₆D₆ (0.5 mL) and hydrolyzed for ¹H NMR analysis. ¹H NMR analysis (FIG. 3) confirmed CTA was synthesized via non-limiting Scheme 6.



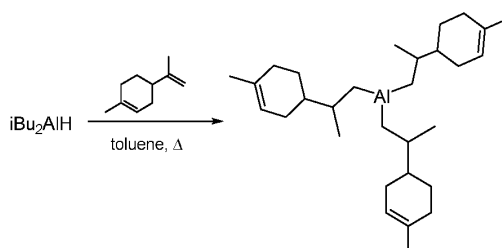
Scheme 6.

[0206] Synthesis of “CTA 7”: The synthesis of CTA 7 is exemplified in non-limiting Scheme 7 and described as follows. It was carried out in two steps. In the first step, trivinylcyclohexane (TVCH) was converted to a diene via intramolecular cyclization in the presence of catalytic amount of DIBAL-H, and in the second step additional DIBAL-H was added to form the CTA. Thus, in a nitrogen-filled drybox, DIBAL-H (0.30 g, 2.11 mmol) was added to TVCH (4.09 mL, 21.1 mmol; d 0.836). The mixture was heated at 160 °C and stirred for 2h to form cyclized-TVCH. In a separate vial additional DIBAL-H (0.35 g, 2.46 mmol) was dissolved in decane (5 mL), followed by addition of a portion of the cyclized-TVCH (2.05 mL, 10.5 mmol) obtained above. The solution was maintained at 130 °C for 2 h to obtain the Al-TVCH solution.



Scheme 7.

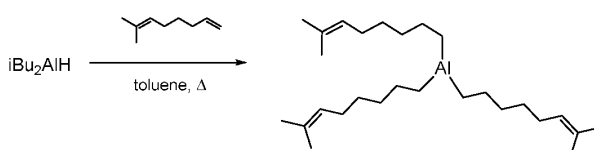
[0207] Synthesis of “CTA 8”: The synthesis of CTA 8 is exemplified in non-limiting Scheme 8 and described as follows. In a nitrogen-filled drybox, a 20 mL vial was equipped with a stirbar and charged with DIBAL-H (2.00 mL, 2.39 mmol; 20 wt% in toluene (1.196 M)) and (R)-(+)-limonene (2.32 mL, 14.35 mmol; d 0.842). The vial was placed in a heating block, a vent needle was inserted through the septum cap, and the solution was heated at 110 – 112 °C for 11 hours. Solvent and excess limonene were removed under vacuum at 50 °C overnight to afford the desired product as a colorless viscous oil (0.870 g, 83%).



Scheme 8.

[0208] Synthesis of “CTA 9”: The synthesis of CTA 9 is exemplified in non-limiting Scheme 9 and described as follows. In a nitrogen-filled drybox a 40 mL vial was equipped with a stirbar

and charged with DIBAL-H (2.00 g, 14.06 mmol), toluene (9.2 mL) and 7-methyl-1,6-octadiene (5.24 g, 42.19 mmol). An immediate exotherm (with some bubbling) was observed. The vial was placed in a heating block, a vent needle was inserted through the septum cap, and the solution was heated at 110 – 112 °C for 3 hours. After 3 hours of reaction time an aliquot showed reaction progress. The solution contained a small amount of suspended white solid particles. The reaction was continued for another 22 hours. The reaction was nearly complete. A small amount of dimer formation from the alkene reagent was observed. The reaction was continued for another 16 hours. Analysis of an aliquot showed no significant changes.



Scheme 9.

Batch Reactor Synthesis of Telechelic Polyolefins

[0209] Exemplary polyolefins and telechelic polyolefins of the present disclosure were synthesized via batch reactor in accordance with the following.

[0210] A batch reactor run was performed with CTA 5, (Cat 1), and Cocat A in accordance with Table 1. With reference to Table 1, B1 used the scavenger MMAO-3A with a (Cat 1):Cocat A:scavenger ratio of 1:1.2:10. Runs B2 to B7 used a procatalyst to cocatalyst ratio of 1:1.2. All runs in Table 1 were carried out without hydrogen. All runs had the following conditions: Ethylene (g): 20, 1-octene (g): 60, pressure (psi): 55, solvent (Isopar E, g): 1325. CTA 5 loading was based on the number of transferrable groups. Runs B1, B2, B4 and B6 were at 120 °C for 10 min. Runs B3, B5 and B7 included an additional heating step to 200 °C for 20 min (excluding the transition time from 120 to 200 °C). The batch reactor run was performed according to the following procedure.

[0211] In each run, a one gallon stirred autoclave reactor is charged with Isopar™ E mixed alkanes solvent, desired mass of propylene and CTA 5. The reactor is heated to 120° C and charged with ethylene. An active catalyst solution is prepared in a drybox under inert atmosphere by mixing (Cat 1) and an activator mixture (a mixture of 1.2 equiv of Cocat A and 10 equiv of modified methyl aluminoxane (MMAO-3A)), where the active catalyst solution has a ratio of (Cat 1) to Cocat A of 1:1.2. The active catalyst solution is injected into the reactor to initiate the polymerization. The reactor pressure and temperature is kept constant by feeding

ethylene during the polymerization and cooling the reactor as needed. After 10 minutes, the reactor was heated to 200 °C and kept at the temperature for 20 minutes. The ethylene feed is shut off and the polymer solution transferred into a nitrogen-purged resin kettle. An additive solution containing a phosphorus stabilizer and phenolic antioxidant (Irgafos® 168 and Irganox® 1010 in a 2:1 ratio by weight in toluene) is added to give a total additive content of approximately 0.1% in the polymer. The polymer is thoroughly dried in a vacuum oven.

Table 1

Run	Cat 1	CTA 5	Polymer (g)	Temp. (°C)	M _n	M _w	M _w /M _n
B1	4.5	-	43.0	120	72,542	739,532	10.2
B2	2.8	2	52.0	120	49,377	208,606	4.2
B3	1.5	2	37.6	120+200	37,531	169,615	4.5
B4	2.5	4	86.0	120	26,232	75,541	2.9
B5	1.5	4	76.0	120+200	22,630	78,956	3.5
B6	2.0	8	87.3	120	15,875	35,117	2.2
B7	1.0	8	119.0	120+200	12,239	31,477	2.6

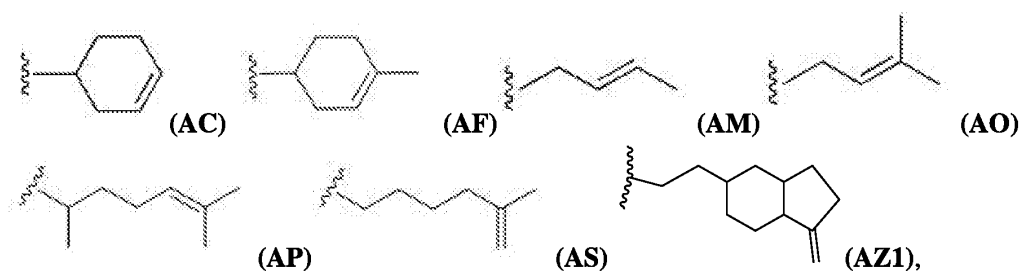
[0212] A similar batch reactor run was done with CTA 6 as seen in Table 2. Here, the procatalyst was Cat 1 and the activator was [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄]. The following conditions were reported: Procatalyst:activator = 1.2. MMAO-3A used in entry 1 only (procatalyst:activator:MMAO = 1:1.2:10). All runs carried out without hydrogen. Ethylene (g): 20, propylene (g): 60, pressure (psig): 155, solvent (Isopar E, g): 1325.

Table 2

Entry	Identification	T (°C)	CTA alkyl groups (mmol)	M _n	M _w	M _w /M _n
1	no CTA	120	0	175,461	899,136	5.1
2	CTA 1	120	4	15,463	47,000	3.0
3	CTA 6	120	4	9,693	42,681	4.4

What is claimed is:

1. An organometallic composition comprising an organoaluminum compound of the formula $\text{Al}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_3$ and an organozinc compound of the formula $\text{Zn}(\text{CH}_2\text{CH}(\text{Y}^2)\text{A}^2)_2$, wherein:
 Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and
 A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.
2. The composition of claim 1, wherein the hindered double bond is selected from the group consisting of the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.
3. The composition of any of the preceding claims, wherein A^2 is a C_3 to C_{30} cyclic hydrocarbyl group or a C_3 to C_{30} acyclic hydrocarbyl group.
4. The composition of any of the preceding claims, wherein A^2 is selected from the group consisting of an unsubstituted cycloalkene, an alkyl-substituted cycloalkene, and an acyclic alkyl group.
5. The composition of any of the preceding claims, wherein A^2 is selected from the group consisting of:



wherein the endocyclic double bond in (AC) and (AF) may be between any two adjacent carbon atoms that are ring members, and wherein the pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.