

CATALYST SYSTEMS AND PROCESSES FOR PRODUCING POLYETHYLENE USING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 63/031,638 filed May 29, 2020 and U.S. Provisional Patent Application No. 63/143,333 filed January 29, 2021, which are incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure are generally directed to processes for producing polyethylene and, in particular, contacting ethylene and, optionally, one or more (C₃–C₁₂) α -olefin comonomers with germanium-bridged bis-phenylphenoxy catalyst systems in a gas-phase polymerization reactor.

BACKGROUND

[0003] Since the discovery of Ziegler and Natta on heterogeneous olefin polymerizations, global polyolefin production reached approximately 150 million tons per year in 2015, and continues to increase due to market demand. The catalyst systems in the polyolefin polymerization process may contribute to the characteristics and properties of such polyolefins. For example, catalyst systems that include bis-phenylphenoxy (BPP) metal-ligand complexes may produce polyolefins that have flat or reverse short-chain branching distributions (SCBD), relatively high levels of comonomer incorporation, high native molecular weights, and/or narrow-medium molecular weight distributions (MWD).

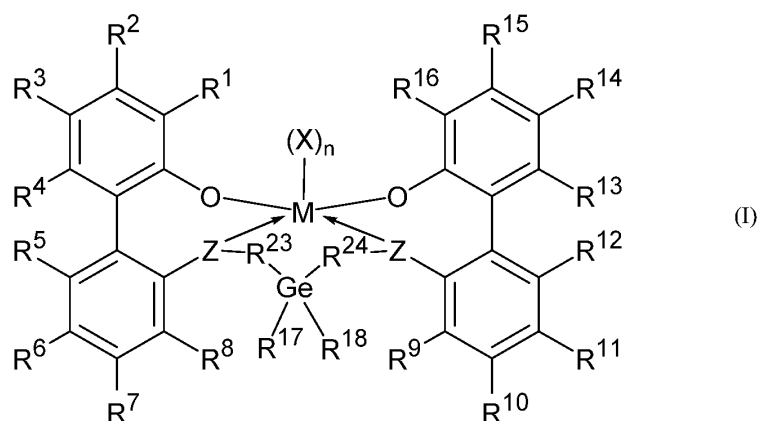
[0004] However, when utilized in some polymerization processes, such as gas-phase polymerization, catalyst systems that include BPP metal-ligand complexes may exhibit generally poor productivity. That is, catalyst systems that include BPP metal-ligand complexes may generally produce less polymer relative to the amount of the catalyst system used. Therefore, the use of catalyst systems that include BPP metal-ligand complexes may not be commercially viable in gas-phase polymerization processes.

SUMMARY

[0005] Accordingly, ongoing needs exist for catalyst systems that are suitable for use in gas-phase reactors and have improved productivity when utilized in gas-phase polymerization processes. Embodiments of the present disclosure address these needs by providing catalyst systems including BPP metal-ligand complexes having germanium-containing bridges. The catalyst systems, when utilized in gas-phase polymerization processes, exhibit a greatly increased

productivity when compared to similar catalyst systems including BPP metal-ligand complexes without germanium-containing bridges.

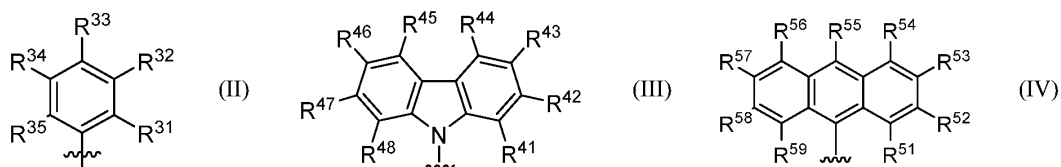
[0006] Embodiments of the present disclosure include a procatalyst. The procatalyst includes a metal-ligand complex disposed on one or more support materials. The metal-ligand complex has a structure according to formula (I):



[0007] In formula (I), M is titanium, zirconium, or hafnium; subscript n of $(X)_n$ is 1, 2, or 3; each X is a monodentate ligand independently chosen from unsaturated (C_2-C_{50}) hydrocarbon, unsaturated (C_2-C_{50}) heterohydrocarbon, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, halogen, $-N(R^N)_2$, and $-N(R^N)COR^C$; and the metal-ligand complex of formula (I) is overall charge-neutral.

[0008] In formula (I), each Z is independently chosen from $-O-$, $-S-$, (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, $N(C_1-C_{40})$ hydrocarbyl, and $P(C_1-C_{40})$ hydrocarbyl.

[0009] In formula (I), R^1 and R^{16} are independently chosen from (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, (C_1-C_{40}) alkyl, (C_3-C_{40}) heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0010] In formulas (II), (III), and (IV), R^{31-35} , R^{41-48} , and R^{51-59} are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$,

$-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen.

[0011] In formula (I), R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently chosen from $-\text{H}$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl, $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, and halogen.

[0012] In formula (I), R^{23} and R^{24} are independently chosen from $-(\text{CR}^{\text{C}})_m-$, wherein subscript m is from 1 to 10.

[0013] In formula (I), R^{17} and R^{18} are independently chosen from linear or branched $(\text{C}_1-\text{C}_{20})$ alkyl.

[0014] In formulas (I), (II), (III), and (IV), each R^{C} , R^{P} , and R^{N} are independently chosen from $-\text{H}$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl, and $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl.

[0015] Embodiments of the present disclosure include methods for producing a catalyst system. The method includes contacting one or more support materials, one or more activators, and a metal-ligand complex in an inert hydrocarbon solvent to produce the catalyst system.

[0016] Embodiments of the present disclosure include a process for producing polyethylene. The process includes contacting ethylene and, optionally, one or more $(\text{C}_3-\text{C}_{12})\alpha$ -olefin comonomers with a catalyst system in a gas-phase polymerization reactor. The catalyst system comprises a metal-ligand complex disposed on one or more support materials.

[0017] These and additional features provided by the embodiments of the present disclosure will be more fully understood in view of the following detailed description.

DETAILED DESCRIPTION

[0018] Specific embodiments of procatalysts, catalyst systems, methods of producing catalyst systems, and processes for producing polyethylene will now be described. However, it should be understood that the systems, methods, and processes of the present disclosure may be embodied in different forms, and should not be construed as limited to the specific embodiments set forth in the present disclosure. Rather, embodiments are provided so that the present disclosure will be thorough and complete, and will fully convey the scope of the disclosed subject matter to those skilled in the art.

[0019] Common abbreviations used in the present disclosure are listed below:

[0020] **Me**: methyl; **Et**: ethyl; **Ph**: phenyl; **Bn**: benzyl; ***i*-Pr**: *iso*-propyl; ***t*-Bu**: *tert*-butyl; ***t*-Oct**: *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf**: trifluoromethane sulfonate; **THF**: tetrahydrofuran; **Et₂O**: diethyl ether; **CH₂Cl₂**: dichloromethane; **CV**: column volume (used in

column chromatography); **EtOAc**: ethyl acetate; **C₆D₆**: deuterated benzene or benzene-*d*₆; **CDCl₃**: deuterated chloroform; **Na₂SO₄**: sodium sulfate; **MgSO₄**: magnesium sulfate; **HCl**: hydrogen chloride; ***n*-BuLi**: butyllithium; ***t*-BuLi**: *tert*-butyllithium; **MAO**: methylaluminoxane; **MMAO**: modified methylaluminoxane; **GC**: gas chromatography; **LC**: liquid chromatography; **NMR**: nuclear magnetic resonance; **MS**: mass spectrometry; **mmol**: millimoles; **mL**: milliliters; **M**: molar; **min or mins**: minutes; **h or hrs**: hours; **d**: days.

[0021] The terms “halogen atom” or “halogen” mean the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means the anionic form of the halogen atom: fluoride (F⁻), chloride (Cl⁻), bromide (Br⁻), or iodide (I⁻).

[0022] The term “independently selected” means that the R groups, such as, R¹, R², and R³, can be identical or different (*e.g.*, R¹, R², and R³ may all be substituted alkyls; or R¹ and R² may be a substituted alkyl, and R³ may be an aryl). A chemical name associated with an R group is intended to convey the chemical structure that is recognized in the art as corresponding to that of the chemical name. As a result, chemical names are intended to supplement and illustrate, not preclude, the structural definitions known to those of skill in the art.

[0023] The term “procatalyst” means a compound that has catalytic activity when combined with an activator. The term “activator” means a compound that chemically reacts with a procatalyst in a manner that converts the procatalyst to a catalytically active compound. As used in the present disclosure, the terms “co-catalyst” and “activator” are interchangeable, and have identical meanings unless clearly specified.

[0024] The term “substitution” means that at least one hydrogen atom (–H) bonded to a carbon atom of a corresponding unsubstituted compound or functional group is replaced by a substituent (*e.g.*, R^S). The term “–H” means a hydrogen or hydrogen radical that is covalently bonded to another atom. As used in the present disclosure, the terms “hydrogen” and “–H” are interchangeable, and have identical meanings unless clearly specified.

[0025] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₅₀)alkyl is an alkyl group having from 1 to 50 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S. An R^S substituted chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–C₅₀)alkyl substituted with exactly one group R^S, where R^S is phenyl (–C₆H₅)”

may contain from 7 to 56 carbon atoms. As a result, when a chemical group defined using the “(C_x–C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^S, the minimum and maximum total number of carbon atoms of the chemical group is determined by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^S.

[0026] The term “(C₁–C₅₀)hydrocarbyl” means a hydrocarbon radical of from 1 to 50 carbon atoms and the term “(C₁–C₅₀)hydrocarbylene” means a hydrocarbon diradical of from 1 to 50 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (having three carbons or more, and including mono- and poly-cyclic, fused and non-fused polycyclic, and bicyclic) or acyclic, and substituted by one or more R^S or unsubstituted. As used in the present disclosure, a (C₁–C₅₀)hydrocarbyl may be an unsubstituted or substituted (C₁–C₅₀)alkyl, (C₃–C₅₀)cycloalkyl, (C₃–C₂₅)cycloalkyl-(C₁–C₂₅)alkylene, (C₆–C₅₀)aryl, or (C₆–C₂₅)aryl-(C₁–C₂₅)alkylene (such as benzyl (–CH₂–C₆H₅)).

[0027] The term “(C₁–C₅₀)alkyl” means a saturated straight or branched hydrocarbon radical containing from 1 to 50 carbon atoms. Each (C₁–C₅₀)alkyl may be unsubstituted or substituted by one or more R^S. In embodiments, each hydrogen atom in a hydrocarbon radical may be substituted with R^S, such as, for example, trifluoromethyl. Examples of unsubstituted (C₁–C₅₀)alkyl are unsubstituted (C₁–C₂₀)alkyl; unsubstituted (C₁–C₁₀)alkyl; unsubstituted (C₁–C₅)alkyl; methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2-butyl; 2-methylpropyl; 1,1-dimethylethyl; 1-pentyl; 1-hexyl; 1-heptyl; 1-nonyl; and 1-decyl. Examples of substituted (C₁–C₅₀)alkyl are substituted (C₁–C₂₀)alkyl, substituted (C₁–C₁₀)alkyl, trifluoromethyl, and [C₄₅]alkyl. The term “[C₄₅]alkyl” means there is a maximum of 45 carbon atoms in the radical, including substituents, and is, for example, a (C₂₇–C₄₀)alkyl substituted by one R^S, which is a (C₁–C₅)alkyl, such as, for example, methyl, trifluoromethyl, ethyl, 1-propyl, 1-methylethyl, or 1,1-dimethylethyl.

[0028] The term “(C₃–C₅₀)cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S. Other cycloalkyl groups (*e.g.*, (C_x–C_y)cycloalkyl) are defined in an analogous manner as having from x to y carbon atoms and being either unsubstituted or substituted with one or more R^S. Examples of unsubstituted (C₃–C₅₀)cycloalkyl are unsubstituted (C₃–C₂₀)cycloalkyl, unsubstituted (C₃–C₁₀)cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C₃–C₅₀)cycloalkyl are substituted (C₃–C₂₀)cycloalkyl, substituted (C₃–C₁₀)cycloalkyl, and 1-fluorocyclohexyl.

[0029] The term “(C₆–C₅₀)aryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic aromatic hydrocarbon radical of from 6 to 50 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms. A monocyclic aromatic hydrocarbon radical includes one aromatic ring; a bicyclic aromatic hydrocarbon radical has two rings; and a tricyclic aromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic aromatic hydrocarbon radical is present, at least one of the rings of the radical is aromatic. The other ring or rings of the aromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Examples of unsubstituted (C₆–C₅₀)aryl include: unsubstituted (C₆–C₂₀)aryl, unsubstituted (C₆–C₁₈)aryl; 2-(C₁–C₅)alkyl-phenyl; phenyl; fluorenyl; tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; and phenanthrene. Examples of substituted (C₆–C₅₀)aryl include: substituted (C₁–C₂₀)aryl; substituted (C₆–C₁₈)aryl; 2,4-bis([C₂₀]alkyl)-phenyl; polyfluorophenyl; pentafluorophenyl; and fluoren-9-one-1-yl.

[0030] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of groups containing one or more than one heteroatom include O, S, S(O), S(O)₂, Si(R^C)₂, P(R^P), N(R^N), –N=C(R^C)₂, –Ge(R^C)₂–, or –Si(R^C)–, where each R^C and each R^P is unsubstituted (C₁–C₁₈)hydrocarbyl or –H, and where each R^N is unsubstituted (C₁–C₁₈)hydrocarbyl. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms of a hydrocarbon are replaced with a heteroatom. The term “(C₁–C₅₀)heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 50 carbon atoms, and the term “(C₁–C₅₀)heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 50 carbon atoms. The heterohydrocarbon of the (C₁–C₅₀)heterohydrocarbyl or the (C₁–C₅₀)heterohydrocarbylene has one or more heteroatoms. The radical of the heterohydrocarbyl may be on a carbon atom or a heteroatom. The two radicals of the heterohydrocarbylene may be on a single carbon atom or on a single heteroatom. Additionally, one of the two radicals of the diradical may be on a carbon atom and the other radical may be on a different carbon atom; one of the two radicals may be on a carbon atom and the other on a heteroatom; or one of the two radicals may be on a heteroatom and the other radical on a different heteroatom. Each (C₁–C₅₀)heterohydrocarbyl and (C₁–C₅₀)heterohydrocarbylene may be unsubstituted or substituted (by one or more R^S), aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic), or acyclic.

[0031] The term “(C₄–C₅₀)heteroaryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi-, or tricyclic heteroaromatic hydrocarbon radical of from 4 to 50 total carbon atoms and from 1 to 10 heteroatoms. A monocyclic heteroaromatic hydrocarbon radical includes one heteroaromatic ring; a bicyclic heteroaromatic hydrocarbon radical has two rings; and a tricyclic heteroaromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic heteroaromatic hydrocarbon radical is present, at least one of the rings in the radical is heteroaromatic. The other ring or rings of the heteroaromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Other heteroaryl groups (e.g., (C_x–C_y)heteroaryl generally, such as (C₄–C₁₂)heteroaryl) are defined in an analogous manner as having from x to y carbon atoms (such as 4 to 12 carbon atoms) and being unsubstituted or substituted by one or more than one R^S. The monocyclic heteroaromatic hydrocarbon radical is a 5-membered ring or a 6-membered ring. The 5-membered ring has 5 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1, 2, or 3; and each heteroatom may be O, S, N, or P. Examples of 5-membered ring heteroaromatic hydrocarbon radicals include pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; and tetrazol-5-yl. The 6-membered ring has 6 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1 or 2 and the heteroatoms may be N or P. Examples of 6-membered ring heteroaromatic hydrocarbon radicals include pyridine-2-yl; pyrimidin-2-yl; and pyrazin-2-yl. The bicyclic heteroaromatic hydrocarbon radical can be a fused 5,6- or 6,6-ring system. Examples of the fused 5,6-ring system bicyclic heteroaromatic hydrocarbon radical are indol-1-yl; and benzimidazole-1-yl. Examples of the fused 6,6-ring system bicyclic heteroaromatic hydrocarbon radical are quinolin-2-yl; and isoquinolin-1-yl. The tricyclic heteroaromatic hydrocarbon radical can be a fused 5,6,5-; 5,6,6-; 6,5,6-; or 6,6,6-ring system. An example of the fused 5,6,5-ring system is 1,7-dihydropyrrolo[3,2-f]indol-1-yl. An example of the fused 5,6,6-ring system is 1H-benzo[f]indol-1-yl. An example of the fused 6,5,6-ring system is 9H-carbazol-9-yl. An example of the fused 6,5,6- ring system is 9H-carbazol-9-yl. An example of the fused 6,6,6-ring system is acrydin-9-yl.

[0032] The term "polymer" refers to polymeric compounds prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus includes homopolymers, which are polymers prepared by polymerizing only one monomer, and copolymers, which are polymers prepared by polymerizing two or more different monomers.

[0033] The term "interpolymer" refers to polymers prepared by polymerizing at least two different types of monomers. The generic term interpolymer thus includes copolymers and other polymers prepared by polymerizing more than two different monomers, such as terpolymers.

[0034] The terms "polyolefin," "polyolefin polymer," and "polyolefin resin" refer to polymers prepared by polymerizing a simple olefin (also referred to as an alkene, which has the general formula C_nH_{2n}) monomer. The generic term polyolefin thus includes polymers prepared by polymerizing ethylene monomer with or without one or more comonomers, such as polyethylene, and polymers prepared by polymerizing propylene monomer with or without one or more comonomers, such as polypropylene.

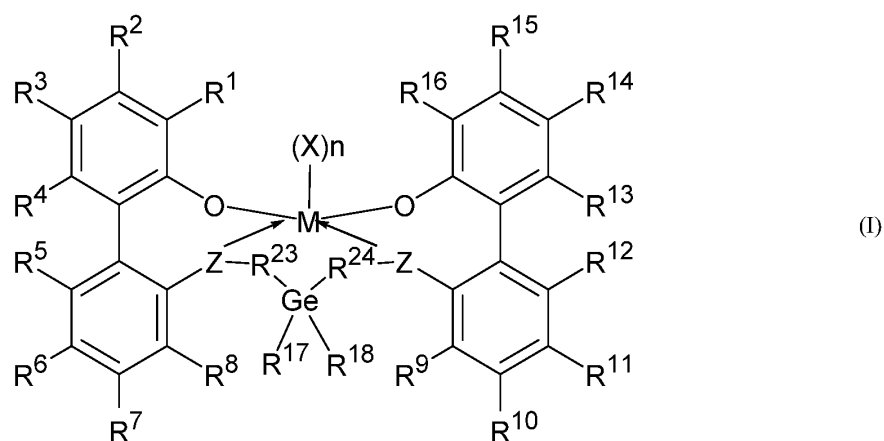
[0035] The terms "polyethylene" and "ethylene-based polymer" refer to polyolefins comprising greater than 50 percent (%) by mole of units that have been derived from ethylene monomer, which includes polyethylene homopolymers and copolymers. Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), Ultra Low Density Polyethylene (ULDPE), Very Low Density Polyethylene (VLDPE), Medium Density Polyethylene (MDPE), and High Density Polyethylene (HDPE).

[0036] The term "molecular weight distribution" means a ratio of two different molecular weights of a polymer. The generic term molecular weight distribution includes a ratio of a weight average molecular weight (M_w) of a polymer to a number average molecular weight (M_n) of the polymer, which may also be referred to as a "molecular weight distribution (M_w/M_n)," and a ratio of a z-average molecular weight (M_z) of a polymer to a weight average molecular weight (M_w) of the polymer, which may also be referred to as a "molecular weight distribution (M_z/M_w)."

[0037] The term "composition" means a mixture of materials that comprises the composition, as well as reaction products and decomposition products formed from the materials of the composition.

[0038] 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, 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.

[0039] In embodiments, the catalyst system includes a procatalyst. The procatalyst includes a metal-ligand complex. The metal-ligand complex may have a structure according to formula (I):

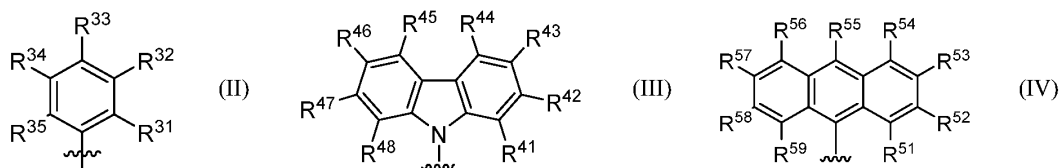


[0040] In formula (I), M is titanium (Ti), zirconium (Zr), or hafnium (Hf). In embodiments, M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4.

[0041] In formula (I), subscript n of (X)_n is 1, 2, or 3, and each X is a monodentate ligand independently chosen from unsaturated (C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, halogen, –N(R^N)₂, and –N(R^N)COR^C. In embodiments, each X is independently chosen from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments, subscript n of (X)_n is 2 and each X is the same. In other embodiments, at least two X are different. For example, subscript n of (X)_n may be 2 and each X may be a different one of methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In embodiments, subscript n of (X)_n is 1 or 2 and at least two X independently are monoanionic monodentate ligands and a third X, if present, is a neutral monodentate ligand. In or more embodiments, subscript n of (X)_n is 2. In formula (I), the metal-ligand complex is overall charge-neutral.

[0042] In formula (I), each Z is independently chosen from –O–, –S–, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, N(C₁–C₅₀)hydrocarbyl, and P(C₁–C₅₀)hydrocarbyl. In embodiments, each Z is the same. For example, each Z may be –O–.

[0043] In formula (I), R¹ and R¹⁶ are independently chosen from (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, (C₁–C₅₀)alkyl, (C₃–C₄₀)heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0044] In formula (II), R³¹, R³², R³³, R³⁴, R³⁵ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, or halogen.

[0045] In formula (III), R⁴¹, R⁴², R⁴³, R⁴⁴, R⁴⁵, R⁴⁶, R⁴⁷, R⁴⁸ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, or halogen.

[0046] In formula (IV), R⁵¹, R⁵², R⁵³, R⁵⁴, R⁵⁵, R⁵⁶, R⁵⁷, R⁵⁸, and R⁵⁹ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, or halogen.

[0047] The groups R¹ and R¹⁶ in the metal-ligand complex of formula (I) are chosen independently of one another. For example, R¹ may be chosen from a radical having formula (II), (III), or (IV), and R¹⁶ may be a (C₄-C₅₀)heteroaryl; or R¹ may be chosen from a radical having formula (II), (III), or (IV), and R¹⁶ may be chosen from a radical having formula (II), (III), or (IV), the same as or different from that of R¹. In embodiments, both R¹ and R¹⁶ are radicals having formula (II), for which the groups R³¹⁻³⁵ are the same or different in R¹ and R¹⁶. In some embodiments, both R¹ and R¹⁶ are radicals having formula (III), for which the groups R⁴¹⁻⁴⁸ are the same or different in R¹ and R¹⁶. In other embodiments, both R¹ and R¹⁶ are radicals having formula (IV), for which the groups R⁵¹⁻⁵⁹ are the same or different in R¹ and R¹⁶.

[0048] In embodiments, at least one of R¹ and R¹⁶ is a radical having formula (II), where at least one of R³² and R³⁴ are *tert*-butyl. In some embodiments, when at least one of R¹ or R¹⁶ is a radical having formula (III), one of or both of R⁴³ and R⁴⁶ is *tert*-butyl and R⁴¹⁻⁴², R⁴⁴⁻⁴⁵, and R⁴⁷⁻⁴⁸ are -H. In other embodiments, one of or both of R⁴² and R⁴⁷ is *tert*-butyl and R⁴¹, R⁴³⁻⁴⁶, and R⁴⁸ are -H. In some embodiments, both R⁴² and R⁴⁷ are -H. In some embodiments, R⁴¹⁻⁴⁸ are -H.

[0049] In formula (I), R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl, -Si(R^C)₃,

$-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, and halogen.

[0050] In some embodiments, at least one of R^5 , R^6 , R^7 , and R^8 is a halogen atom; and at least one of R^9 , R^{10} , R^{11} , and R^{12} is a halogen atom. In some embodiments, at least two of R^5 , R^6 , R^7 , and R^8 are halogen atoms; and at least two of R^9 , R^{10} , R^{11} , and R^{12} are halogen atoms. In various embodiments, at least three of R^5 , R^6 , R^7 , and R^8 are halogen atoms; and at least three of R^9 , R^{10} , R^{11} , and R^{12} are halogen atoms.

[0051] In embodiments, R^3 and R^{14} are $(\text{C}_1-\text{C}_{24})$ alkyl. In various embodiments, R^3 and R^{14} are $(\text{C}_1-\text{C}_{20})$ alkyl. In some embodiments, R^3 and R^{14} are $(\text{C}_4-\text{C}_{24})$ alkyl. In one or more embodiments, R^3 and R^{14} are $(\text{C}_8-\text{C}_{12})$ alkyl. In some embodiments, R^3 and R^{14} are 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methyl-1-butyl, hexyl, 4-methyl-1-pentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl. In embodiments, R^3 and R^{14} are $-\text{OR}^{\text{C}}$, wherein R^{C} is $(\text{C}_1-\text{C}_{20})$ hydrocarbon, and in some embodiments, R^{C} is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl.

[0052] In embodiments, R^3 and R^{14} are methyl. In other embodiments, R^3 and R^{14} are $(\text{C}_4-\text{C}_{24})$ alkyl. In some embodiments, R^8 and R^9 are 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methyl-1-butyl, hexyl, 4-methyl-1-pentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0053] In some embodiments, R^6 and R^{11} are halogen. In other embodiments, R^6 and R^{11} are $(\text{C}_1-\text{C}_{24})$ alkyl. In some embodiments, R^6 and R^{11} independently are chosen from methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl. In some embodiments, R^6 and R^{11} are *tert*-butyl. In embodiments, R^6 and R^{11} are $-\text{OR}^{\text{C}}$, wherein R^{C} is $(\text{C}_1-\text{C}_{20})$ hydrocarbyl, and in some embodiments, R^{C} is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl. In other embodiments, R^6 and R^{11} are $-\text{SiR}^{\text{C}}_3$, wherein each R^{C} is independently $(\text{C}_1-\text{C}_{20})$ hydrocarbyl, and in some embodiments, R^{C} is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl.

[0054] In some embodiments, R^3 and R^{14} are methyl and R^6 and R^{11} are halogen. In other embodiments, R^6 and R^{11} are *tert*-butyl. In other embodiments, R^3 and R^{14} are *tert*-octyl or *n*-octyl.

[0055] In formula (I), R^{23} and R^{24} are independently chosen from $-(CR^C)_m-$, wherein subscript m is from 1 to 10. In one or more embodiments, each subscript m is 1 or 2.

[0056] In formula (I), R^{17} and R^{18} are independently chosen from linear or branched (C_1-C_{20}) alkyl. In some embodiments, R^{17} and R^{18} are independently chosen from linear or branched (C_2-C_{20}) alkyl, (C_3-C_7) alkyl, or (C_4-C_7) cycloalkyl.

[0057] In formulas (I), (II), (III), and (IV), each R^C , R^P , and R^N are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, and (C_1-C_{50}) heterohydrocarbyl.

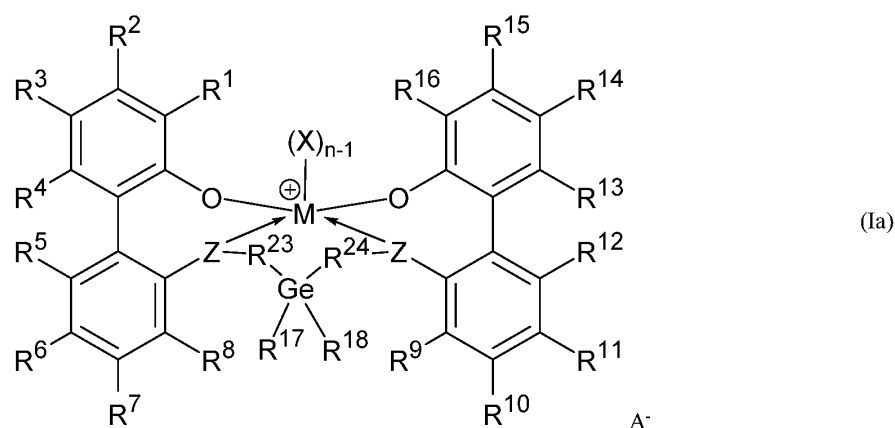
[0058] In embodiments, the procatalyst may be rendered catalytically active by contacting it to, or combining it with, an activator. A procatalyst that has been rendered catalytically active by contacting it to, or combining it with, an activator may be referred to as a “catalyst system.” That is, as used in the present disclosure, a catalyst system may include a procatalyst and one or more activators. The term “activator” may include any combination of reagents that increases the rate at which a transition metal compound oligomerizes or polymerizes unsaturated monomers, such as olefins. An activator may also affect the molecular weight, degree of branching, comonomer content, or other properties of the oligomer or polymer. The transition metal compounds may be activated for oligomerization and/or polymerization catalysis in any manner sufficient to allow coordination or cationic oligomerization and or polymerization.

[0059] Alumoxane activators may be utilized as an activator for one or more of the catalyst compositions. Alumoxane(s) or aluminoxane(s) are generally oligomeric compounds containing $--Al(R)--O--$ subunits, where R is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is a halide. Mixtures of different alumoxanes and modified alumoxanes may also be used. For further descriptions, see U.S. Patent Nos. 4,665,208; 4,952,540; 5,041,584; 5,091,352; 5,206,199; 5,204,419; 4,874,734; 4,924,018; 4,908,463; 4,968,827; 5,329,032; 5,248,801; 5,235,081; 5,157,137; 5,103,031; and EP 0 561 476; EP 0 279 586; EP 0 516 476; EP 0 594 218; and WO 94/10180.

[0060] When the activator is an alumoxane (modified or unmodified), the maximum amount of activator may be selected to be a 5000-fold molar excess Al/M over the catalyst precursor (per metal catalytic site). Alternatively, or additionally the minimum amount of activator-to-catalyst-precursor may be set at a 1:1 molar ratio.

[0061] Aluminum alkyl or organoaluminum compounds that may be utilized as activators (or scavengers) include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

[0062] When the metal–ligand complex is rendered catalytically active by an activator, the metal of the metal–ligand complex may have a formal charge of positive one (+1). In embodiments in which the procatalyst includes the metal–ligand complex, the metal–ligand complex has a structure according to formula (I) and is overall charge neutral. In embodiments in which the catalyst system includes the metal–ligand complex, the metal–ligand complex may have a structure according to formula (Ia) and has an overall formal charge of positive one (+1):



[0063] In formula (Ia), A^- is an anion, and M, subscript n of $(X)_n$, each X, each Z, R^1 - R^{16} , R^{17-18} , and R^{23-24} are as described previously with regard to the metal–ligand complex of formula (I).

[0064] Formula (Ia) is an illustrative depiction of an active catalyst.

[0065] In embodiments, the metal–ligand complex, the activator, or both, may be disposed on one or more support materials. For example, the metal–ligand complex may be deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, one or more support materials. The metal–ligand complex may be combined with one or more support materials using one of the support methods well known in the art or as described below. As used in the present disclosure, the metal–ligand complex is in a supported form, for example, when deposited on, contacted with, or incorporated within, adsorbed or absorbed in, or on, one or more support materials.

[0066] Suitable support materials, such as inorganic oxides, include oxides of metals of Group 2, 3, 4, 5, 13 or 14 of the IUPAC periodic table. In embodiments, support materials include silica, which may or may not be dehydrated, fumed silica, alumina (*e.g.*, as described in International Patent Application No. 1999/060033), silica-alumina, and mixtures of these. The fumed silica may be hydrophilic (untreated), alternatively hydrophobic (treated). In embodiments, the support material is hydrophobic fumed silica, which may be prepared by treating an untreated fumed silica with a treating agent, such as dimethyldichlorosilane, a polydimethylsiloxane fluid, or hexamethyldisilazane. In some embodiments, support materials include magnesia, titania, zirconia, magnesium chloride (*e.g.*, as described in U.S. Patent No. 5,965,477), montmorillonite (*e.g.*, as described in European Patent No. 0 511 665), phyllosilicate, zeolites, talc, clays (*e.g.*, as described in U.S. Patent No. 6,034,187), and mixtures of these. In other embodiments, combinations of these support materials may be used, such as, for example, silica-chromium, silica-alumina, silica-titania, and combinations of these. Additional support materials may also include those porous acrylic polymers described in European Patent No. 0 767 184. Other support materials may also include nanocomposites described in International Patent Application No. 1999/047598; aerogels described in International Patent Application No. 1999/048605; spherulites described in U.S. Patent No. 5,972,510; and polymeric beads described in International Patent Application No. 1999/050311.

[0067] In embodiments, the support material has a surface area of from 10 square meters per gram (m^2/g) to 700 m^2/g , a pore volume of from 0.1 cubic meters per gram (cm^3/g) to 4.0 cm^3/g , and an average particle size of from 5 microns (μm) to 500 μm . In some embodiments, the support material has a surface area of from 50 m^2/g to 500 m^2/g , a pore volume of from 0.5 cm^3/g to 3.5 cm^3/g , and an average particle size of from 10 μm to 200 μm . In other embodiments, the support material may have a surface area of from 100 m^2/g to 400 m^2/g , a pore volume from 0.8 cm^3/g to 3.0 cm^3/g , and an average particle size of from 5 μm to 100 μm . The average pore size of the support material is typically from 10 Angstroms ($\text{\AA}$) to 1,000 $\text{\AA}$, such as from 50 $\text{\AA}$ to 500 $\text{\AA}$ or from 75 $\text{\AA}$ to 350 $\text{\AA}$.

[0068] There are various suitable methods to produce the catalyst systems of the present disclosure. In one or more embodiments, methods for producing the catalyst system include contacting one or more support materials, one or more activators, and a metal-ligand complex in an inert hydrocarbon solvent to produce the catalyst system. In some embodiments, the method for producing the catalyst system may include disposing the one or more activators on the one or more support materials to produce a supported activator, and contacting the supported activator

with a solution of the metal-ligand complex in an inert hydrocarbon solvent (often referred to as a “trim catalyst” or a “trim feed”). For example, in some embodiments, methods for producing the catalyst system include contacting a spray-dried supported activator (*i.e.*, a supported activator produced via spray drying) with a solution of the metal-ligand complex in an inert hydrocarbon solvent. In some embodiments, the supported activator may be included in a slurry, such as, for example a mineral oil slurry.

[0069] In some embodiments, the method for producing the catalyst system may include mixing one or more support materials, one or more activators, and a metal-ligand complex to produce a catalyst system precursor. The methods may further include drying the catalyst system precursor to produce the catalyst system. More specifically, the methods may include making a mixture of the metal-ligand complex, one or more support materials, one or more activators, or a combinations of these, and an inert hydrocarbon solvent. The inert hydrocarbon solvent may then be removed from the mixture so as to produce the metal-ligand complex, the one or more activators, or combinations of these, disposed on the one or more support materials. In embodiments, the removing step may be achieved via conventional evaporating of the inert hydrocarbon solvent from the mixture (*i.e.*, conventional concentrating method), which yields an evaporated/supported catalyst system. In other embodiments, the removing step may be achieved by spray-drying the mixture, which produces spray-dried particles. It should be understood that the drying and/or removing steps may not result in the complete removal of liquids from the resulting catalyst system. That is, the catalyst system may include residual amounts (*i.e.*, from 1 wt.% to 3 wt.%) of the inert hydrocarbon solvent.

[0070] As noted above, the catalyst systems of the present disclosure may be utilized in processes for producing polymers, such as polyethylene, via the polymerization of olefins, such as ethylene. In embodiments, one or more olefins may be contacted with the catalyst systems of the present disclosure in a gas-phase polymerization reactor, such as a gas-phase fluidized bed polymerization reactor. Exemplary gas-phase systems are described in U.S. Patent Nos. 5,665,818; 5,677,375; and 6,472,484; and European Patent Nos. 0 517 868 and 0 794 200. For example, in some embodiments, ethylene and, optionally, one or more (C₃–C₁₂) α -olefin comonomers may be contacted with the catalyst systems of the present disclosure in a gas-phase polymerization reactor. The catalyst system may be fed to the gas-phase polymerization reactor in neat form (*i.e.*, as a dry solid), as a solution, or as a slurry. For example, in some embodiments, spray-dried particles of the catalyst system may be fed directly to the gas-phase polymerization reactor. In other embodiments, a solution or slurry of the catalyst system in a solvent, such as an

inert hydrocarbon or mineral oil, may be fed to the reactor. For example, the procatalyst may be fed to the reactor in an inert hydrocarbon solution and the activator may be fed to the reactor in a mineral oil slurry.

[0071] In embodiments, the gas-phase polymerization reactor comprises a fluidized bed reactor. A fluidized bed reactor may include a “reaction zone” and a “velocity reduction zone.” The reaction zone may include a bed of growing polymer particles, formed polymer particles, and a minor amount of the catalyst system fluidized by the continuous flow of the gaseous monomer and diluent to remove heat of polymerization through the reaction zone. Optionally, some of the re-circulated gases may be cooled and compressed to form liquids that increase the heat removal capacity of the circulating gas stream when readmitted to the reaction zone. A suitable rate of gas flow may be readily determined by simple experiment. Make up of gaseous monomer to the circulating gas stream may be at a rate equal to the rate at which particulate polymer product and monomer associated therewith may be withdrawn from the reactor and the composition of the gas passing through the reactor may be adjusted to maintain an essentially steady state gaseous composition within the reaction zone. The gas leaving the reaction zone may be passed to the velocity reduction zone where entrained particles are removed. Finer entrained particles and dust may be removed in a cyclone and/or fine filter. The gas may be passed through a heat exchanger where the heat of polymerization may be removed, compressed in a compressor, and then returned to the reaction zone. Additional reactor details and means for operating the reactor are described in, for example, U.S. Patent Nos. 3,709,853; 4,003,712; 4,011,382; 4,302,566; 4,543,399; 4,882,400; 5,352,749; and 5,541,270; European Patent No. 0 802 202; and Belgian Patent No. 839,380.

[0072] In embodiments, the reactor temperature of the gas-phase polymerization reactor is from 30 °C to 150 °C. For example, the reactor temperature of the gas-phase polymerization reactor may be from 30 °C to 120 °C, from 30 °C to 110 °C, from 30 °C to 100 °C, from 30 °C to 90 °C, from 30 °C to 50 °C, from 30 °C to 40 °C, from 40 °C to 150 °C, from 40 °C to 120 °C, from 40 °C to 110 °C, from 40 °C to 100 °C, from 40 °C to 90 °C, from 40 °C to 50 °C, from 50 °C to 150 °C, from 50 °C to 120 °C, from 50 °C to 110 °C, from 50 °C to 100 °C, from 50 °C to 90 °C, from 90 °C to 150 °C, from 90 °C to 120 °C, from 90 °C to 110 °C, from 90 °C to 100 °C, from 100 °C to 150 °C, from 100 °C to 120 °C, from 100 °C to 110 °C, from 110 °C to 150 °C, from 110 °C to 120 °C, or from 120 °C to 150 °C. Generally, the gas-phase polymerization reactor may be operated at the highest temperature feasible, taking into account the sintering temperature of the polymer product within the reactor. Regardless of the process used to make the

polyethylene, the reactor temperature should be below the melting or “sintering” temperature of the polymer product. As a result, the upper temperature limit may be the melting temperature of the polymer product.

[0073] In embodiments, the reactor pressure of the gas-phase polymerization reactor is from 690 kPa (100 psig) to 3,448 kPa (500 psig). For example, the reactor pressure of the gas-phase polymerization reactor may be from 690 kPa (100 psig) to 2,759 kPa (400 psig), from 690 kPa (100 psig) to 2,414 kPa (350 psig), from 690 kPa (100 psig) to 1,724 kPa (250 psig), from 690 kPa (100 psig) to 1,379 kPa (200 psig), from 1,379 kPa (200 psig) to 3,448 kPa (500 psig), from 1,379 kPa (200 psig) to 2,759 kPa (400 psig), from 1,379 kPa (200 psig) to 2,414 kPa (350 psig), from 1,379 kPa (200 psig) to 1,724 kPa (250 psig), from 1,724 kPa (250 psig) to 3,448 kPa (500 psig), from 1,724 kPa (250 psig) to 2,759 kPa (400 psig), from 1,724 kPa (250 psig) to 2,414 kPa (350 psig), from 2,414 kPa (350 psig) to 3,448 kPa (500 psig), from 2,414 kPa (350 psig) to 2,759 kPa (400 psig), or from 2,759 kPa (400 psig) to 3,448 kPa (500 psig).

[0074] In embodiments, hydrogen gas may be used in during polymerization to control the final properties of the polyethylene. The amount of hydrogen in the polymerization may be expressed as a mole ratio relative to the total polymerizable monomer, such as, for example, ethylene or a blend of ethylene and 1-hexene. The amount of hydrogen used in the polymerization process may be an amount necessary to achieve the desired properties of the polyethylene, such as, for example, melt flow rate (MFR). In embodiments, the mole ratio of hydrogen to total polymerizable monomer (H_2 :monomer) is greater than 0.0001. For example, the mole ratio of hydrogen to total polymerizable monomer (H_2 :monomer) may be from 0.0001 to 10, from 0.0001 to 5, from 0.0001 to 3, from 0.0001 to 0.10, from 0.0001 to 0.001, from 0.0001 to 0.0005, from 0.0005 to 10, from 0.0005 to 5, from 0.0005 to 3, from 0.0005 to 0.10, from 0.0005 to 0.001, from 0.001 to 10, from 0.001 to 5, from 0.001 to 3, from 0.001 to 0.10, from 0.10 to 10, from 0.10 to 5, from 0.10 to 3, from 3 to 10, from 3 to 5, or from 5 to 10.

[0075] In embodiments, the catalyst systems of the present disclosure may be utilized to polymerize a single type of olefin, producing a homopolymer. However, additional α -olefins may be incorporated into the polymerization scheme in other embodiments. The additional α -olefin comonomers typically have no more than 20 carbon atoms. For example, the catalyst systems of the present disclosure may be utilized to polymerize ethylene and one or more (C_3 – C_{12}) α -olefin comonomers. Exemplary α -olefin comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. For example, the one or more α -olefin co-monomers may be selected from the group consisting

of propylene, 1-butene, 1-hexene, and 1-octene; or, in the alternative, from the group consisting of 1-hexene and 1-octene.

[0076] In embodiments, the one or more (C₃–C₁₂) α -olefin comonomers may not be derived from propylene. That is, the one or more (C₃–C₁₂) α -olefin comonomers may be substantially free of propylene. The term “substantially free” of a compound means the material or mixture includes less than 1.0 wt.% of the compound. For example, the one or more (C₃–C₁₂) α -olefin comonomers, which may be substantially free of propylene, may include less than 1.0 wt.% propylene, such as less than 0.8 wt.% propylene, less than 0.6 wt.% propylene, less than 0.4 wt.% propylene, or less than 0.2 wt.% propylene.

[0077] In embodiments, the polyethylene produced, for example homopolymers and/or interpolymers (including copolymers) of ethylene and, optionally, one or more comonomers may include at least 50 mole percent (mol.%) monomer units derived from ethylene. For example, the polyethylene may include at least 60 mol.%, at least 70 mol.%, at least 80 mol.%, or at least 90 mol.% monomer units derived from ethylene. In embodiments, the polyethylene includes from 50 mol.% to 100 mol.% monomer units derived from ethylene. For example, the polyethylene may include from 50 mol.% to 90 mol.%, from 50 mol.% to 80 mol.%, from 50 mol.% to 70 mol.%, from 50 mol.% to 60 mol.%, from 60 mol.% to 100 mol.%, from 60 mol.% to 90 mol.%, from 60 mol.% to 80 mol.%, from 60 mol.% to 70 mol.%, from 70 mol.% to 100 mol.%, from 70 mol.% to 90 mol.%, from 70 mol.% to 80 mol.%, from 80 mol.% to 100 mol.%, from 80 mol.% to 90 mol.%, or from 90 mol.% to 100 mol.% monomer units derived from ethylene.

[0078] In embodiments, the polyethylene produced includes at least 90 mol.% monomer units derived from ethylene. For example, the polyethylene may include at least 93 mol.%, at least 96 mol.%, at least 97 mol.%, or at least 99 mol.% monomer units derived from ethylene. In embodiments, the polyethylene includes from 90 mol.% to 100 mol.% monomer units derived from ethylene. For example, the polyethylene may include from 90 mol.% to 99.5 mol.%, from 90 mol.% to 99 mol.%, from 90 mol.% to 97 mol.%, from 90 mol.% to 96 mol.%, from 90 mol.% to 93 mol.%, from 93 mol.% to 100 mol.%, from 93 mol.% to 99.5 mol.%, from 93 mol.% to 99 mol.%, from 93 mol.% to 97 mol.%, from 93 mol.% to 96 mol.%, from 96 mol.% to 100 mol.%, from 96 mol.% to 99.5 mol.%, from 96 mol.% to 99 mol.%, from 96 mol.% to 97 mol.%, from 97 mol.% to 100 mol.%, from 97 mol.% to 99.5 mol.%, from 97 mol.% to 99 mol.%, from 99 mol.% to 100 mol.%, from 99 mol.% to 99.5 mol.%, or from 99.5 mol.% to 100 mol.% monomer units derived from ethylene.

[0079] In embodiments, the polyethylene produced includes less than 50 mol.% monomer units derived from an additional α -olefin. For example, the polyethylene may include less than 40 mol%, less than 30 mol.%, less than 20 mol.% or less than 10 mol.% monomer units derived from an additional α -olefin. In embodiments, the polyethylene includes from 0 mol.% to 50 mol.% monomer units derived from an additional α -olefin. For example, the polyethylene may include from 0 mol.% to 40 mol.%, from 0 mol.% to 30 mol.%, from 0 mol.% to 20 mol.%, from 0 mol.% to 10 mol.%, from 0 mol.% to 5 mol.%, from 0 mol.% to 1 mol.%, from 1 mol.% to 50 mol.%, from 1 mol.% to 40 mol.%, from 1 mol.% to 30 mol.%, from 1 mol.% to 20 mol.%, from 1 mol.% to 10 mol.%, from 1 mol.% to 5 mol.%, from 5 mol.% to 50 mol.%, from 5 mol.% to 40 mol.%, from 5 mol.% to 30 mol.%, from 5 mol.% to 20 mol.%, from 5 mol.% to 10 mol.%, from 10 mol.% to 50 mol.%, from 10 mol.% to 40 mol.%, from 10 mol.% to 30 mol.%, from 10 mol.% to 20 mol.%, from 20 mol.% to 50 mol.%, from 20 mol.% to 40 mol.%, from 20 mol.% to 30 mol.%, from 30 mol.% to 50 mol.%, from 30 mol.% to 40 mol.%, or from 40 mol.% to 50 mol.% monomer units derived from an additional α -olefin.

[0080] In embodiments, the polyethylene produced further includes one or more additives. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, pigments, primary antioxidants, secondary antioxidants, processing aids, ultraviolet (UV) stabilizers, and combinations of these. The polyethylene may include any amounts of additives. In embodiments, the produced polyethylene further includes fillers, which may include, but are not limited to, organic or inorganic fillers, such as, for example, calcium carbonate, talc, or $\text{Mg}(\text{OH})_2$.

[0081] The produced polyethylene may be used in a wide variety of products and end-use applications. The produced polyethylene may also be blended and/or co-extruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylene, elastomers, plastomers, high pressure low density polyethylene, high density polyethylene, polypropylenes, and the like. The produced polyethylene and blends including the produced polyethylene may be used to produce blow-molded components or products, among various other end uses. The produced polyethylene and blends including the produced polyethylene may be useful in forming operations such as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films may include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food

packaging, medical packaging, industrial liners, and membranes in food-contact and non-food contact applications. Fibers may include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, and geotextiles. Extruded articles may include medical tubing, wire and cable coatings, pipe, geomembranes, and pond liners. Molded articles may include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys.

TEST METHODS

Polymerization Activity

[0082] Unless indicated otherwise, all polymerization activities (also referred to as productivities) presently disclosed were determined as a ratio of polymer produced to the amount of catalyst added to the reactor and are reported in grams of polymer per grams of catalyst per hour (gPE/gcat/hr).

Comonomer Content

[0083] Unless indicated otherwise, all comonomer contents (*i.e.*, the amount of comonomer incorporated into a polymer) presently disclosed were determined by rapid FT-IR spectroscopy on dissolved polymer in a Gel Permeation Chromatography (GPC) measurement and are reported in weight percent (wt.%). The comonomer content of a polymer can be determined with respect to polymer molecular weight by use of an infrared detector, such as an IR5 detector, in a GPC measurement, as described in Lee et al., *Toward absolute chemical composition distribution measurement of polyolefins by high-temperature liquid chromatography hyphenated with infrared absorbance and light scattering detectors*, 86 ANAL. CHEM. 8649 (2014).

High Load Melt Index (I₂₁)

[0084] Unless indicated otherwise, all high load melt indices (I₂₁) disclosed herein were measured according to ASTM D1238-10, Method B, at 190 °C and a 21.6 kg load, and are reported in decigrams per minute (dg/min).

Melt Temperature (T_m)

[0085] Unless indicated otherwise, all melt temperatures (T_m) disclosed herein were measured according to ASTM D3418-08 and are reported in degrees Celsius (°C). Unless indicated otherwise, a scan rate of 10 degrees Celsius per minute (°C/min) on a 10 milligram (mg) sample was used, and the second heating cycle was used to determine the melt temperature (T_m).

Uptake Ratio

[0086] Unless indicated otherwise, all uptake ratios presently disclosed were determined as a ratio of an amount of monomer units derived from a comonomer (*e.g.*, a (C₃–C₁₂) α -olefin comonomer) to an amount of monomer units derived from ethylene.

Molecular Weight

[0087] Unless indicated otherwise, all molecular weights disclosed herein, including weight average molecular weight (M_w), number average molecular weight (M_n), and z-average molecular weight (M_z), were measured using conventional GPC and are reported in grams per mole (g/mol).

[0088] The chromatographic system consisted of a High Temperature Gel Permeation Chromatography (Polymer Laboratories), equipped with a differential refractive index detector (DRI). Three Polymer Laboratories PLgel 10 μ m Mixed-B columns were used. The nominal flow rate was 1.0 mL/min, and the nominal injection volume was 300 μ L. The various transfer lines, columns, and differential refractometer (the DRI detector) were contained in an oven maintained at 160°C. The solvent for the experiment was prepared by dissolving 6 grams of butylated hydroxytoluene as an antioxidant in 4 liters of Aldrich reagent-grade 1,2,4-trichlorobenzene (TCB). The TCB mixture was then filtered through a 0.1 μ m Teflon filter. The TCB was then degassed with an online degasser before entering the GPC instrument.

[0089] The polymer solutions were prepared by placing dry polymer in glass vials, adding the desired amount of TCB, then heating the mixture at 160 °C with continuous shaking for about 2 hours. All quantities were measured gravimetrically. The injection concentration was from 0.5 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. Prior to running each sample the DRI detector was purged. The flow rate in the apparatus was then increased to 1.0 ml/minute, and the DRI was allowed to stabilize for 8 hours before injecting the first sample. The molecular weight was determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards. The MW was calculated at each elution volume with following equation:

$$\log M_X = \frac{\log(K_X / K_{PS})}{a_X + 1} + \frac{a_{PS} + 1}{a_X + 1} \log M_{PS}$$

where the variables with subscript “X” stand for the test sample while those with subscript “PS” stand for PS. In this method, $a_{PS} = 0.67$ and $K_{PS} = 0.000175$, while a_X and K_X were obtained from published literature. Specifically, $a/K = 0.695/0.000579$ for PE and $0.705/0.0002288$ for PP.

[0090] The concentration, c , at each point in the chromatogram was calculated from the baseline-subtracted DRI signal, IDRI, using the following equation:

$$c = \frac{KDRI \times IDRI}{dn/dc}$$

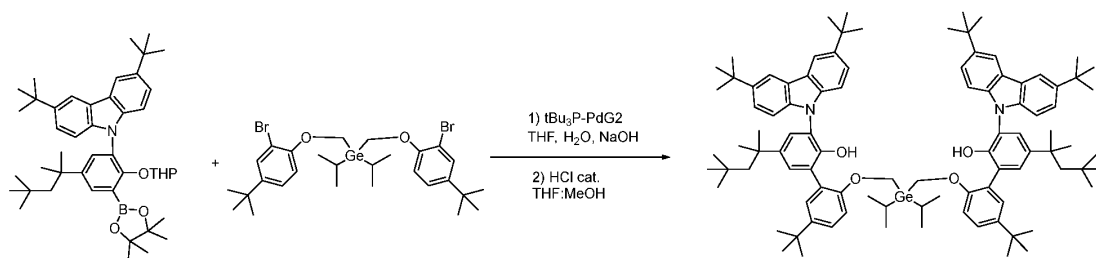
where KDRI is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. Specifically, $dn/dc = 0.109$ for polyethylene.

[0091] The mass recovery was calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume.

EXAMPLES

Synthesis of Metal-Ligand Complex 1 (MLC-1)

Synthesis of 2-[5-tert-butyl-2-[[[4-tert-butyl-2-[3-(3,6-ditert-butylcarbazol-9-yl)-2-hydroxy-5-(1,1,3,3-tetramethylbutyl)phenyl]phenoxy]methyl-diisopropyl-germyl]methoxy]phenyl]-6-(3,6-ditert-butylcarbazol-9-yl)-4-(1,1,3,3-tetramethylbutyl)phenol

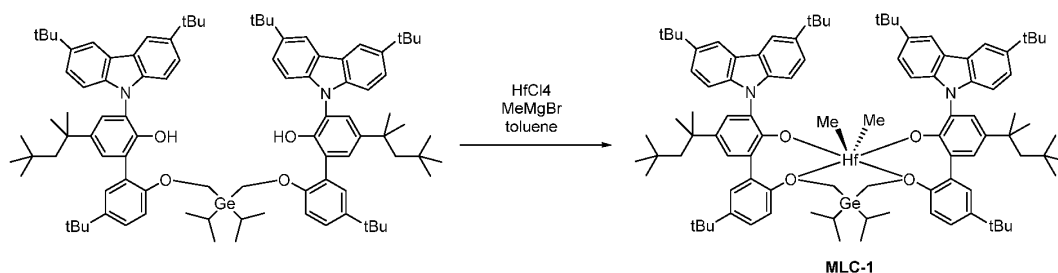


[0092] Degassed toluene (15 ml) and degassed water (5 mL) were added to a 40 mL vial charged with 3,6-di-tert-butyl-9-[2-tetrahydropyran-2-yloxy-5-(1,1,3,3-tetramethylbutyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]carbazole (4.14 g, 5.97 mmol), bis[(2-bromo-4-tert-butyl-phenoxy)methyl]-diisopropyl-germane (1.6 g, 2.49 mmol), $t\text{Bu}_3\text{P-PdG2}$ (0.05 g, 0.1 mmol), and NaOH (0.5 g, 12.4 mmol). The reaction was warmed to 50 °C and maintained at this temperature for 18 h. After this time, the reaction was cooled to room temperature. The mixture was transferred to a separatory funnel, Et_2O (20 mL) and H_2O (10 mL) were added, and the layers were separated. The aqueous phase was extracted with additional Et_2O (10 mL). The combined organics were washed with brine (10 mL), dried (Na_2SO_4), and filtered into a 100 mL roundbottom flask. The solvent was removed under reduced pressure. The crude residue was dissolved in MeOH/THF (1:1, 20 mL), concentrated HCl (5 drops from a glass pipet) was added,

a reflux condenser was fitted to the flask, then the solution was warmed to 70 °C while stirring. After 18 hours the solvent was removed under reduced pressure. The yellow oil was rotovapped from MeOH (3 x 3 mL), and a tan solid formed. MeOH (20 mL) was added to the solid, which was then collected by filtration. The solid was washed with MeOH (2 x 8 mL). Acetone (10 mL) was added to the solid in the filter funnel affording a heterogeneous solution. The heterogeneous mixture was stirred using a spatula, then the acetone was pulled through the filter using vacuum. Acetone (10 mL) was again added to the solid in the filter. The heterogeneous mixture was stirred using a spatula, then the acetone was pulled through the filter using vacuum. The material was dried under vacuum to provide 2.1 g (58%) desired product as a tan solid:

[0093] ^1H NMR (400 MHz, Chloroform- d) δ 8.22 (br s, 4H), 7.47 – 7.30 (m, 4H), 7.26 (d, J = 2.5 Hz, 2H), 7.22 (d, J = 2.4 Hz, 2H), 7.11 – 6.86 (m, 6H), 6.72 (br s, 2H), 5.78 – 5.19 (m, 4H), 3.80 – 3.44 (m, 4H), 1.66 (s, 4H), 1.45 (s, 36H), 1.30 (s, 12H), 1.24 – 1.11 (m, 20H), 0.87 (d, J = 7.4 Hz, 12H), 0.76 (s, 18H).

Synthesis of (MLC-1)



[0094] 3M MeMgBr in Et₂O (1.96 mL) was added to a -30 °C mixture of tetrachlorohafnium (0.46 g, 1.43 mmol) in toluene (30 mL). After stirring for 3 minutes the solid 2-[5-tert-butyl-2-[[[4-tert-butyl-2-[3-(3,6-ditert-butylcarbazol-9-yl)-2-hydroxy-5-(1,1,3,3-tetramethylbutyl)phenyl]phenoxy]methyl-diisopropyl-germyl]methoxy]phenyl]-6-(3,6-ditert-butylcarbazol-9-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (2.05 g, 1.42 mmol) was added.

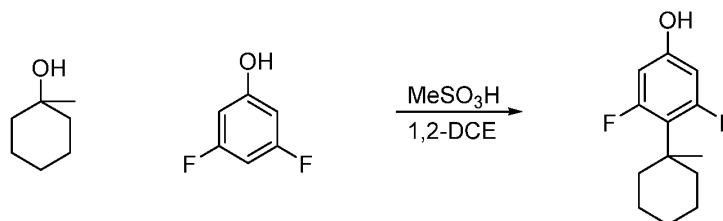
[0095] After 18 h additional 3M MeMgBr in Et₂O (200 μ L) was added, and the reaction was stirred for 1 hour. After this time the solvent was removed under reduced pressure to provide a dark solid.

[0096] Hexanes/toluene (2:1, 30 mL) was added to the jar, the solution was stirred for 5 minutes at room temperature, then this material was passed through a fritted funnel CELITE

plug. The frit was extracted with hexanes/toluene (2:1 15 mL). The combined organics were dried under vacuum to provide IMLC-1 (2.10 g, yield: 89 %) as an off-white solid:

[0097] ^1H NMR (400 MHz, Benzene- d_6) δ 8.71 (t, J = 1.3 Hz, 2H), 8.37 (dd, J = 2.0, 0.7 Hz, 2H), 7.70 – 7.62 (m, 6H), 7.53 (dd, J = 7.4, 2.5 Hz, 4H), 7.47 (dd, J = 8.7, 0.6 Hz, 2H), 7.30 (dd, J = 8.7, 1.9 Hz, 2H), 7.19 – 7.11 (m, 2H), 5.29 (d, J = 8.7 Hz, 2H), 4.52 (d, J = 12.2 Hz, 2H), 3.52 (d, J = 12.2 Hz, 2H), 1.81 (d, J = 14.5 Hz, 2H), 1.64 (d, J = 14.5 Hz, 2H), 1.58 (s, 18H), 1.42 (s, 6H), 1.36 (s, 6H), 1.30 (s, 18H), 1.22 (s, 18H), 0.93 (s, 18H), 0.74 – 0.61 (m, 8H), 0.59 (d, J = 6.6 Hz, 6H), -1.20 (s, 6H).

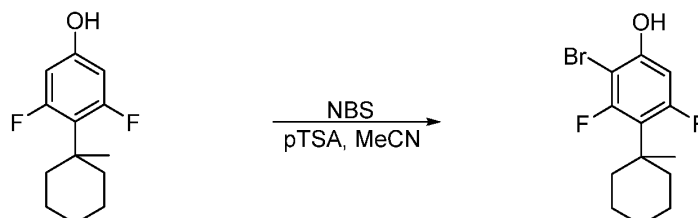
Synthesis of Metal-Ligand Complex 2 (MLC-2)



[0098] In a glovebox, a 40 mL vial equipped with a stir bar was charged with 3,5-difluorophenol (1.58 g, 12.2 mmol, 1.0 eq), concentrated MeSO_3H (0.79 mL, 12.2 mmol, 1.0 eq) and 1,2-dichloroethane (1.2 mL). The resulting mixture was stirred at ambient temperature until the 3,5-difluorophenol was fully dissolved and was then cooled in an ice-bath before 1-methylcyclohexanol (1.51 mL, 12.2 mmol, 1.0 eq) was added dropwise over 20 minutes. The resulting reaction mixture was stirred for 1 hour at 0 °C and for 16 hours at room temperature before being cooled back to 0 °C and adding additional 1-methylcyclohexanol (0.5 mL) over 5 minutes. After the resulting mixture was stirred at 0 °C for 10 minutes, the vial was removed from the cold bath and stirred at room temperature for 4 hours before being diluted with Et_2O (15 mL) and neutralized with aqueous 1N NaOH. The resulting mixture was then transferred to a separatory funnel, Et_2O was added (10 mL), the layers were separated, and the aqueous phase was further extracted with Et_2O (10 mL). The combined organics were washed with brine (10 mL), dried over Na_2SO_4 , filtered, and concentrated to dryness. Et_2O (10 mL) was added to the concentrate, then Celite® was added to the organic phase. The solvent was removed under reduced pressure and the resulting solid material was directly loaded onto a pre-column and purified using flash column chromatography (40 g SiO_2 , 40 mL/min, 0% EtOAc to 10% EtOAc /hexanes over 18 min), which produced 3,5-difluoro-4-(1-methylcyclohexyl)phenol (1.00 g, yield: 35%) as a white solid:

[0099] ^1H NMR (400 MHz, CDCl_3) δ 6.37 - 6.27 (m, 2H), 5.01 (s, 1H), 2.47 - 2.35 (m, 2H), 1.67 - 1.30 (m, 8H), 1.29 (s, 3H).

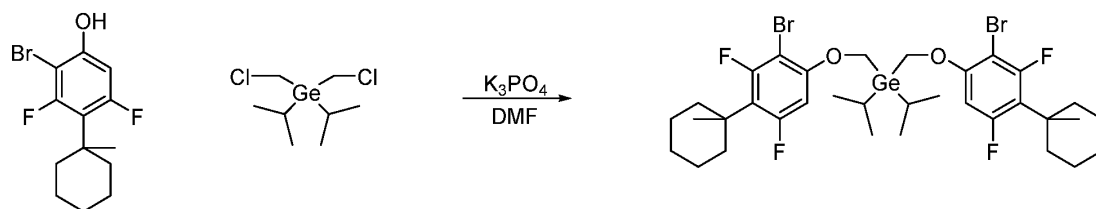
[0100] $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -104.67.



[0101] NBS (0.787 g, 4.42 mmol, 1.0 eq) was slowly added to a 0 °C solution of the 3,5-difluoro-4-(1-methylcyclohexyl)phenol (1.00 g, 4.42 mmol, 1.0 eq) and 4-methylbenzenesulfonic acid-hydrate (0.841 g, 4.42 mmol, 1.0 eq) in acetonitrile (10 mL). The resulting mixture was stirred for 3 days. The solvent was removed under reduced pressure, then the resulting residue was purified directly using flash chromatography (12 g load cartridge, 40 g SiO_2 , 40 mL/min, 0% ethyl acetate to 10% ethyl acetate/hexanes over 17 min), which produced 2-bromo-3,5-difluoro-4-(1-methylcyclohexyl)phenol (1.00 g, yield: 74%) as a slightly yellow oil:

[0102] ^1H NMR (400 MHz, CDCl_3) δ 6.57 (dd, J = 14.3, 2.3 Hz, 1H), 5.60 (d, J = 1.3 Hz, 1H), 2.42 (dt, J = 13.3, 3.4 Hz, 2H), 1.62 (ddt, J = 9.1, 6.2, 3.2 Hz, 2H), 1.55 - 1.26 (m, 9H).

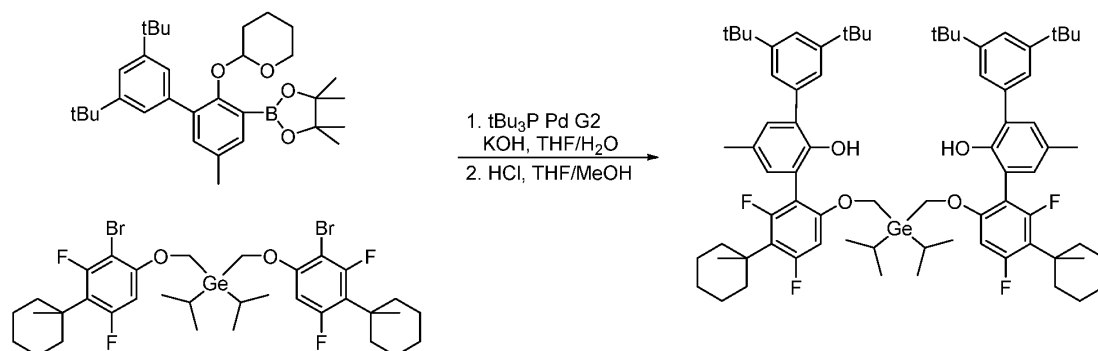
[0103] $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -97.78 (d, J = 6.2 Hz), -105.01 (d, J = 6.2 Hz).



[0104] In a glovebox, a 40 mL vial was charged with a germanium-containing bridge (described in International Publication No. WO 2018/183056 A1; 0.385 g, 1.50 mmol, 0.48 eq), phenol (0.95 g, 3.11 mmol, 1.0 eq), K_3PO_4 (1.98 g, 9.34 mmol, 3.0 eq), and DMF (3 mL). The resulting mixture was stirred at 80 °C overnight. After cooling down to room temperature, the reaction mixture was purified by column chromatography, which provided bis((2-bromo-3,5-difluoro-4-(1-methylcyclohexyl)phenoxy)methyl)diisopropylgermane (1.24 g, yield: 68%) as a colorless oil:

[0105] ^1H NMR (400 MHz, CDCl_3) δ 6.60 (dd, J = 15.1, 2.0 Hz, 2H), 4.12 (s, 4H), 2.43 (dd, J = 13.3, 6.0 Hz, 4H), 1.70 (p, J = 7.4 Hz, 2H), 1.60 (ddq, J = 12.7, 6.8, 3.1 Hz, 4H), 1.53 - 1.16 (m, 32H).

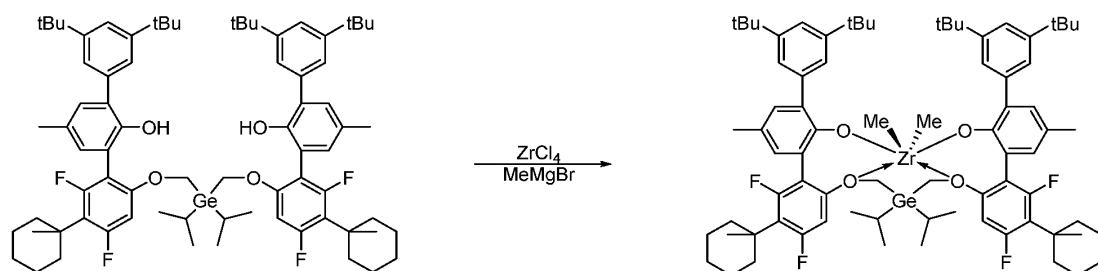
[0106] ^{19}F NMR (376 MHz, CDCl_3) δ -97.35 (d, J = 5.9 Hz, 2F), -104.75 (d, J = 6.4 Hz, 2F).



[0107] In a glove box, a 40 mL vial was charged with 2-(3',5'-di-tert-butyl-5-methyl-2-((tetrahydro-2H-pyran-2-yl)oxy)-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.256 g, 2.48 mmol, 3.0 eq), bis((2-bromo-3,5-difluoro-4-(1-methylcyclohexyl)phenoxy)methyl)diisopropylgermane (0.657 g, 0.83 mmol, 1.0 eq), tBu_3P Pd G2 (0.066 g, 0.08 mmol, 0.08 eq), toluene (4 mL), and KOH solution (4M, 0.83 mL, 3.30 mmol, 4.0 eq). The vial was heated under nitrogen at 80 °C overnight. When completed, the top organic layer was transferred to another 40 mL vial by rinsing the reaction vial with THF (5 mL). MeOH (10 mL) and concentrated HCl (1 mL) were then added. The resulting mixture was stirred at 85 °C for 2 hours. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel (rinsed with ether). Solvents were removed under reduced pressure and the residue was purified by reverse phase column chromatography, which provided a ligand (0.24 g, yield: 23%) as a white solid:

[0108] ^1H NMR (400 MHz, CDCl_3) δ 7.41 (q, J = 1.8 Hz, 2H), 7.31 – 7.28 (m, 4H), 7.12 – 7.08 (m, 2H), 6.90 – 6.86 (m, 2H), 6.50 – 6.41 (m, 2H), 5.06 (d, J = 6.3 Hz, 2H), 3.77 – 3.68 (m, 4H), 2.50 – 2.42 (m, 4H), 2.30 (s, 6H), 1.64 – 1.56 (m, 4H), 1.43 (s, 6H), 1.40 – 1.28 (m, 48H), 1.20 – 1.11 (m, 2H), 0.88 – 0.78 (m, 12H).

[0109] ^{19}F NMR (376 MHz, CDCl_3) δ -104.34 (dd, J = 18.1, 6.5 Hz, 2F), -105.19 (dd, J = 15.4, 6.3 Hz, 2F).

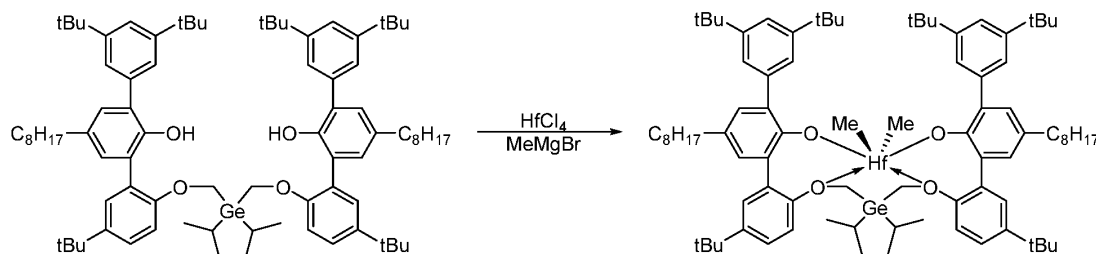


[0110] In a glovebox, MeMgBr in diethyl ether (3 M, 0.281 mL, 0.86 mmol, 4.3 eq) was added to a -30 °C suspension of ZrCl₄ (0.046 g, 0.2 mmol, 1.0 eq) in anhydrous toluene (6 mL). After stirring for 2 minutes, the solid ligand (0.24 g, 0.2 mmol, 1.0 eq) was added portionwise. The resulting mixture was stirred overnight before the solvent was removed under reduced pressure overnight to afford a dark residue, which was extracted with hexanes (12 mL) and filtered. Any remaining solids were then extracted with toluene (10 mL). The hexane extract was concentrated to approximately 2 mL and placed in a freezer for one day. Any remaining solvent was decanted and the remaining material (98 mg) was dried under vacuum, and combined with the toluene extract (dried under vacuum; 141 mg), which provided a metal-ligand complex (0.239 g, yield: 91%) as a white powder:

[0111] ¹H NMR (400 MHz, C₆D₆) δ 8.07 (br s, 2H), 7.82 (q, J = 1.5 Hz, 2H), 7.54 (br s, 2H), 7.28 – 7.19 (m, 4H), 5.37 (dd, J = 13.4, 1.7 Hz, 2H), 4.72 (d, J = 11.5 Hz, 2H), 3.65 (d, J = 11.5 Hz, 2H), 2.72 – 2.55 (m, 4H), 2.19 (s, 6H), 1.69 – 1.26 (m, 56H), 0.63 – 0.42 (m, 14H), 0.14 (s, 6H).

[0112] ¹⁹F{¹H} NMR (376 MHz, C₆D₆) δ -101.44 (d, J = 5.5 Hz, 2F), -104.43 (d, J = 5.7 Hz, 2F).

Synthesis of Metal-Ligand Complex 3 (MLC-3)

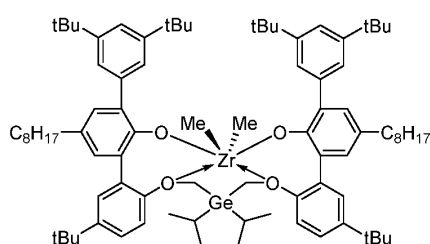


[0113] In a glovebox, MeMgBr (methylmagnesium bromide) in diethyl ether (3.0 M, 0.88 mmol, 4.4 eq) was added to a -30 °C suspension of HfCl₄ (64 mg, 0.2 mmol, 1.0 eq) in anhydrous toluene (6.0 mL). After stirring the resulting mixture for 2 minutes, the ligand (described in International Publication No. WO 2018/183056 A1; 0.254 g, 0.2 mmol, 1.0 eq) was added portionwise. The resulting mixture was stirred overnight before the solvent was removed under vacuum to afford a dark residue, which was extracted with hexanes (12 mL) followed by toluene (12 mL). The hexane extract was concentrated to approximately 3-4 mL and then kept in a freezer for one day before the top solution was decanted and the white solid was dried under vacuum yielding a white solid (150 mg). The toluene extract was dried under vacuum to afford a white

solid (60 mg). The hexane extract and the toluene extract were then combined, which provided a metal-ligand complex (210 mg, yield: 71%) as a white powder:

[0114] ^1H NMR (400 MHz, C_6D_6) δ 8.14 (br s, 2H), 7.80 (t, $J = 1.8$ Hz, 2H), 7.65 (br s, 2H), 7.58 (d, $J = 2.5$ Hz, 2H), 7.42 – 7.29 (m, 4H), 7.22 (dd, $J = 8.6, 2.5$ Hz, 2H), 5.71 (d, $J = 8.6$ Hz, 2H), 4.97 (d, $J = 11.8$ Hz, 2H), 3.78 (d, $J = 11.8$ Hz, 2H), 2.74 – 2.53 (m, 4H), 1.75 – 1.61 (m, 4H), 1.59 – 1.20 (m, 74H), 0.94 – 0.88 (m, 6H), 0.82 – 0.78 (m, 2H), 0.70 – 0.60 (m, 12H), -0.23 (s, 6H).

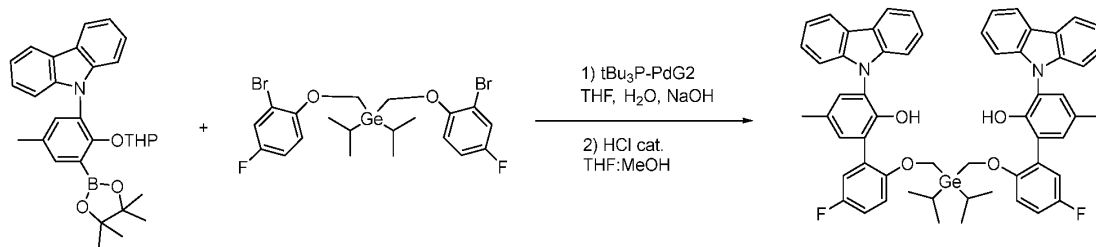
Synthesis of Metal-Ligand Complex 4 (MLC-4)



[0115] The metal-ligand complex was prepared in the manner described in International Publication No. WO 2018/183056 A1:

[0116] ^1H NMR (400 MHz, C_6D_6) δ 8.04 (br s, 2H), 7.76 (t, $J = 1.9$ Hz, 2H), 7.61 (br s, 2H), 7.43 (t, $J = 2.8$ Hz, 2H), 7.34 (d, $J = 2.4$ Hz, 2H), 7.08 (t, $J = 8.8$ Hz, 2H), 5.50 (dd, $J = 8.8, 1.1$ Hz, 2H), 4.75 (d, $J = 11.5$ Hz, 2H), 3.69 (d, $J = 11.4$ Hz, 2H), 2.69– 2.49 (m, 4H), 1.71– 1.60 (m, 4H), 1.58– 1.19 (m, 74H), 0.96– 0.87 (m, 6H), 0.73– 0.57 (m, 14H), -0.04 (s, 6H). ^{19}F { ^1H } NMR (376 MHz, C_6D_6) δ -108.63 (m, 2F).

Synthesis of Metal-Ligand Complex 5 (MLC-5)



[0117] Degassed THF (3 mL) and degassed water (1 mL) were added to a 40 mL vial charged with 9-[5-methyl-2-tetrahydropyran-2-yloxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]carbazole (as described in International Publication No. WO 2016/003879 A1; 0.72 g, 1.49 mmol), bis[(2-bromo-4-fluorophenoxy)methyl]-diisopropyl-germane (0.36 g, 0.64 mmol), $\text{tBu}_3\text{P-PdG2}$ (0.013 g, 0.03 mmol), and NaOH (0.13 g, 3.18 mmol). The resulting mixture was warmed to 50 °C and maintained at this temperature for 18 hours. After this time, the reaction was

cooled to room temperature. Et₂O (10 mL) and brine (3 mL) were added to the mixture. The resulting solution was shaken and, after the layers settled, the organic phase was removed using a pipet, and transferred to a 40 mL vial. MeOH (6 mL) was added followed by concentrated HCl (5 drops from a glass pipet). The resulting solution was stirred at room temperature for 3 hours before the solvent was removed under reduced pressure.

[0118] The resulting yellow oil was rotovapped from CH₃CN (3 x 3 mL), and a tan solid formed. CH₃CN (6 mL) was added to the solid, which was then collected by filtration. The solid was washed with CH₃CN (2 x 3 mL). The material was dissolved in Et₂O (4 mL) and passed through a plug of silica. The plug was washed with additional Et₂O (20 mL). The combined Et₂O was concentrated to dryness to provide 2-carbazol-9-yl-6-[2-[[[2-(3-carbazol-9-yl-2-hydroxy-5-methyl-phenyl)-4-fluoro-phenoxy]methyl-diisopropyl-germyl]methoxy]-5-fluoro-phenyl]-4-methyl-phenol (0.430 g, yield: 71%) as a white solid:

[0119] ¹H NMR (400 MHz, Chloroform-d) δ 8.20 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 4H), 7.34 (ddd, *J* = 8.1, 7.2, 1.4 Hz, 4H), 7.29 (td, *J* = 7.4, 1.2 Hz, 4H), 7.18 (d, *J* = 2.2 Hz, 2H), 7.14 – 7.10 (m, 4H), 7.04 (dd, *J* = 2.2, 0.7 Hz, 2H), 6.92 (dd, *J* = 8.8, 3.1 Hz, 2H), 6.50 – 6.36 (m, 2H), 5.95 – 5.81 (m, 2H), 5.49 (s, 2H), 3.60 (s, 4H), 2.31 (s, 6H), 1.13 (h, *J* = 7.3 Hz, 2H), 0.81 (d, *J* = 7.5 Hz, 12H).

[0120] ¹⁹F NMR (376 MHz, CDCl₃) δ -123.49.



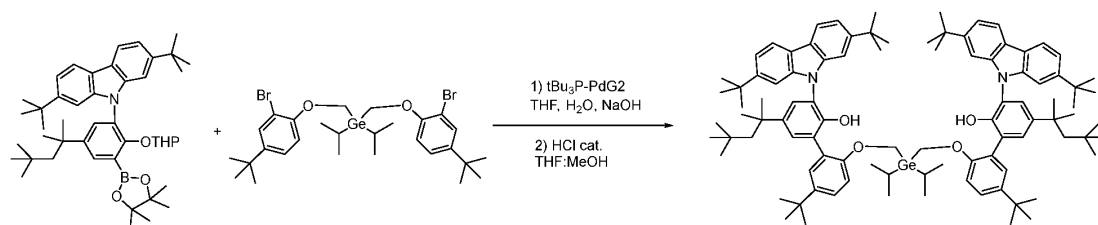
[0121] In a glovebox, MeMgBr in diethyl ether (3 M, 0.37 mL) was added to a -30 °C suspension of ZrCl₄ (0.06 g, 0.27 mmol) in anhydrous toluene (5 mL). After stirring the resulting mixture for 3 minutes, the 2-carbazol-9-yl-6-[2-[[[2-(3-carbazol-9-yl-2-hydroxy-5-methyl-phenyl)-4-fluoro-phenoxy]methyl-diisopropyl-germyl]methoxy]-5-fluoro-phenyl]-4-methyl-phenol (0.25 g, 0.26 mmol) was added as a solution in toluene/CH₂Cl₂ (2:1, 3 mL). The resulting mixture was stirred for four hours before the solvent was removed under vacuum to afford a dark residue. Hexanes (4 mL) was added to the dark residue, then this mixture was passed through a CELITE pad. The residue was washed with additional hexanes (4 mL). A new collection vial was

put on, and the residue was then extracted with toluene (3 x 8 mL). The combined toluene extracts were concentrated to dryness to provide a tan semi-solid. The solid was evaporated from pentane (3 x 2 mL) to provide a metal-ligand complex (0.150 g, yield: 53%) as a tan solid:

[0122] ^1H NMR (400 MHz, Benzene- d_6) δ 8.12 (dt, $J = 7.7, 0.9$ Hz, 2H), 8.03 (dt, $J = 7.7, 1.0$ Hz, 2H), 7.48 (dq, $J = 8.3, 1.0$ Hz, 4H), 7.36 (ddd, $J = 8.2, 7.1, 1.3$ Hz, 2H), 7.25 (ddd, $J = 8.4, 7.2, 1.2$ Hz, 4H), 7.20 – 7.11 (m, 2H), 7.03 (dd, $J = 2.4, 0.8$ Hz, 2H), 6.88 – 6.80 (m, 4H), 6.66 (ddd, $J = 9.0, 7.3, 3.2$ Hz, 2H), 4.91 (dd, $J = 9.0, 4.8$ Hz, 2H), 4.30 (d, $J = 12.1$ Hz, 2H), 3.26 (d, $J = 12.1$ Hz, 2H), 2.07 (s, 6H), 1.31 – 1.15 (m, 1H), 0.61 – 0.48 (m, 14H), -0.93 (s, 6H).

[0123] ^{19}F NMR (376 MHz, C_6D_6) δ -117.32.

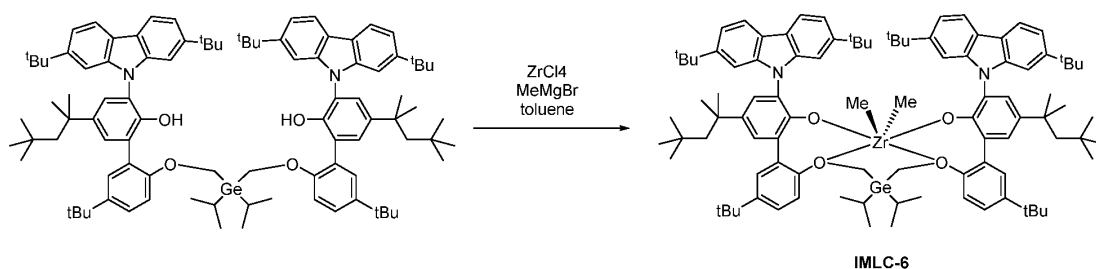
Synthesis of Metal-Ligand Complex 6 (MLC-6)



[0124] Degassed toluene (6 mL) and degassed water (3 mL) were added to a 40 mL vial charged with 2,7-di-tert-butyl-9-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]carbazole (1.62 g, 2.33 mmol), bis[(2-bromo-4-tert-butyl-phenoxy)methyl]-diisopropyl-germane (as described in International Publication No. WO 2018/183056 A1; 0.6 g, 0.93 mmol), $\text{tBu}_3\text{P-PdG2}$ (0.02 g, 0.04 mmol), and NaOH (0.19 g, 4.67 mmol). The resulting mixture was warmed to 75 °C and maintained at this temperature for 18 hours. After this time, the reaction was cooled to room temperature. The mixture was transferred to a separatory funnel, Et_2O (20 mL) and H_2O (10 mL) were added, and the layers were separated. The aqueous phase was extracted with additional Et_2O (10 mL). The combined organics were washed with brine (10 mL), dried (Na_2SO_4), and filtered into a 100 mL roundbottom flask. The solvent was removed under reduced pressure. The crude residue was dissolved in MeOH/THF (1:1, 20 mL), concentrated HCl (5 drops from a glass pipet) was added, a reflux condenser was fitted to the flask, then the solution was warmed to 70 °C while stirring. After 4 hours, the solvent was removed under reduced pressure. The yellow oil was rotovapped from CH_3CN (3x5 mL), and a tan solid formed. CH_3CN (15 mL) was added to the solid, which was then collected by filtration. The solid was washed with CH_3CN (2 x 4 mL). The solid was isolated and dried under vacuum to produce 6',6'''-(((diisopropylgermanediyl)bis(methylene))bis(oxy))bis(3'-(tert-butyl)-3-(2,7-di-tert-butyl-9H-

carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol) (0.7 g, yield: 52%) as a tan powder:

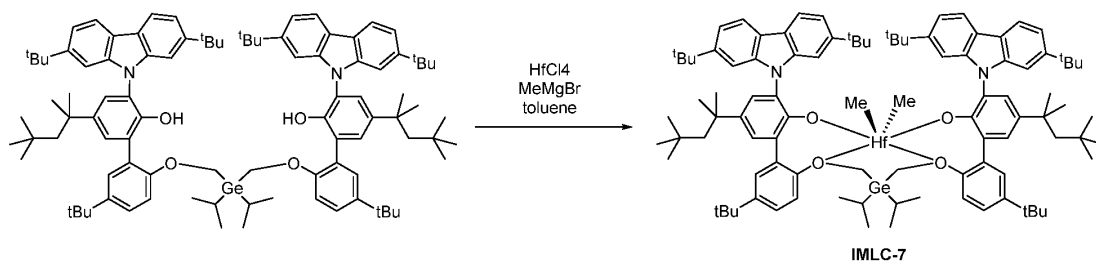
[0125] ^1H NMR (400 MHz, Chloroform- d) δ 8.05 (d, J = 8.2 Hz, 4H), 7.35 – 7.29 (m, 6H), 7.24 (d, J = 2.5 Hz, 2H), 7.21 – 7.10 (m, 6H), 6.71 (d, J = 8.6 Hz, 2H), 6.25 (d, J = 7.2 Hz, 2H), 5.35 (s, 2H), 3.78 (s, 4H), 1.67 (s, 4H), 1.33 (s, 12H), 1.30 (s, 36H), 1.23 – 1.12 (m, 20H), 0.79 (d, J = 7.4 Hz, 12H), 0.77 (s, 18H).



[0126] In a glovebox, MeMgBr in diethyl ether (3 M, 0.30 mL) was added to a $-30\text{ }^{\circ}\text{C}$ suspension of ZrCl_4 (0.05 g, 0.22 mmol) in anhydrous toluene (8 mL). After stirring the resulting mixture for 3 minutes, a $-30\text{ }^{\circ}\text{C}$ solution of the 6',6'''-(((diisopropylgermanediyl)bis(methylene))bis(oxy))bis(3'-(tert-butyl)-3-(2,7-di-tert-butyl-9H-carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol) (0.3 g, 0.21 mmol) in toluene (2 mL) was added. The resulting mixture was stirred for 2 hours before the solvent was removed under vacuum to afford a dark residue. Hexanes (10 mL) was added to the vial, the solution was shaken for a few minutes at room temperature, then this material was passed through a fritted funnel CELITE plug. The frit was extracted with hexanes (5 mL), the vial was replaced, and the CELITE plug was extracted with toluene (2 x 10 mL). The toluene was removed using vacuum to provide a metal-ligand complex (0.18 g, yield: 55%) as a tan powder:

[0127] ^1H NMR (400 MHz, Benzene- d_6) δ 8.40 (d, J = 8.2 Hz, 2H), 8.09 (dd, J = 8.2, 0.6 Hz, 2H), 7.75 (d, J = 1.6 Hz, 2H), 7.68 – 7.63 (m, 4H), 7.61 – 7.55 (m, 4H), 7.50 (d, J = 2.5 Hz, 2H), 7.29 (dd, J = 8.3, 1.7 Hz, 2H), 7.09 (dd, J = 8.7, 2.6 Hz, 2H), 5.19 (d, J = 8.6 Hz, 2H), 4.64 (d, J = 12.2 Hz, 2H), 3.67 (d, J = 12.2 Hz, 2H), 1.79 – 1.61 (m, 4H), 1.48 – 1.43 (m, 24H), 1.40 (s, 6H), 1.22 (s, 18H), 1.16 (s, 18H), 0.94 (s, 20H), 0.75 (d, J = 7.4 Hz, 6H), 0.64 (d, J = 7.5 Hz, 6H), -1.01 (s, 6H).

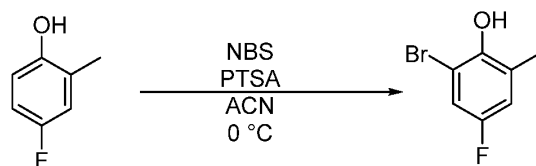
Synthesis of Metal-Ligand Complex 7 (MLC-7)



[0128] In a glovebox, MeMgBr in diethyl ether (3 M, 0.30 mL) was added to a $-30\text{ }^{\circ}\text{C}$ suspension of HfCl_4 (0.07 g, 0.21 mmol) in anhydrous toluene (8 mL). After stirring the resulting mixture for 3 minutes, a $-30\text{ }^{\circ}\text{C}$ solution of the 6',6'''-(((diisopropylgermanediyl)bis(methylene))bis(oxy))bis(3'-(tert-butyl)-3-(2,7-di-tert-butyl-9H-carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol) (0.3 g, 0.21 mmol) in toluene (2 mL) was added. The resulting mixture was stirred for 18 hours before the solvent was removed under vacuum to afford a dark residue. Hexanes (5 mL) was added to the vial, the solution was shaken for a few minutes at room temperature, then this material was passed through a fritted funnel CELITE plug. The frit was extracted with hexanes (3 mL), the vial was replaced, and the CELITE plug was extracted with toluene (2 x 10 mL). The toluene was removed using vacuum to provide a metal-ligand complex (0.14 g, yield: 41%) as a tan powder:

[0129] ^1H NMR (400 MHz, Benzene- d_6) δ 8.41 (d, $J = 8.4$ Hz, 2H), 8.10 (dd, $J = 8.2, 0.6$ Hz, 2H), 7.75 (d, $J = 1.6$ Hz, 2H), 7.66 (d, $J = 2.5$ Hz, 2H), 7.63 – 7.60 (m, 4H), 7.57 (dd, $J = 8.3, 1.7$ Hz, 2H), 7.49 (d, $J = 2.5$ Hz, 2H), 7.29 (dd, $J = 8.3, 1.7$ Hz, 2H), 7.10 (dd, $J = 8.2, 2.1$ Hz, 2H), 5.19 (d, $J = 8.7$ Hz, 2H), 4.74 (d, $J = 12.3$ Hz, 2H), 3.74 (d, $J = 12.4$ Hz, 2H), 1.78 – 1.60 (m, 4H), 1.47 – 1.44 (m, 24H), 1.40 (s, 6H), 1.21 (s, 18H), 1.15 (s, 18H), 0.93 (s, 20H), 0.75 (d, $J = 7.4$ Hz, 6H), 0.63 (d, $J = 7.5$ Hz, 6H), -1.23 (s, 6H).

Synthesis of Metal-Ligand Complex 8 (MLC-8)

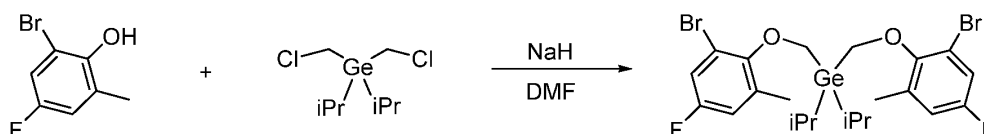


[0130] A 1L glass bottle was charged with acetonitrile (400 mL), 4-fluoro-6-methyl-phenol (50 g, 396.4 mmol), and *p*-toluenesulfonic acid (monohydrate; 75.6 g, 396 mmol), making sure everything was in solution. The solution was cooled to $0\text{ }^{\circ}\text{C}$ with ice for 25 min, providing a precipitate. The cooled solution was slowly treated with *N*-bromosuccinimide (70.55 g, 396.4 mmol) over the course of approximately 5 minutes, and was allowed to reach room temperature

while stirring overnight. The volatiles were removed under vacuum, and the resulting solid was treated with dichloromethane (600 mL), cooled in the freezer (0 °C), and filtered through a large plug of silica gel. The silica gel was washed several times with cold CH₂Cl₂. The volatiles were removed under vacuum to provide 2-bromo-4-fluoro-6-methyl-phenol (46 g, yield: 56%):

[0131] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.05 (ddd, *J* = 7.7, 3.0, 0.7 Hz, 1H), 6.83 (ddt, *J* = 8.7, 3.0, 0.8 Hz, 1H), 5.35 (s, 1H), 2.29 (d, *J* = 0.7 Hz, 3H).

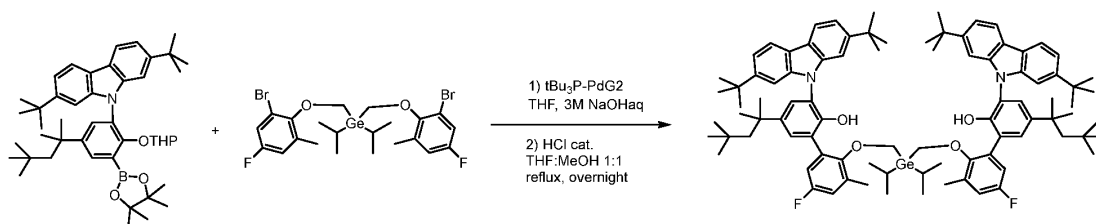
[0132] ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -122.84.



[0133] In a glovebox, in a 250 mL flask equipped with a magnetic stir bar, 95% NaH (1.76 g) (Caution H₂ is generated) was slowly added to a solution of 2-bromo-4-fluoro-6-methyl-phenol (15 g, 73.2 mmol) in *N,N*-dimethylformamide (DMF) (35 mL) until hydrogen evolution ceased. This mixture was stirred for 30 minutes at room temperature. After this time, the diisopropyl germyl dichloride (6.29 g, 24.4 mmol) was added. The mixture was warmed to 55 °C and held at this temperature for 18 hours. The reaction was removed from the glove box and quenched with saturated aqueous NH₄Cl (20 mL) and H₂O (8 mL). Et₂O (30 mL) was added and the phases were transferred to a separatory funnel and separated. The aqueous phase was further extracted with Et₂O (20 mL), and the combined organic extracts were washed with brine (10 mL). The organic layer was then dried (MgSO₄), filtered, and concentrated to dryness. The crude residue was dry loaded onto silica gel and then purified using flash column chromatography (100 mL/min, pure hexanes with ethyl acetate ramping to 10% over 20 minutes) to afford the product as a pale-yellow oil. All clean fractions (some fractions contained <10% of starting phenol) were combined, and the final product was dried under vacuum overnight, which provided bis((2-bromo-4-fluoro-6-methylphenoxy)methyl)diisopropylgermane (9 g, yield: 62%):

[0134] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.10 (dd, *J* = 7.7, 3.0 Hz, 2H), 6.84 (ddd, *J* = 8.8, 3.1, 0.8 Hz, 2H), 4.14 (s, 4H), 2.33 (s, 6H), 1.74 (hept, *J* = 7.4 Hz, 2H), 1.35 (d, *J* = 7.4 Hz, 12H).

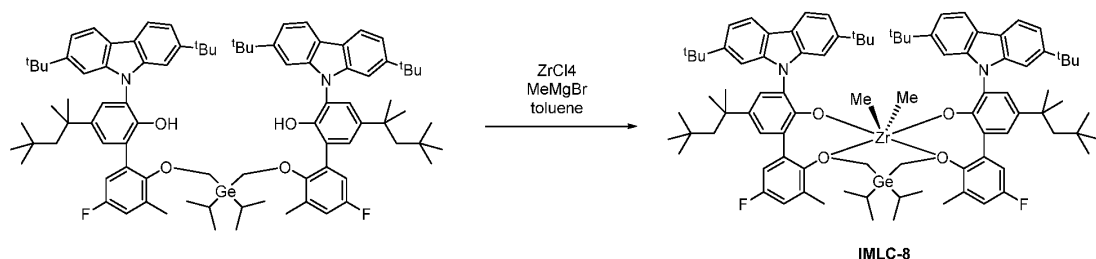
[0135] ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -118.03.



[0136] A 500 mL glass-bottle, equipped with a stir bar, was charged with 2,7-di-tert-butyl-9-(2-((tetrahydro-2H-pyran-2-yl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(2,4,4-trimethylpentan-2-yl)phenyl)-9H-carbazole (as described in International Publication No. WO 2014/105411 A1; 29.0 g, 41.9 mmol), bis((2-bromo-4-fluoro-6-methylphenoxy)methyl)diisopropylgermane (6.00 g, 8.65 mmol, contains 10% 2-bromo-4-fluoro-2-methyl-phenol), and THF (80 mL). The solution was heated to 55 °C and, while stirring, was treated with chloro[(tri-tert-butylphosphine)-2-(2-aminobiphenyl)] palladium (II) ($\text{tBu}_3\text{P-PdG2}$) (199 mg, 0.346 mmol, 4 mol%). An aqueous solution of NaOH (17.3 mL, 51.9 mmol, 3M) was purged with nitrogen for 20 min, and then added to the THF solution. The reaction was stirred overnight at 55 °C. The aqueous phase was separated and discarded, and the remaining organic phase was diluted with diethyl ether and washed with brine twice. The solution was passed through a short plug of silica gel. The filtrate was dried on a rotary evaporator, dissolved in THF/methanol (40 mL/40 mL), treated with HCl (2 mL), and stirred overnight at 70 °C. The solution was dried under vacuum, and purified by C18 reverse-phase column chromatography to provide a ligand (6.5 g, yield: 54%) as an off-white solid:

[0137] ^1H NMR (400 MHz, Chloroform- d) δ 8.01 (d, J = 8.2 Hz, 4H), 7.42 (dd, J = 25.5, 2.4 Hz, 4H), 7.32 (dd, J = 8.2, 1.6 Hz, 4H), 7.17 (s, 4H), 6.87 (ddd, J = 16.4, 8.8, 3.0 Hz, 4H), 6.18 (s, 2H), 3.79 (s, 4H), 2.12 (s, 6H), 1.71 (s, 6H), 1.56 (s, 4H), 1.38 (s, 12H), 1.31 (s, 36H), 0.83 – 0.73 (m, 30H).

[0138] ^{19}F NMR (376 MHz, Chloroform- d) δ -119.02.



[0139] In a glovebox, MeMgBr in diethyl ether (3 M, 2.4 mL, 7.1 mmol) was added to a -30 °C suspension of ZrCl_4 (402 mg, 1.72 mmol) in anhydrous toluene (83 mL). After stirring the

resulting mixture for 3 minutes, the ligand (2.3 g, 1.64 mmol) was added portion wise. The reaction was stirred overnight at room temperature, and then filtered through a fritted plastic funnel. The filtrate was dried under vacuum, re-dissolved in toluene (40 mL), filtered again through a plug of CELITE, and dried again under vacuum. The resulting solid was washed with pentane (approximately 5 mL) and dried under vacuum, which provided a metal-ligand complex (2.1 g, yield: 84%) as an off-white powder:

[0140] ^1H NMR (400 MHz, Benzene- d_6) δ 8.20 (dd, $J = 8.2, 0.5$ Hz, 2H), 8.11 (dd, $J = 8.2, 0.6$ Hz, 2H), 7.88 – 7.82 (m, 4H), 7.77 (d, $J = 2.6$ Hz, 2H), 7.50 (dd, $J = 8.3, 1.7$ Hz, 2H), 7.42 – 7.37 (m, 4H), 6.99 (dd, $J = 8.7, 3.1$ Hz, 2H), 6.20 – 6.10 (m, 2H), 4.29 (d, $J = 12.2$ Hz, 2H), 3.90 (d, $J = 12.2$ Hz, 2H), 1.56 (s, 4H), 1.53 (s, 18H), 1.29 (s, 24H), 1.27 (s, 6H), 1.18 (s, 6H), 1.04 – 0.94 (m, 2H), 0.81 (d, $J = 7.4$ Hz, 6H), 0.80 (s, 18H), 0.74 (d, $J = 7.4$ Hz, 6H), -0.47 (s, 6H).

[0141] ^{19}F NMR (376 MHz, Benzene- d_6) δ -116.24.

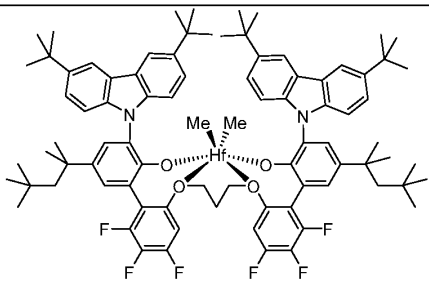
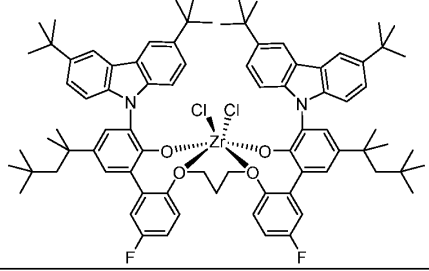
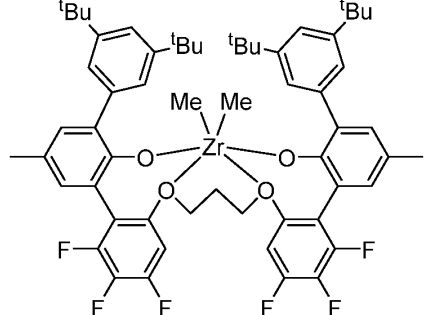
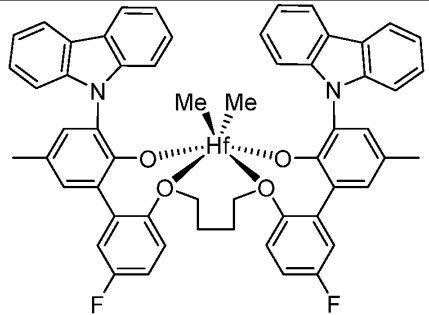
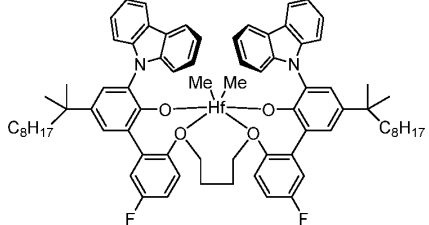
Production of Catalyst Systems

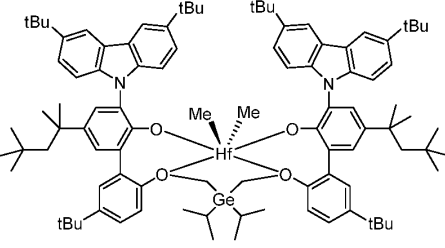
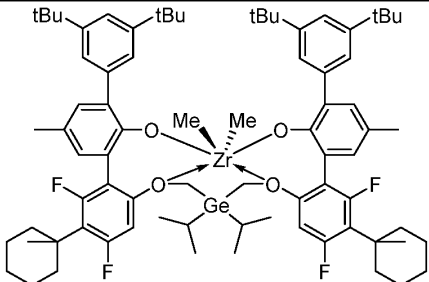
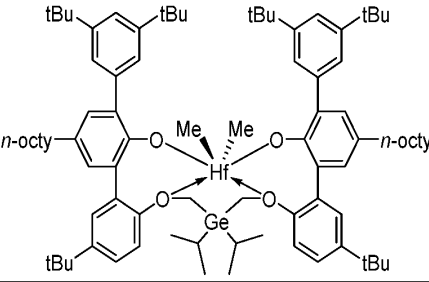
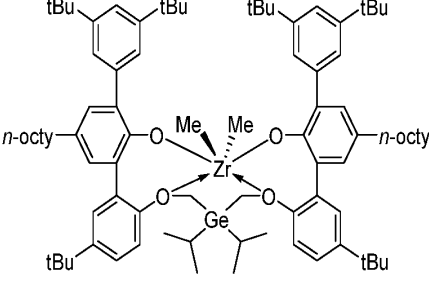
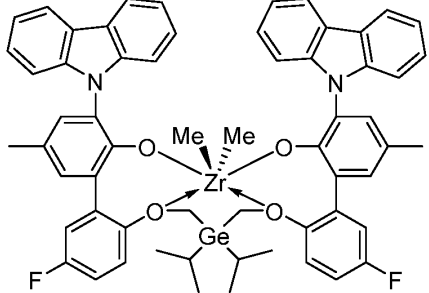
[0142] Various catalyst systems were produced via spray drying. Specifically, fumed silica (commercially available as CAB-O-SIL® from Cabot Corporation) and methylaluminoxane (10 wt.% in toluene) were dissolved in toluene and mixed for 15 minutes. A metal-ligand complex was added to the resulting slurry and mixed for an additional 30 to 60 minutes. The resulting catalyst system precursor was then dried using a spray dryer (commercially available as Mini Spray Dryer B-290 from BUCHI Corporation) with an inlet temperature of 185 °C, an outlet temperature of 100 °C, an aspirator speed of 95 rotations per minute (rpm), and a pump speed of 150 rpm.

[0143] The structures of the different metal-ligand complexes are reported in Table 1. The specific metal-ligand complex, as well as the amounts of each component, used to produce each catalyst system are reported in Table 2.

Table 1

Metal-Ligand Complex	Structure
CMLC-1	

CMLC-2	
CMLC-3	
CMLC-4	
CMLC-5	
CMLC-6	

MLC-1	 MLC-1
MLC-2	
MLC-3	
MLC-4	
MLC-5	

MLC-6	
MLC-7	
MLC-8	

Table 2

Catalyst System	Metal-Ligand Complex	Mass of Metal-Ligand Complex (g)	Mass of Fumed Silica (g)	Mass of MAO (g)	Mass of Toluene (g)
Comparative Sample 1	CMLC-1	0.161	1.325	11.00	37.5
Comparative Sample 2	CMLC-2	0.101	0.795	6.60	22.5
Comparative Sample 3	CMLC-3	0.186	1.590	13.20	45.0
Comparative Sample 4	CMLC-4	0.070	0.795	6.60	22.5
Comparative Sample 5	CMLC-5	0.070	1.325	11.00	37.5
Comparative Sample 6	CMLC-6	0.089	1.325	11.00	37.5
Sample 1	MLC-1	0.083	0.750	6.50	21.0
Sample 2	MLC-1	0.042	0.800	6.60	21.0
Sample 3	MLC-2	0.079	0.790	6.90	22.0
Sample 4	MLC-2	0.038	0.800	6.60	21.0
Sample 5	MLC-2	0.041	0.690	9.10	23.0
Sample 6	MLC-3	0.088	0.800	6.90	22.0
Sample 7	MLC-4	0.740	0.660	5.90	37.5
Sample 8	MLC-5	0.061	0.785	6.65	21.0
Sample 9	MLC-5	0.030	0.800	6.50	21.0
Sample 10	MLC-6	0.045	0.800	6.60	21.0
Sample 11	MLC-7	0.045	0.750	6.30	20.0
Sample 12	MLC-8	0.043	0.800	6.60	20.0
Sample 13	MLC-8	0.091	0.800	6.98	20.0
Sample 14	MLC-8	0.046	0.680	9.05	20.0

Production of Polyethylene

[0144] Various polyethylene samples were produced by contacting ethylene and 1-hexene with the catalyst systems reported in Table 2 in a gas-phase polymerization reactor. Specifically, a gas-phase polymerization reactor (*i.e.*, a 2-liter, stainless steel autoclave equipped with a mechanical agitator) was dried for 1 hour, charged with sodium chloride (200 grams), and dried again at 100 °C under nitrogen for 30 minutes. Supported methylaluminoxane (SMAO; 3 grams) was then introduced to the reactor under nitrogen pressure, the reactor was sealed, and the components were stirred. The reactor was then charged with hydrogen and 1-hexene pressurized with ethylene. Once steady state operation was achieved, a catalyst system was charged into the reactor at 80 °C to initiate polymerization. The reactor was then heated to a desired reaction temperature and maintained for a desired run time. After the run was complete, the reactor was cooled, vented, and opened. The resulting poly(ethylene-*co*-1-hexene) copolymer was collected, washed with water and methanol, and dried.

[0145] The reaction conditions used for each run are reported in Table 3. The reactor data for each run are reported in Table 4. The properties of the poly(ethylene-*co*-1-hexene) copolymer produced by each run are reported in Table 5.

Table 3

Condition	Temperature (°C)	C ₆ /C ₂ Ratio	H ₂ /C ₂ Ratio	C ₂ Partial Pressure (psi)	Run Time (hours)
1	90	0.016	0.0011	220	1
2	100	0.004	0.0068	230	1
3	90	0.003	0.0040	100	1

Table 4

Run	Catalyst System	Condition	Catalyst Charge (mg)	Yield (g)	Productivity (gPE/gcat/hr)	Uptake Ratio
1	Comparative Sample 1	1	20.3	38.59	1,901	0.352
2	Comparative Sample 2	1	101.3	0.00	0	0.322
3	Comparative Sample 3	1	10.7	69.60	6,504	0.234
4	Sample 1	1	3.4	226.20	66,528	0.178
5	Sample 2	1	3.2	108.00	33,749	0.272
6	Comparative Sample 4	1	100.3	65.07	649	0.444
7	Sample 3	1	6.3	37.80	6,000	0.382
8	Sample 4	1 ^a	6.0	11.60	1,933	0.339
9	Sample 5	1	6.8	16.19	2,381	0.344
10	Sample 6	1	3.3	157.60	47,757	0.115
11	Sample 7	1	10.5	131.20	12,495	0.163

12	Comparative Sample 5	1	10.1	30.60	3,030	0.299
13	Comparative Sample 6	1	10.6	35.40	3,339	0.275
14	Sample 8	1	3.5	224.59	64,170	0.172
15	Sample 9	1	3.2	98.20	30,687	0.243
16	Sample 10	1	3.2	120.60	37,687	0.104
17	Sample 11	1	3.1	124.60	40,192	0.189
18	Comparative Sample 1	2	10.5	25.60	2,438	0.097
19	Comparative Sample 2	2	100.3	1.40	14	0.063
20	Comparative Sample 3	2	11.4	69.00	6,052	0.042
21	Sample 1	2	3.2	250.39	130,414	0.044
22	Sample 2	2	3.3	216.00	77,922	0.046
23	Comparative Sample 4	2	101.4	36.79	363	0.116
24	Sample 3	2	6.6	184.39	27,938	0.055
25	Sample 4	2	6.1	105.59	17,310	0.078
26	Sample 5	2	6.4	133.60	20,875	0.069
27	Sample 6	2	3.0	125.39	41,798	0.024
28	Sample 7	2	9.9	239.20	24,161	-
29	Comparative Sample 5	2	10.0	18.80	1,880	0.049
30	Comparative Sample 6	2	10.7	34.60	3,233	0.062
31	Sample 8	2	3.4	127.80	37,588	0.049
32	Sample 9	2	3.3	115.60	35,030	0.050
33	Sample 10	2	3.3	265.40	182,781	0.018
34	Sample 11	2	3.4	231.40	68,058	0.030
35	Sample 12	2	0.9	255.39	283,771	0.002
36	Sample 13	2	1.5	127.20	84,798	0.002
37	Sample 14	2	1.7	141.40	83,173	0.003

^a Temperature: 90 °C, H₂/C₂ Ratio: 0.05, C₂ Partial Pressure: 220 psi

Table 5

Polymer	Run	Number Average Molecular Weight (Mn) (g/mol)	Weight Average Molecular Weight (Mw) (g/mol)	Z-Average Molecular Weight (Mz) (g/mol)	Molecular Weight Distribution (Mw/Mn)	C6 (wt.%; corrected)
1	1	240,753	547,803	1,072,132	2.28	33.69
2	2	-	-	-	-	-
3	3	34,855	298,450	6,430,772	8.56	23.97
4	4	930,512	3,224,405	5,799,490	3.47	22.98
5	5	1,179,181	3,018,247	5,173,552	2.56	29.42
6	6	-	-	-	-	-

7	7	553,434	1,540,663	3,231,380	2.78	36.64
8	8	522,730	1,416,028	2,899,172	2.71	37.44
9	9	492,307	1,377,471	2,812,961	2.80	38.08
10	10	1,597,149	3,898,075	5,912,058	2.44	13.18
11	11	192,418	349,504	574,185	1.82	16.56
12	12	443,250	1,422,312	3,611,631	3.21	28.05
13	13	406,942	1,262,083	2,917,624	3.10	28.27
14	14	115,134	338,639	1,746,880	2.94	22.16
15	15	126,682	335,590	1,102,257	2.65	32.48
16	16	127,239	336,781	1,150,180	2.65	12.41
17	17	374,867	1,160,036	2,527,365	3.09	20.67
18	18	296,915	694,880	1,294,183	2.34	10.72
19	19	-	-	-	-	-
20	20	42,586	524,854	2,935,115	12.32	5.70
21	21	787,035	2,376,573	4,530,925	3.02	6.45
22	22	846,156	2,197,426	4,222,654	2.60	7.91
23	23	-	-	-	-	-
24	24	326,941	781,694	1,615,079	2.39	8.83
25	25	307,420	729,725	1,503,284	2.37	10.15
26	26	305,427	724,332	1,475,912	2.37	9.61
27	27	1,593,447	3,627,487	5,593,940	2.28	6.07
28	28	229,722	417,325	680,751	1.82	5.17
29	29	362,138	1,242,309	3,044,292	3.43	6.67
30	30	360,676	1,094,521	2,638,737	3.03	8.44
31	31	126,510	337,170	1,061,156	2.67	7.09
32	32	362,138	1,242,309	3,044,292	3.43	6.67
33	33	108,549	297,826	807,091	2.74	3.39
34	34	305,707	1,013,894	2,377,207	3.32	5.53
35	35	-	-	-	-	-
36	36	-	-	-	-	-
37	37	-	-	-	-	-

[0146] As indicated by Table 4, catalyst systems including a metal-ligand complex having a germanium-containing bridge provide a higher productivity than catalyst systems including metal-ligand complexes having carbon bridges (*i.e.*, bridges that contain only carbon connecting atoms). Put more simply, the catalyst systems of the present disclosure provide a greater productivity than comparative catalyst systems. This increase in productivity was unexpected because corresponding changes in the bridge structure generally do not improve productivity or efficiency in unsupported catalyst systems that include such metal-ligand complexes (which are typically used in solution-phase polymerization processes).

[0147] The effect of the bridge of the metal-ligand complex on the catalyst system is more clearly indicated when comparing runs conducted under similar conditions and using catalyst

systems including metal-ligand complexes having similar “top groups” (*i.e.*, R¹ and R¹⁶ of formula (I)). For example, Runs 1-5 were each conducted under Condition 1 and used catalyst systems including metal-ligand complexes having 3,6-*t*Bu₂-carbazolyl as both top groups. However, Run 4, which used Sample 1, produced more than 60,000 grams more of polymer per gram of catalyst system compared to Runs 1 and 3, which used Comparative Samples 1 and 3, and Run 2 did not produce polymer at all. An even greater increase in productivity can be seen when comparing Runs 18-22, which used the same catalyst systems as Runs 1-5, but were conducted under Condition 2. Similar increases in productivity provided by a metal-ligand complex having a germanium-containing bridge are indicated by comparing Runs 6-11 and 23-28, which used catalyst systems including metal-ligand complexes having *t*Bu₂-phenyl as both top groups, Runs 12-15 and 29-32, which used catalyst systems including metal-ligand complexes having unsubstituted carbazolyl as both top groups.

[0148] Additional polyethylene samples were produced by contacting ethylene and 1-hexene with the catalyst systems reported in Table 2 in a gas-phase polymerization reactor in a manner consistent with that described previously. The reaction conditions and reactor data for each run are reported in Table 6. The properties of the poly(ethylene-*co*-1-hexene) copolymer produced by each run are reported in Table 7.

Table 6

Run	Catalyst System	Temp (°C)	C ₆ /C ₂ Ratio	H ₂ /C ₂ Ratio	C ₂ Partial Pressure (psi)	Catalyst Charge (mg)	Yield (g)	Productivity (gPE/gcat/hr)	Efficiency (gPE/gM)
38	Sample 4	90	0.003	0.500	100	10.8	16.40	1,518	0.416
39	Sample 4	90	0.003	0.100	100	10.4	58.40	5,615	1.539
40	Sample 4	90	0.003	0.050	100	10.5	99.79	9,504	2.605
41	Sample 4	90	0.003	0.010	100	10.8	163.79	15,166	4.156
42	Sample 4	90	0.003	0.007	100	10.9	200.40	18,385	5.039
43	Sample 4	90	0.003	0.004	100	10.9	143.40	18,529	3.606
44	Sample 4	90	0.003	0.002	100	6.0	102.40	17,066	4.677
45	Sample 4	90	0.003	-	100	10.4	218.39	13,207	5.755
46	Comparative Sample 1	90	0.003	0.500	100	50.2	13.19	263	0.032
47	Comparative Sample 1	90	0.003	0.100	100	49.9	18.39	369	0.045
48	Comparative Sample 1	90	0.003	0.050	100	49.7	17.20	346	0.042

49	Comparative Sample 1	90	0.003	0.010	100	51.2	72.60	1,418	0.173
50	Comparative Sample 1	90	0.003	0.007	100	50.4	46.79	928	0.113
51	Comparative Sample 1	90	0.003	0.004	100	50.6	54.40	1,075	0.131
52	Comparative Sample 1	90	0.003	0.002	100	50.5	51.80	1,026	0.125
53	Comparative Sample 1	90	0.003	-	100	20.4	36.20	1,774	0.217

Table 7

Polymer	Run	Number Average Molecular Weight (Mn) (g/mol)	Weight Average Molecular Weight (Mw) (g/mol)	Z-Average Molecular Weight (Mz) (g/mol)	Molecular Weight Distribution (Mw/Mn)	C6 (wt.%; corrected)	Tm (°C)
38	38	25,557	57,890	116,393	2.27	3.92	130.970
39	39	103,752	204,941	371,016	1.98	3.70	125.100
40	40	170,535	335,123	599,335	1.97	3.57	120.640
41	41	602,989	1,510,715	4,737,696	2.51	3.41	120.330
42	42	720,921	2,002,291	7,133,634	2.78	3.29	120.620
43	43	1,060,048	1,868,861	3,031,907	1.76	2.49	120.170
44	44	2,483,135	6,622,652	17,924,947	2.67	2.30	129.370
45	45	-	-	-	-	-	-
46	46	9,676	42,051	641,460	4.35	10.43	125.730
47	47	42,137	110,911	504,815	2.63	9.07	122.730
48	48	66,535	198,224	2,406,089	2.98	10.60	119.120
49	49	193,861	600,213	3,878,324	3.10	5.43	124.620
50	50	266,499	742,976	3,812,580	2.79	7.57	123.210
51	51	-	-	-	-	-	122.300
52	52	-	-	-	-	-	118.052
53	53	-	-	-	-	-	-

[0149] As indicated by Table 6, catalyst systems including a metal-ligand complex having a germanium-containing bridge provide a higher productivity than catalyst systems including metal-ligand complexes having carbon bridges under the same and/or similar conditions and relatively low ethylene partial pressure. For example, runs that used Sample 4 provided a greater productivity than runs that used Comparative Sample 1 when under the same reaction conditions. The increased productivity is important for use in dual reactor applications with relatively low ethylene partial pressures in the first reactor, which are utilized to increase the lifetime of catalysts systems to produce polymer in two reactors.

[0150] Additional polyethylene samples were produced by contacting ethylene with the catalyst systems reported in Table 2 in a gas-phase polymerization reactor in a manner consistent

with that described previously, with the exception of the inclusion of 1-hexene. The reaction conditions and reactor data for each run are reported in Table 8. The properties of the poly(ethylene-*co*-1-hexene) copolymer produced by each run are reported in Table 9.

Table 8

Run	Catalyst System	Temperature (°C)	H ₂ /C ₂ Ratio	C ₂ Partial Pressure (psi)	Catalyst Charge (mg)	Yield (g)	Productivity (gPE/gcat/hr)	Efficiency (gPE/gM)
54	Sample 4	90	0.018	230	5.3	244.59	46,150	12.60
55	Sample 4	90	0.010	230	5.2	254.39	48,922	13.40
56	Sample 4	90	0.007	230	5.0	223.59	44,718	12.30
57	Sample 4	90	0.004	230	5.1	251.20	49,254	13.50
58	Sample 4	90	0.010	165	5.8	174.00	29,999	8.20
59	Sample 4	90	0.010	100	5.1	78.91	15,472	4.20
60	Sample 4	105	0.010	230	4.8	101.19	21,081	5.80
61	Sample 4	80	0.010	230	5.0	245.78	49,157	13.50
62	Sample 4	80	0.010	230	1.9	111.57	58,723	16.10
63	Comparative Sample 1	100	0.050	230	20.3	146.60	7,222	0.88
64	Comparative Sample 1	100	0.100	230	10.2	131.80	12,922	1.58
65	Comparative Sample 1	100	0.500	230	9.9	90.00	9,091	1.11
66	Comparative Sample 1	100	1.000	230	10.4	66.39	6,383	0.78
67	Comparative Sample 1	100	0.050	230	9.7	48.40	4,990	0.61
68	Comparative Sample 1	100	0.100	230	10.2	39.17	3,840	0.47
69	Comparative Sample 1	100	0.500	230	10.0	21.20	2,119	0.26
70	Comparative Sample 1	100	1.000	230	10.1	16.92	1,675	0.20

Table 9

Polymer	Run	Number Average Molecular Weight (Mn) (g/mol)	Weight Average Molecular Weight (Mw) (g/mol)	Z-Average Molecular Weight (Mz) (g/mol)	Molecular Weight Distribution (Mw/Mn)	Molecular Weight Distribution (Mz/Mw)	T _m (°C)
54	54	294,577	721,512	1,917,434	2.45	2.66	143.30
55	55	475,106	1,193,394	2,943,059	2.51	2.47	-
56	56	655,118	1,509,293	3,682,816	2.30	2.44	-
57	57	1,070,457	2,438,370	5,462,562	2.28	2.24	-
58	58	487,073	1,222,617	3,061,832	2.51	2.50	-
59	59	485,973	1,360,793	3,472,563	2.80	2.55	-
60	60	478,576	1,208,172	2,850,833	2.52	2.36	-

61	61	402,555	1,136,576	3,153,277	2.82	2.77	-
62	62	680,336	1,432,085	3,071,158	2.10	2.14	-
63	63	483,431	1,742,038	3,831,521	3.60	2.20	134.21
64	64	593,252	1,635,019	3,600,097	2.76	2.20	133.86
65	65	276,569	835,806	2,399,047	3.02	2.87	136.65
66	66	196,004	655,099	2,646,403	3.34	4.04	137.17
67	67	61,726	262,804	2,341,962	4.26	8.91	138.03
68	68	32,427	175,067	1,811,919	5.40	10.35	139.69
69	69	7,765	49,055	401,747	6.32	8.19	134.68
70	70	4,074	24,395	234,260	5.99	9.60	-

[0151] Additional polyethylene samples were produced by contacting ethylene and 1-hexene with the catalyst systems reported in Table 2 in a gas-phase polymerization reactor in a manner consistent with that described previously. The reaction conditions and reactor data for each run are reported in Table 10.

Table 10

Run	Catalyst System	Temperature (°C)	C ₆ /C ₂ Ratio	H ₂ /C ₂ Ratio	C ₂ Partial Pressure (psi)	Catalyst Charge (mg)	Yield (g)	Productivity (gPE/gcat/hr)	Efficiency (gPE/gM)	Melt Index (I ₂₁) (dg/min)
71	Sample 4	90	0.004	0.0500	200	9.9	239.20	24,161	6.62	0.21
72	Sample 4	93	0.016	0.0500	200	10.5	131.20	12,495	3.42	0.32
73	Comparative Sample 4	90	0.016	0.0011	220	101.4	36.79	363	0.08	0.02
74	Comparative Sample 4	100	0.004	0.0068	230	100.3	65.07	649	0.15	0.85

[0152] In Table 10, Runs 71-74 were each conducted under similar conditions; however, Runs 71 and 72 used Sample 4, and Runs 73 and 74 used Comparative Sample 4. The primary difference between the metal-ligand complexes of Sample 4 and Comparative Sample 4 are the bridges. Specifically, the metal-ligand complex of Comparative Sample 4 has a $-\text{CH}_3\text{CH}_3\text{CH}_3-$ bridge and the metal-ligand complex of Sample 4 has a $-\text{CH}_2\text{Ge}(\text{iPr})_2\text{CH}_2-$ bridge. However, as a result of this difference, Runs 71 and 72 had productivities at least nineteen times greater than the productivities of Runs 73 and 74, and efficiencies at least twenty-two times greater than the efficiencies of Runs 73 and 74. That is, given similar conditions, catalyst systems that include a metal-ligand complex having a germanium-containing bridge may result in polymerization

processes that are significantly more productive and efficient than those that utilize catalyst systems that include a similar metal-ligand complex having a carbon bridge.

[0153] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 g/cm³” is intended to mean “about 40 g/cm³.”

[0154] Notations used in the equations included herein refer to their standard meaning as understood in the field of mathematics. For example, “=” means equal to, “×” denotes the multiplication operation, “+” denotes the addition operation, “-” denotes the subtraction operation, “>” is a “greater than” sign, “<” is a “less than” sign, “and “/” denotes the division operation.

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