

HYDROCARBYL-MODIFIED METHYLALUMINOXANE COCATALYSTS FOR BIS-PHENYLPHENOXY METAL-LIGAND COMPLEXES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 63/053,342, filed on July 17, 2020, the entire disclosure of which is hereby incorporated by reference.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to hydrocarbyl-modified methylaluminoxane activators for catalysts systems including bis-phenylphenoxy metal-ligand complexes.

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 it is rising due to increasing market demand. This success is based in part on a series of important breakthroughs in co-catalyst technology. The co-catalysts discovered include aluminoxanes, boranes, and borates with triphenylcarbenium or ammonium cations. These co-catalysts activate the homogeneous single-site olefin polymerization procatalysts, and polyolefins have been produced using these co-catalysts in industry.

[0004] As part of the catalyst composition in α -olefin polymerization reactions, the activator may have characteristics that are beneficial for the production of the α -olefin polymer and for final polymer compositions including the α -olefin polymer. Activator characteristics that increase the production of α -olefin polymers include, but are not limited to: rapid procatalyst activation, high catalyst efficiency, high temperature capability, consistent polymer composition, and selective deactivation.

[0005] Borate based co-catalysts in particular have contributed significantly to the fundamental understanding of olefin polymerization mechanisms, and have enhanced the ability for precise control over polyolefin microstructures by deliberately tuning catalyst structures and

processes. This results in stimulated interest in mechanistic studies and lead to the development of novel homogeneous olefin polymerization catalyst systems that have precise control over polyolefin microstructures and performance. However, once the cations of the activator or co-catalyst activate the procatalyst, the counter ion of the activator may remain in the polymer composition. As a result, the borate anions may affect the polymer composition. In particular, the size of the borate anion, the charge of the borate anion, the interaction of the borate anion with the surrounding medium, and the dissociation energy of the borate anion with available counterions will affect the ion's ability to diffuse through a surrounding medium such as a solvent, a gel, or a polymer material.

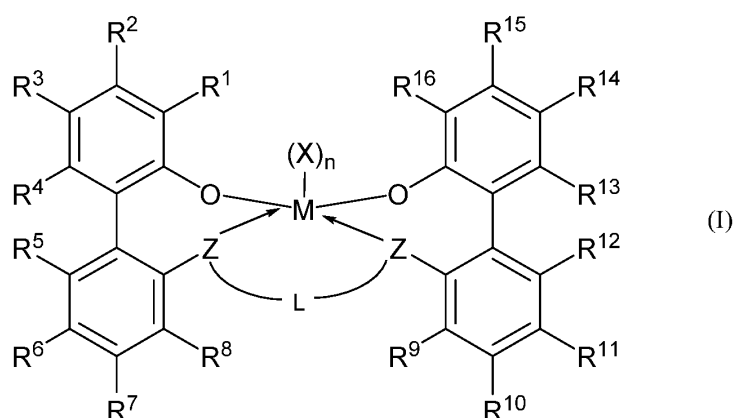
[0006] Modified methylaluminoxanes (MMAOs) can be described as a mixture of aluminoxane structures and trihydrocarbylaluminum species. Trihydrocarbylaluminum species, like trimethylaluminum are used as scavengers to remove impurities in the polymerization process which may contribute to the deactivation of the olefin polymerization catalyst. However, it is believed that trihydrocarbylaluminum species may be active in some polymerization systems. Catalyst inhibition has been noted when trimethylaluminum is present in propylene homopolymerizations with hafnocene catalysts at 60 °C (Busico, V. et. al. *Macromolecules* **2009**, *42*, 1789-1791). However, these observations convolute differences in MAO-activation versus borate activation, and even in direct comparison only possibly capture differences between some trimethylaluminum and none. Additionally, it is unclear that such observations extend to other catalysts systems, to ethylene polymerization, or to polymerizations conducted at higher temperatures. Regardless, the preference for soluble MAOs necessitates the use of MMAO and hence the presence of trihydrocarbylaluminum species.

[0007] Modified methylaluminoxanes (MMAO) are used as activators in some PE processes in place of borate based activators. However, MMAO has been found to have negative impact on the performance of some catalysts, such as some bis-phenylphenoxy procatalysts, and have negatively impacted the production of polymer resins. The negative impact on the polymerization process includes decreasing catalyst activity, broadening composition distribution of the produced polymer, and negatively affecting the pellet handling.

SUMMARY

[0008] There is an ongoing need to create a catalyst system while maintaining catalyst efficiency, reactivity, and the ability to produce polymers with good physical properties.

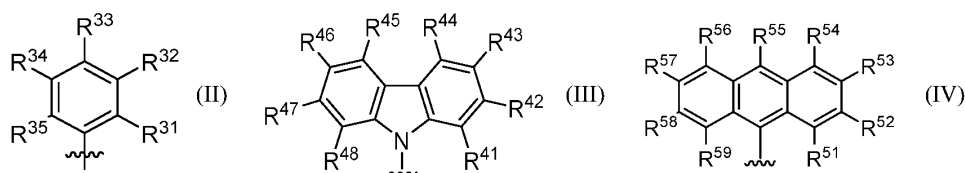
[0009] Embodiments of this disclosure includes processes of polymerizing olefin monomers. In one or more embodiments, the process includes reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system. The catalyst system includes hydrocarbyl-modified methylaluminoxane and a metal-ligand complex. The hydrocarbyl-modified methylaluminoxane having less than 25 mole percent trihydrocarbyl aluminum compound $\text{AlR}^{\text{A}}\text{R}^{\text{B}}\text{R}^{\text{C}}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A} , R^{B} , and R^{C} are independently $(\text{C}_1\text{--C}_{40})$ alkyl; and one or more metal-ligand complexes according to formula (I):



[0010] In formula (I), M is titanium, zirconium, hafnium, yttrium, or an element of the lanthanide series of the periodic table having a formal oxidation state of +2, +3, or +4. Subscript n of $(\text{X})_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(\text{C}_2\text{--C}_{50})$ hydrocarbon, unsaturated $(\text{C}_2\text{--C}_{50})$ heterohydrocarbon, saturated $(\text{C}_2\text{--C}_{50})$ heterohydrocarbon, $(\text{C}_1\text{--C}_{50})$ hydrocarbyl, $(\text{C}_6\text{--C}_{50})$ aryl, $(\text{C}_6\text{--C}_{50})$ heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(\text{C}_4\text{--C}_{12})$ diene, halogen, $-\text{N}(\text{R}^{\text{N}})_2$, and $-\text{N}(\text{R}^{\text{N}})\text{COR}^{\text{C}}$. The metal-ligand complex is overall charge-neutral. Each Z is independently chosen from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^{\text{N}})-$, or $-\text{P}(\text{R}^{\text{P}})-$. L is $(\text{C}_1\text{--C}_{40})$ hydrocarbylene or $(\text{C}_2\text{--C}_{40})$ heterohydrocarbylene.

[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 selected from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen.

[0012] In formula (I), R^1 and R^{16} are independently selected from the group consisting of $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N=C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0013] In formulas (II), (III), and (IV), each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, or halogen.

[0014] In formulas (I), (II), (III), and (IV), each R^C , R^P , and R^N is independently a (C_1-C_{30}) hydrocarbyl, (C_1-C_{30}) heterohydrocarbyl, or $-H$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a chart of the catalyst efficiency of bis-phenylphenoxy 4 (BPP-4) and BPP-11 as a function of MMAO.

[0016] FIG. 2 is a chart of the catalyst efficiency of BPP-2 and BPP-4 as a function of MMAO.

[0017] FIG. 3 is a chart of the catalyst efficiency of BPP-1 to BPP-6 and BPP-12 as a function of MMAO.

[0018] FIG. 4 is a chart of the catalyst efficiency of BPP-9 and BPP-10 as a function of MMAO.

DETAILED DESCRIPTION

[0019] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0020] Common abbreviations are listed below:

[0021] **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** : *n*-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.

[0022] The term “independently selected” is used herein to indicate that the R groups, such as, R¹, R², R³, R⁴, and R⁵, can be identical or different (e.g., R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc). 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. Thus, 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” refers to a transition metal compound that has olefin polymerization catalytic activity when combined with an activator. The term “activator” refers to a compound that chemically reacts with a procatalyst in a manner that converts the procatalyst to a catalytically active catalyst. As used herein, the terms “co-catalyst” and “activator” are interchangeable terms.

[0024] 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. Thus, in general 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.

[0025] 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. “Hydrogen” and “–H” are interchangeable, and unless clearly specified have identical meanings.

[0026] The term “(C₁–C₅₀)alkyl” means a saturated straight or branched hydrocarbon radical containing from 1 to 50 carbon atoms; and the term “(C₁–C₃₀)alkyl” means a saturated straight or branched hydrocarbon radical of from 1 to 30 carbon atoms. Each (C₁–C₅₀)alkyl and (C₁–C₃₀)alkyl may be unsubstituted or substituted by one or more R^S. In some examples, 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–C₄₀)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.

[0027] The term (C₃–C₅₀)alkenyl means a branched or unbranched, cyclic or acyclic monovalent hydrocarbon radical containing from 3 to 50 carbon atoms, at least one double bond

and is unsubstituted or substituted by one or more R^S . Examples of unsubstituted (C_3 – C_{50})alkenyl: n-propenyl, isopropenyl, n-butenyl, isobutenyl, octenyl, decenyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, and cyclohexadienyl. Examples of substituted (C_3 – C_{50})alkenyl: (2-trifluoromethyl)pent-1-enyl, (3-methyl)hex-1-enyl, (3-methyl)hexa-1,4-dienyl and (Z)-1-(6-methylhept-3-en-1-yl)cyclohex-1-enyl.

[0028] The term “(C_3 – C_{50})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 (C_3 – C_{40})cycloalkyl are unsubstituted (C_3 – C_{20})cycloalkyl, unsubstituted (C_3 – C_{10})cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C_3 – C_{40})cycloalkyl are substituted (C_3 – C_{20})cycloalkyl, substituted (C_3 – C_{10})cycloalkyl, and 1-fluorocyclohexyl.

[0029] The term “halogen atom” or “halogen” means the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means anionic form of the halogen atom: fluoride (F^-), chloride (Cl^-), bromide (Br^-), or iodide (I^-).

[0030] The term “saturated” means lacking carbon–carbon double bonds, carbon–carbon triple bonds, and (in heteroatom-containing groups) carbon–nitrogen, carbon–phosphorous, and carbon–silicon double bonds. Where a saturated chemical group is substituted by one or more substituents R^S , one or more double or triple bonds optionally may be present in substituents R^S . The term “unsaturated” means containing one or more carbon–carbon double bonds or carbon–carbon triple bonds, or (in heteroatom-containing groups) one or more carbon–nitrogen double bonds, carbon–phosphorous double bonds, or carbon–silicon double bonds, not including double bonds that may be present in substituents R^S , if any, or in aromatic rings or heteroaromatic rings, if any.

[0031] The term “hydrocarbyl-modified methylaluminoxane” refers to a methylaluminoxane (MMAO) structure comprising an amount of trihydrocarbyl aluminum. The hydrocarbyl-modified methylaluminoxane includes a combination of a hydrocarbyl-modified methylaluminoxane matrix and trihydrocarbylaluminum. A total molar amount of aluminum in the hydrocarbyl-modified methylaluminoxane is composed of the aluminum contribution from the

moles of aluminum from the hydrocarbyl-modified methylaluminoxane matrix and moles of aluminum from the trihydrocarbyl aluminum. The hydrocarbyl-modified methylaluminoxane includes greater than 2.5 mole percent of trihydrocarbylaluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. These additional hydrocarbyl substituents can impact the subsequent aluminosilane structure and result in differences in the distribution and size of aluminosilane clusters (Bryliakov, K. P et. al. *Macromol. Chem. Phys.* **2006**, 207, 327-335). The additional hydrocarbyl substituents can also impart increased solubility of the aluminosilane in hydrocarbon solvents such as, but not limited to, hexane, heptane, methylcyclohexane, and ISOPAR E™ as demonstrated in US5777143. Modified methylaluminoxane compositions are generically disclosed and can be prepared as described in US5066631 and US5728855, both of which are incorporated herein by reference.

[0032] Embodiments of this disclosure includes processes of polymerizing olefin monomers. In one or more embodiments, the process includes reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system.

[0033] In some embodiments, the olefin monomer is (C₃–C₂₀) α -olefin. In other embodiments, the olefin monomer is not (C₃–C₂₀) α -olefin. In various embodiments, the olefin monomer is cyclic olefin.

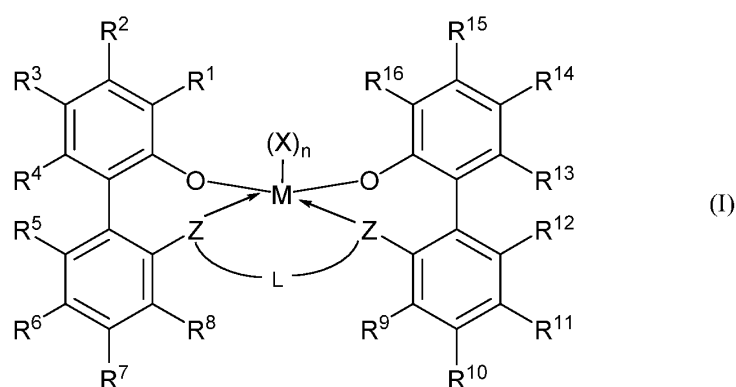
[0034] In one or more embodiments, the catalyst system includes hydrocarbyl-modified methylaluminoxane and a metal–ligand complex. The hydrocarbyl-modified methylaluminoxane having less than 25 mole percent trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. The trihydrocarbyl aluminum has a formula of AlR^{A1}R^{B1}R^{C1}, where R^{A1}, R^{B1}, and R^{C1} are independently (C₁–C₄₀)alkyl.

[0035] In embodiments, the hydrocarbyl-modified methylaluminoxane in the polymerization process has less than 20 mole percent and greater than 5 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. In some embodiments, the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. In one or more embodiments, the hydrocarbyl-modified methylaluminoxane has less than 10 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum

in the hydrocarbyl-modified methylaluminoxane. In various embodiments, the hydrocarbyl-modified methylaluminoxane is modified methylaluminoxane.

[0036] In some embodiments, the trihydrocarbyl aluminum has a formula of $\text{AlR}^{\text{A1}}\text{R}^{\text{B1}}\text{R}^{\text{C1}}$, where R^{A1} , R^{B1} , and R^{C1} are independently $(\text{C}_1\text{--C}_{10})$ alkyl. In one or more embodiments, R^{A1} , R^{B1} , and R^{C1} are independently methyl, ethyl, propyl, 2-propyl, butyl, *tert*-butyl, or octyl. In some embodiment, R^{A1} , R^{B1} , and R^{C1} are the same. In other embodiments, at least one of R^{A1} , R^{B1} , and R^{C1} is different from the other R^{A1} , R^{B1} , and R^{C1} .

[0037] In embodiments, the catalyst system includes hydrocarbyl-modified methylaluminoxane and a metal–ligand complex. In some embodiments, the catalyst system includes one or more metal–ligand complexes according to formula (I):

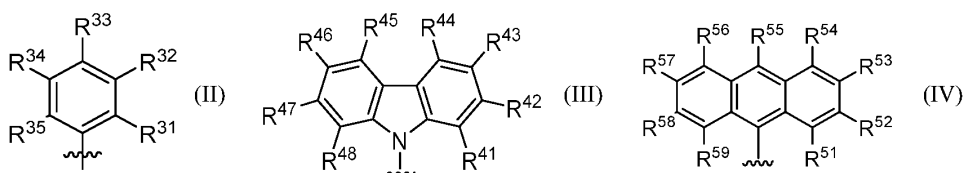


[0038] In formula (I), M is titanium, zirconium, hafnium, scandium, yttrium, or an element of the lanthanide series of the periodic table having a formal oxidation state of +2, +3, or +4. In some embodiments, M is Zr or Sc.

[0039] Subscript n of $(\text{X})_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(\text{C}_2\text{--C}_{50})$ hydrocarbon, unsaturated $(\text{C}_2\text{--C}_{50})$ heterohydrocarbon, saturated $(\text{C}_2\text{--C}_{50})$ heterohydrocarbon, $(\text{C}_1\text{--C}_{50})$ hydrocarbyl, $(\text{C}_6\text{--C}_{50})$ aryl, $(\text{C}_6\text{--C}_{50})$ heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(\text{C}_4\text{--C}_{12})$ diene, halogen, $-\text{N}(\text{R}^{\text{N}})_2$, and $-\text{N}(\text{R}^{\text{N}})\text{COR}^{\text{C}}$. The metal–ligand complex is overall charge-neutral. Each Z is independently chosen from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^{\text{N}})-$, or $-\text{P}(\text{R}^{\text{P}})-$. L is $(\text{C}_1\text{--C}_{40})$ hydrocarbylene or $(\text{C}_2\text{--C}_{40})$ heterohydrocarbylene.

[0040] 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 selected from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^C\text{S}(\text{O})-$, $\text{R}^C\text{S}(\text{O})_2-$, $(\text{R}^C)_2\text{C}=\text{N}-$, $\text{R}^C\text{C}(\text{O})\text{O}-$, $\text{R}^C\text{OC}(\text{O})-$, $\text{R}^C\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^C)_2\text{NC}(\text{O})-$, and halogen.

[0041] In formula (I), R^1 and R^{16} are independently selected from the group consisting of $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^C\text{S}(\text{O})-$, $\text{R}^C\text{S}(\text{O})_2-$, $-\text{N}=\text{C}(\text{R}^C)_2$, $\text{R}^C\text{C}(\text{O})\text{O}-$, $\text{R}^C\text{OC}(\text{O})-$, $\text{R}^C\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^C)_2\text{NC}(\text{O})-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0042] When present in the metal–ligand complex of formula (I) as part of a radical having formula (II), formula (III), or formula (IV), the groups R^{31-35} , R^{41-48} , and R^{51-59} of the metal–ligand complex of formula (I) are each independently chosen from (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^C\text{S}(\text{O})-$, $\text{R}^C\text{S}(\text{O})_2-$, $(\text{R}^C)_2\text{C}=\text{N}-$, $\text{R}^C\text{C}(\text{O})\text{O}-$, $\text{R}^C\text{OC}(\text{O})-$, $\text{R}^C\text{C}(\text{O})\text{N}(\text{R}^N)-$, $(\text{R}^N)_2\text{NC}(\text{O})-$, halogen, hydrogen ($-H$), or combinations thereof. Independently each R^C , R^P , and R^N are unsubstituted (C_1-C_{18}) hydrocarbyl, (C_1-C_{30}) heterohydrocarbyl, or $-H$.

[0043] In formulas (I), (II), (III), and (IV), each R^C , R^P , and R^N is independently a (C_1-C_{30}) hydrocarbyl, (C_1-C_{30}) heterohydrocarbyl, or $-H$.

[0044] In one or more embodiments, the metal–ligand complex of formula (I) is a procatalyst.

[0045] In some embodiments, the groups R^1 and R^{16} in the metal–ligand complex of formula (I) are chosen independently of one another. For example, R^1 may be chosen from a radical having formula (II), (III), or (IV) and R^{16} may be a (C_1-C_{40}) hydrocarbyl; or R^1 may be chosen from a radical having formula (II), (III), or (IV) and R^{16} may be chosen from a radical having formula (II), (III), or (IV) the same as or different from that of R^1 . Both R^1 and R^{16} may be radicals having formula (II), for which the groups R^{31-35} are the same or different in R^1 and R^{16} . In other examples, both R^1 and R^{16} may be radicals having formula (III), for which the groups R^{41-48}

⁴⁸ are the same or different in R¹ and R¹⁶; or both R¹ and R¹⁶ may be radicals having formula (IV), for which the groups R⁵¹⁻⁵⁹ are the same or different in R¹ and R¹⁶.

[0046] In some embodiments, at least one of R¹ and R¹⁶ is a radical having formula (II), where R³² and R³⁴ are *tert*-butyl. In one or more embodiments, R³² and R³⁴ are (C₁–C₁₂)hydrocarbyl or –Si[(C₁–C₁₀)alkyl]₃.

[0047] 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 R⁴⁷⁻⁴⁸ are –H. In some embodiments, both R⁴² and R⁴⁷ are –H. In various embodiments, R⁴² and R⁴⁷ are (C₁–C₂₀)hydrocarbyl or –Si[(C₁–C₁₀)alkyl]₃. In other embodiments, R⁴³ and R⁴⁶ are (C₁–C₂₀)hydrocarbyl or –Si(C₁–C₁₀)alkyl]₃.

[0048] In embodiments, when at least one of R¹ or R¹⁶ is a radical having formula (IV), each R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ are –H, (C₁–C₂₀)hydrocarbyl, –Si[(C₁–C₂₀)hydrocarbyl]₃, or –Ge[(C₁–C₂₀)hydrocarbyl]₃. In some embodiments, at least one of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ is (C₃–C₁₀)alkyl, –Si[(C₃–C₁₀)alkyl]₃, or –Ge[(C₃–C₁₀)alkyl]₃. In one or more embodiments, at least two of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ is a (C₃–C₁₀)alkyl, –Si[(C₃–C₁₀)alkyl]₃, or –Ge[(C₃–C₁₀)alkyl]₃. In various embodiments, at least three of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ is a (C₃–C₁₀)alkyl, –Si[(C₃–C₁₀)alkyl]₃, or –Ge[(C₃–C₁₀)alkyl]₃.

[0049] In some embodiments, when at least one of R¹ or R¹⁶ is a radical having formula (IV), at least two of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ are (C₁–C₂₀)hydrocarbyl or –Si[(C₁–C₂₀)hydrocarbyl]₃.

[0050] Examples of (C₃–C₁₀)alkyl include, but are not limited to: 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.

[0051] In formula (I), R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ is independently selected from –H, (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)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)–, (R^C)₂NC(O)–, and halogen.

[0052] In one or more embodiments, R^2 , R^4 , R^5 , R^{12} , R^{13} , and R^{15} are hydrogen; and each Z is oxygen.

[0053] In various 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, R^8 and R^9 are independently (C_1-C_4) alkyl.

[0054] In some embodiments, R^3 and R^{14} are (C_1-C_{20}) alkyl. In one or more embodiments, R^3 and R^{14} are methyl and R^6 and R^{11} are halogen. In 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 various embodiments, R^3 and R^{14} are (C_1-C_{24}) alkyl. In one or more embodiments, R^3 and R^{14} are (C_4-C_{24}) 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 $-OR^C$, wherein R^C is (C_1-C_{20}) hydrocarbon, and in some embodiments, R^C is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl.

[0056] In one or more embodiments, one of R^8 and R^9 is not $-H$. In various embodiments, at least one of R^8 and R^9 is (C_1-C_{24}) alkyl. In some embodiments, both R^8 and R^9 are (C_1-C_{24}) alkyl. In some embodiments, R^8 and R^9 are methyl. In other embodiments, R^8 and R^9 are halogen.

[0057] In some embodiments, R^3 and R^{14} are methyl; In one or more embodiments, R^3 and R^{14} are (C_4-C_{24}) 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.

[0058] In various embodiments, in the metal-ligand complex of formula (I), R^6 and R^{11} are halogen. In some embodiments, R^6 and R^{11} are (C_1-C_{24}) alkyl. In various 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, *n*-pentyl, 3-methylbutyl, *n*-hexyl, 4-methylpentyl, *n*-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.

[0059] In some embodiments, any or all of the chemical groups (e.g., X and R^{1-59}) of the metal-ligand complex of formula (I) may be unsubstituted. In other embodiments, none, any, or all of the chemical groups X and R^{1-59} of the metal-ligand complex of formula (I) may be substituted with one or more than one R^{S} . When two or more than two R^{S} are bonded to a same chemical group of the metal-ligand complex of formula (I), the individual R^{S} of the chemical group may be bonded to the same carbon atom or heteroatom or to different carbon atoms or heteroatoms. In some embodiments, none, any, or all of the chemical groups X and R^{1-59} may be persubstituted with R^{S} . In the chemical groups that are persubstituted with R^{S} , the individual R^{S} may all be the same or may be independently chosen. In one or more embodiments, R^{S} is chosen from $(\text{C}_1\text{--C}_{20})$ hydrocarbyl, $(\text{C}_1\text{--C}_{20})$ alkyl, $(\text{C}_1\text{--C}_{20})$ heterohydrocarbyl, or $(\text{C}_1\text{--C}_{20})$ heteroalkyl.

[0060] In formula (I), L is $(\text{C}_1\text{--C}_{40})$ hydrocarbylene or $(\text{C}_1\text{--C}_{40})$ heterohydrocarbylene; and each Z is independently chosen from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^{\text{N}})-$, or $-\text{P}(\text{R}^{\text{P}})-$. In one or more embodiments, L includes from 1 to 10 atoms.

[0061] In formulas (I), (II), (III), and (IV), each R^{C} , R^{P} , and R^{N} is independently a $(\text{C}_1\text{--C}_{30})$ hydrocarbyl, $(\text{C}_1\text{--C}_{30})$ heterohydrocarbyl, or $-\text{H}$.

[0062] In some embodiments of formula (I), the L may be chosen from $(\text{C}_3\text{--C}_7)$ alkyl 1,3-diradicals, such as $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}_2\text{C}^*\text{H}(\text{CH}_3)$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{C}^*\text{H}(\text{CH}_3)$, $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2-$, cyclopentan-1,3-diyl, or cyclohexan-1,3-diyl, for example. In some embodiments, the L may be chosen from $(\text{C}_4\text{--C}_{10})$ alkyl 1,4-diradicals, such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CH}_2-$, cyclohexane-1,2-diyl dimethyl, and bicyclo[2.2.2]octane-2,3-diyl dimethyl, for example. In some embodiments, L may be chosen from $(\text{C}_5\text{--C}_{12})$ alkyl 1,5-diradicals, such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, and 1,3-bis(methylene)cyclohexane. In some embodiments, L may be chosen from $(\text{C}_6\text{--C}_{14})$ alkyl 1,6-diradicals, such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ or 1,2-bis(ethylene)cyclohexane, for example.

[0063] In one or more embodiments, L is $(\text{C}_2\text{--C}_{40})$ heterohydrocarbylene. In some embodiments, L is $-\text{CH}_2\text{Ge}(\text{R}^{\text{C}})_2\text{CH}_2-$, where each R^{C} is $(\text{C}_1\text{--C}_{30})$ hydrocarbyl. In some

embodiments, L is $-\text{CH}_2\text{Ge}(\text{CH}_3)_2\text{CH}_2-$, $-\text{CH}_2\text{Ge}(\text{ethyl})_2\text{CH}_2-$, $-\text{CH}_2\text{Ge}(\text{2-propyl})_2\text{CH}_2-$, $-\text{CH}_2\text{Ge}(\textit{t}\text{-butyl})_2\text{CH}_2-$, $-\text{CH}_2\text{Ge}(\text{cyclopentyl})_2\text{CH}_2-$, or $-\text{CH}_2\text{Ge}(\text{cyclohexyl})_2\text{CH}_2-$.

[0064] In one or more embodiments, L is chosen from $-\text{CH}_2-$; $-\text{CH}_2\text{CH}_2-$; $-\text{CH}_2(\text{CH}_2)_m\text{CH}_2-$, $\text{CH}_2(\text{C(H)R}^C)_m\text{CH}_2-$ and $-\text{CH}_2(\text{CR}^C)_m\text{CH}_2-$, where subscript m is from 1 to 3; $-\text{CH}_2\text{Si}(\text{R}^C)_2\text{CH}_2-$; $-\text{CH}_2\text{Ge}(\text{R}^C)_2\text{CH}_2-$; $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}^*(\text{CH}_3)$; and $-\text{CH}_2(\text{phen-1,2-di-yl})\text{CH}_2-$; where each R^C in L is $(\text{C}_1-\text{C}_{20})$ hydrocarbyl.

[0065] Examples of such $(\text{C}_1-\text{C}_{12})$ alkyl include, but are not limited to methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl, cyclopentyl, or cyclohexyl, butyl, *tert*-butyl, pentyl, hexyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpent-2-yl), nonyl, decyl, undecyl, and dodecyl.

[0066] In some embodiments, in the metal–ligand complex according to formula (I), both R^8 and R^9 are methyl. In other embodiments, one of R^8 and R^9 is methyl and the other of R^8 and R^9 is $-\text{H}$.

[0067] In the metal–ligand complex according to formula (I), X bonds with M through a covalent bond or an ionic bond. In some embodiments, X may be a monoanionic ligand having a net formal oxidation state of -1 . Each monoanionic ligand may independently be hydride, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl carbanion, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, sulfate, HC(O)O^- , HC(O)N(H)^- , $(\text{C}_1-\text{C}_{40})$ hydrocarbyl C(O)O^- , $(\text{C}_1-\text{C}_{40})$ hydrocarbyl $\text{C(O)N}((\text{C}_1-\text{C}_{20})\text{hydrocarbyl})^-$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl C(O)N(H)^- , $\text{R}^K\text{R}^L\text{B}^-$, $\text{R}^K\text{R}^L\text{N}^-$, R^KO^- , R^KS^- , $\text{R}^K\text{R}^L\text{P}^-$, or $\text{R}^M\text{R}^K\text{R}^L\text{Si}^-$, where each R^K , R^L , and R^M independently is hydrogen, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, or $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl, or R^K and R^L are taken together to form a $(\text{C}_2-\text{C}_{40})$ hydrocarbylene or $(\text{C}_1-\text{C}_{20})$ heterohydrocarbylene and R^M is as defined above.

[0068] In some embodiments, X is a halogen, unsubstituted $(\text{C}_1-\text{C}_{20})$ hydrocarbyl, unsubstituted $(\text{C}_1-\text{C}_{20})$ hydrocarbyl C(O)O^- , or $\text{R}^K\text{R}^L\text{N}^-$, wherein each of R^K and R^L independently is an unsubstituted $(\text{C}_1-\text{C}_{20})$ hydrocarbyl. In some embodiments, each monodentate ligand X is a chlorine atom, $(\text{C}_1-\text{C}_{10})$ hydrocarbyl (e.g., (C_1-C_6) alkyl or benzyl), unsubstituted $(\text{C}_1-\text{C}_{10})$ hydrocarbyl C(O)O^- , or $\text{R}^K\text{R}^L\text{N}^-$, wherein each of R^K and R^L independently is an unsubstituted $(\text{C}_1-\text{C}_{10})$ hydrocarbyl.

[0069] In further embodiments, X is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. X is methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In one embodiment, n is 2 and at least two X independently are monoanionic monodentate ligands. In a specific embodiment, n is 2 and the two X groups join to form a bidentate ligand. In further embodiments, the bidentate ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0070] In one or more embodiments, each X is independently $-(CH_2)SiR^X_3$, in which each R^X is independently a (C_1-C_{30}) alkyl or a (C_1-C_{30}) heteroalkyl and at least one R^X is (C_1-C_{30}) alkyl. In some embodiments, when one of R^X is a (C_1-C_{30}) heteroalkyl, the heteroatom is silica or oxygen atom. In some embodiments, R^X is methyl, ethyl, propyl, 2-propyl, butyl, 1,1-dimethylethyl (or *tert*-butyl), pentyl, hexyl, heptyl, n-octyl, *tert*-octyl, or nonyl.

[0071] In one or more embodiments X is $-(CH_2)Si(CH_3)_3$, $-(CH_2)Si(CH_3)_2(CH_2CH_3)$; $-(CH_2)Si(CH_3)(CH_2CH_3)_2$, $-(CH_2)Si(CH_2CH_3)_3$, $-(CH_2)Si(CH_3)_2(n\text{-butyl})$, $-(CH_2)Si(CH_3)_2(n\text{-hexyl})$, $-(CH_2)Si(CH_3)(n\text{-Oct})R^X$, $-(CH_2)Si(n\text{-Oct})R^X_2$, $-(CH_2)Si(CH_3)_2(2\text{-ethylhexyl})$, $-(CH_2)Si(CH_3)_2(\text{dodecyl})$, $-CH_2Si(CH_3)_2CH_2Si(CH_3)_3$ (herein referred to as $-CH_2Si(CH_3)_2CH_2TMS$). Optionally, in some embodiments, the metal–ligand complex according to formula (I), exactly two R^X are covalently linked or exactly three R^X are covalently linked.

[0072] In some embodiments, X is $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$, $-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, in which subscript Q is 0, 1, 2 or 3 and each R^C is independently a substituted or unsubstituted (C_1-C_{30}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl.

Cocatalyst Component

[0073] The catalyst system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, the precatalyst according to a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Additionally, the metal–ligand complex according to formula (I) includes both a precatalyst form, which is neutral, and a catalytic form, which may be positively charged due to the loss of a monoanionic ligand, such as a methyl, benzyl

or phenyl. Suitable activating co-catalysts for use herein include oligomeric alumoxanes or hydrocarbyl-modified methylaluminoxanes.

[0074] In embodiments, the catalyst system does not contain a borate activator. In one or more embodiments, the borate activator is tetrakis(pentafluorophenyl)borate(1-) anion and a countercation. In some embodiments, the borate activator is bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate.

Polyolefins

[0075] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene and propylene, to form ethylene-based polymers or propylene-based polymers. In some embodiments, there is only a single type of olefin or α -olefin in the polymerization scheme, creating a homopolymer. However, additional α -olefins may be incorporated into the polymerization procedure. The additional α -olefin co-monomers typically have no more than 20 carbon atoms. For example, the α -olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α -olefin co-monomers 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] The ethylene-based polymers, for example homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins, may comprise from at least 50 mole percent (mol%) monomer units derived from ethylene. All individual values and subranges encompassed by "from at least 50 mole percent" are disclosed herein as separate embodiments; for example, the ethylene based polymers, homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins may comprise at least 60 mole percent monomer units derived from ethylene; at least 70 mole percent monomer units derived from ethylene; at least 80 mole percent monomer units derived from ethylene; or from 50 to 100 mole percent monomer units derived from ethylene; or from 80 to 100 mole percent monomer units derived from ethylene.

[0077] In some embodiments, the ethylene-based polymers may comprise at least 90 mole percent units derived from ethylene. All individual values and subranges from at least 90 mole

percent are included herein and disclosed herein as separate embodiments. For example, the ethylene based polymers may comprise at least 93 mole percent units derived from ethylene; at least 96 mole percent units; at least 97 mole percent units derived from ethylene; or in the alternative, from 90 to 100 mole percent units derived from ethylene; from 90 to 99.5 mole percent units derived from ethylene; or from 97 to 99.5 mole percent units derived from ethylene.

[0078] In some embodiments of the ethylene-based polymer, the amount of additional α -olefin is less than 50 mol%; other embodiments include at least 1 mole percent (mol%) to 25 mol%; and in further embodiments the amount of additional α -olefin includes at least 5 mol% to 100 mol%. In some embodiments, the additional α -olefin is 1-octene.

[0079] Any conventional polymerization processes may be employed to produce the ethylene based polymers. Such conventional polymerization processes include, but are not limited to, solution polymerization processes, slurry phase polymerization processes, and combinations thereof using one or more conventional reactors such as loop reactors, isothermal reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[0080] In one embodiment, the ethylene-based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described herein, and optionally one or more co-catalysts. In another embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system in this disclosure, and as described herein, and optionally one or more other catalysts. The catalyst system, as described herein, can be used in the first reactor, or second reactor, optionally in combination with one or more other catalysts. In one embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described herein, in both reactors.

[0081] In another embodiment, the ethylene based polymer may be produced via solution polymerization in a single reactor system, for example a single loop reactor system, in which ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst

system, as described within this disclosure, and optionally one or more co-catalysts, as described in the preceding paragraphs.

[0082] The ethylene based polymers may further comprise 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, UV stabilizers, and combinations thereof. The ethylene based polymers may contain any amounts of additives. The ethylene based polymers may comprise from about 0 to about 10 percent by the combined weight of such additives, based on the weight of the ethylene based polymers and the one or more additives. The ethylene based polymers may further comprise fillers, which may include, but are not limited to, organic or inorganic fillers. The ethylene based polymers may contain from about 0 to about 20 weight percent fillers such as, for example, calcium carbonate, talc, or $\text{Mg}(\text{OH})_2$, based on the combined weight of the ethylene based polymers and all additives or fillers. The ethylene based polymers may further be blended with one or more polymers to form a blend.

[0083] In some embodiments, a polymerization process for producing an ethylene-based polymer may include polymerizing ethylene and at least one additional α -olefin in the presence of a catalyst system according to the present disclosure. The polymer resulting from such a catalyst system that incorporates the metal-ligand complex of formula (I) may have a density according to ASTM D792 (incorporated herein by reference in its entirety) from 0.850 g/cm³ to 0.970 g/cm³, from 0.880 g/cm³ to 0.920 g/cm³, from 0.880 g/cm³ to 0.910 g/cm³, or from 0.880 g/cm³ to 0.900 g/cm³, from 0.950 g/cm³ to 0.965 g/cm³ for example.

[0084] In another embodiment, the polymer resulting from the catalyst system according to the present disclosure has a melt flow ratio (I_{10}/I_2) from 5 to 15, where the melt index, I_2 , is measured according to ASTM D1238 (incorporated herein by reference in its entirety) at 190 °C and 2.16 kg load, and melt index I_{10} is measured according to ASTM D1238 at 190 °C and 10 kg load. In other embodiments the melt flow ratio (I_{10}/I_2) is from 5 to 10, and in others, the melt flow ratio is from 5 to 9.

[0085] In some embodiments, the polymer resulting from the catalyst system according to the present disclosure has a molecular-weight distribution (MWD) from 1 to 25, where MWD is defined as M_w/M_n with M_w being a weight-average molecular weight and M_n being a number-average molecular weight. In other embodiments, the polymers resulting from the catalyst system

have a MWD from 1 to 6. Another embodiment includes a MWD from 1 to 3; and other embodiments include MWD from 1.5 to 2.5.

[0086] Embodiments of the catalyst systems described in this disclosure yield a catalyst system having a high efficiency in comparison to catalyst systems lacking the hydrocarbyl-modified methylaluminoxane.

[0087] One or more features of the present disclosure are illustrated in view of the examples as follows:

EXAMPLES

[0088] **Procedure for Continuous Process Reactor Polymerization :** Raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked ISOPAR E commercially available from ExxonMobil Corporation) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized to above reaction pressure. The solvent and comonomer feed is pressurized to above reaction pressure. The individual catalyst components (metal ligand complex and cocatalysts) are manually batch diluted to specified component concentrations with purified solvent and pressured to above reaction pressure. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

[0089] The continuous solution polymerizations are carried out in a continuously stirred-tank reactor (CSTR). The combined solvent, monomer, comonomer and hydrogen feed to the reactor is temperature controlled between 5° C and 50° C and is typically 15-25° C. All of the components are fed to the polymerization reactor with the solvent feed. The catalyst is fed to the reactor to reach a specified conversion of ethylene. The cocatalyst component(s) is/are fed separately based on a calculated specified molar or ppm ratios. The effluent from the polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exits the reactor and is contacted with water. In addition, various additives such as antioxidants, can be added at this point. The stream then goes through a static mixer to evenly disperse the mixture.

[0090] Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passes through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower-boiling components. The stream then passes through the reactor pressure control valve, across which the pressure is greatly reduced. From there, it enters a two stage separation system consisting of a devolatilizer and a vacuum extruder, where solvent and unreacted hydrogen, monomer, comonomer, and water are removed from the polymer. At the exit of the extruder, the strand of molten polymer formed goes through a cold-water bath, where it solidifies. The strand is then fed through a strand chopper, where the polymer is cut it into pellets after being air-dried.

[0091] **Procedure for Batch Reactor Polymerization.** Raw materials (ethylene, 1-octene) and the process solvent (ISOPAR E) are purified with molecular sieves before introduction into the reaction environment. A stirred autoclave reactor was charged with ISOPAR E, and 1-octene. The reactor was then heated to a temperature and charged with ethylene to reach a pressure. Optionally, hydrogen was also added. The catalyst system was prepared in a drybox under inert atmosphere by mixing the metal-ligand complex and optionally one or more additives, with additional solvent. The catalyst system was then injected into the reactor. The reactor pressure and temperature were kept constant by feeding ethylene during the polymerization and cooling the reactor as needed. After 10 minutes, the ethylene feed was shut off and the solution transferred into a nitrogen-purged resin kettle. The polymer was thoroughly dried in a vacuum oven, and the reactor was thoroughly rinsed with hot ISOPAR E between polymerization runs.

[0092] **TEST METHODS**

[0093] Unless otherwise indicated herein, the following analytical methods are used in describing aspects of the present disclosure:

[0094] **Melt index**

[0095] Melt indices I_2 (or I_2) and I_{10} (or I_{10}) of polymer samples were measured in accordance to ASTM D-1238 (method B) at 190 °C and at 2.16 kg and 10 kg load, respectively. Their values are reported in g/10 min.

[0096] **Density**

[0097] Samples for density measurement were prepared according to ASTM D4703. Measurements were made, according to ASTM D792, Method B, within one hour of sample pressing.

[0098] Gel Permeation Chromatography (GPC)

[0099] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 160° Celsius and the column compartment was set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns and a 20-um pre-column. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00100] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were dissolved at 80 degrees Celsius with gentle agitation for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (\text{EQ 1})$$

where M is the molecular weight, A has a value of 0.4315 and B is equal to 1.0.

[00101] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points. A small adjustment to A (from approximately 0.375 to 0.445) was made to correct for column resolution and band-broadening effects such that linear homopolymer polyethylene standard is obtained at 120,000 Mw.

[00102] The total plate count of the GPC column set was performed with decane (prepared at 0.04 g in 50 milliliters of TCB and dissolved for 20 minutes with gentle agitation.) The plate count

(Equation 2) and symmetry (Equation 3) were measured on a 200 microliter injection according to the following equations:

$$Plate\ Count = 5.54 * \left(\frac{(RV_{Peak\ Max})}{Peak\ Width\ at\ \frac{1}{2}height} \right)^2 \quad (EQ\ 2)$$

where RV is the retention volume in milliliters, the peak width is in milliliters, the peak max is the maximum height of the peak, and $\frac{1}{2}$ height is $\frac{1}{2}$ height of the peak maximum.

$$Symmetry = \frac{(Rear\ Peak\ RV_{one\ tenth\ height} - RV_{Peak\ max})}{(RV_{Peak\ max} - Front\ Peak\ RV_{one\ tenth\ height})} \quad (EQ\ 3)$$

where RV is the retention volume in milliliters and the peak width is in milliliters, Peak max is the maximum position of the peak, one tenth height is 1/10 height of the peak maximum, and where rear peak refers to the peak tail at later retention volumes than the peak max and where front peak refers to the peak front at earlier retention volumes than the peak max. The plate count for the chromatographic system should be greater than 18,000 and symmetry should be between 0.98 and 1.22.

[00103] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under “low speed” shaking.

[00104] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 4-6, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

$$Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(\frac{IR_i}{M_{polyethylene_i}} \right)} \quad (EQ\ 4)$$

$$M_{W(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ 5)$$

$$M_{Z(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (EQ 6)$$

[00105] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. To facilitate the highest accuracy of a RV measurement of the flow marker peak, a least-squares fitting routine is used to fit the peak of the flow marker concentration chromatogram to a quadratic equation. The first derivative of the quadratic equation is then used to solve for the true peak position. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 7. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (EQ 7)$$

[00106] Analysis of Hydrocarbyl-Modified Methylaluminioxanes

[00107] *Example 1 is the analytical procedure for determination of aluminum concentration in a solution.*

[00108] In a nitrogen atmosphere glovebox, aluminum-based analyte having the formula $AlR^{Al}R^{BI}R^{Cl}$ was transferred to a tared bottle and the mass of the sample was recorded. The sample was diluted with methylcyclohexane and then quenched with methanol. The mixture was

swirled and allowed to react over 15 minutes prior to removal of the sample from the glovebox. The sample was further hydrolyzed by addition of H₂SO₄. The bottle was capped shaken for five minutes. Periodic venting of the bottle may be necessary depending on aluminum concentration. The solution was transferred to a separatory funnel. The bottle was rinsed repeatedly with water adding each rinseate from this process to the separatory funnel. The organic layer was discarded and the remaining aqueous solution was transferred to a volumetric flask. The separatory funnel was further rinsed with water, each rinseate being added to the volumetric flask. The flask was diluted to a known volume, thoroughly mixed, and analyzed by complexation with excess EDTA and subsequent back-titration with ZnCl₂ using xylenol orange as an indicator.

[00109] Calculation of the AlR^{A1}R^{B1}R^{C1} Compound in the Hydrocarbyl-Modified Methylaluminoxane

$$\text{Molarity Al in titrant} = \frac{[(M \text{ EDTA} * mL \text{ EDTA}) - (M \text{ ZnCl}_2 * mL \text{ ZnCl}_2)]}{mL, \text{aqueous solution used in titrated}} \quad (1)$$

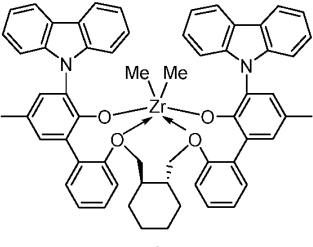
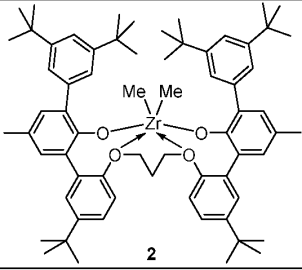
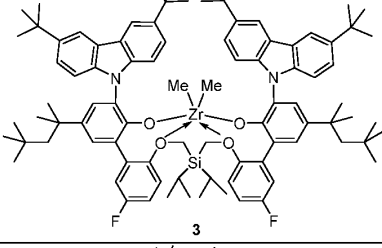
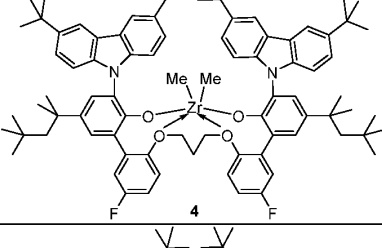
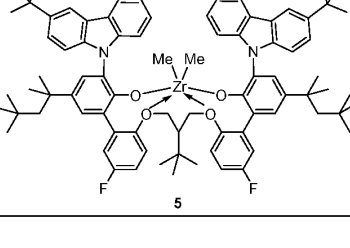
$$\text{mole \% Al in sample} = \frac{(\text{Molarity Al in titrant} * \text{Volume of Volumetric Dilution}) * 26.98 \frac{g}{mol \text{ Al}}}{\text{Mass of Analyte Sample}} * 100 \quad (2)$$

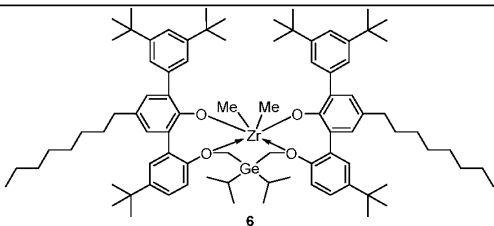
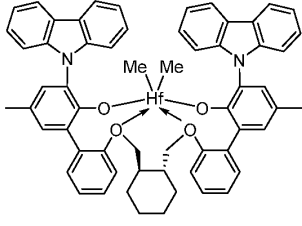
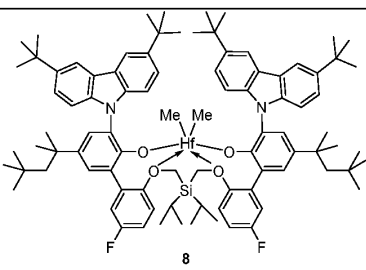
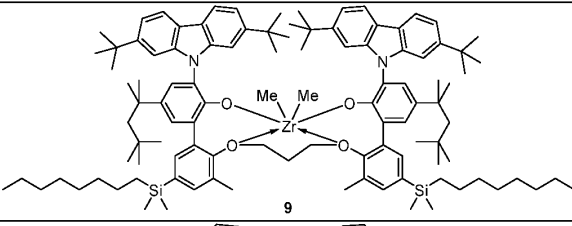
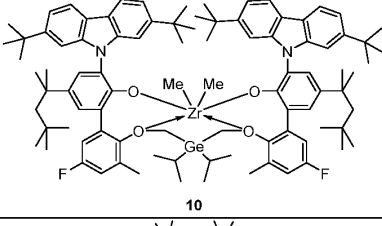
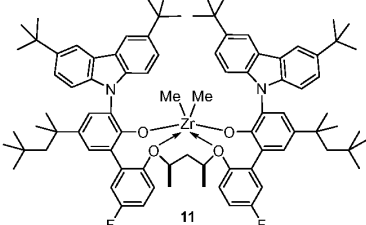
[00110] The AlR^{A1}R^{B1}R^{C1} Compound content is analyzed using previously described methods (*Macromol. Chem. Phys.* **1996**, 197, 1537; WO2009029857A1; *Analytical Chemistry* **1968**, 40 (14), 2150-2153; and *Organometallics* **2013**, 32(11), 3354-3362)

[00111] The metal-complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of transition metal and a neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding transition metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. The techniques employed are the same as of analogous to those disclosed in United States Patent Nos. 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, US-A-2004/0220050.

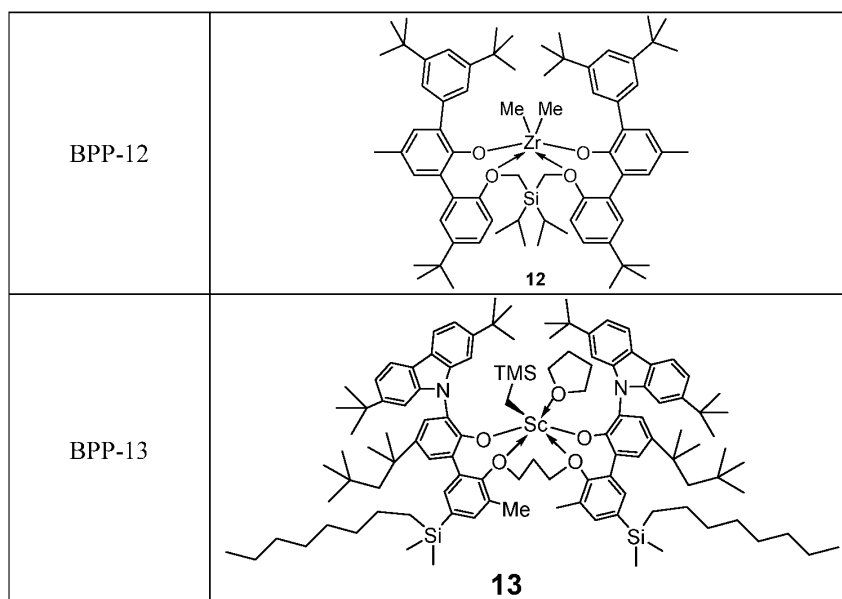
[00112] The synthetic procedures for synthesizing metal-ligand complexes **1** to **12** may be found in in the procedures below and, where previously disclosed, in the following publications US20040010103A1, WO2007136494A2, WO2012027448A1, WO2016003878A1, WO2016014749A1, WO2017058981A1, WO2018022975A1

[00113] The Bis-phenylphenoxy (BPP) Complexes BPP-1 to BPP-13 have a structure according to formula (I) and are as follows:

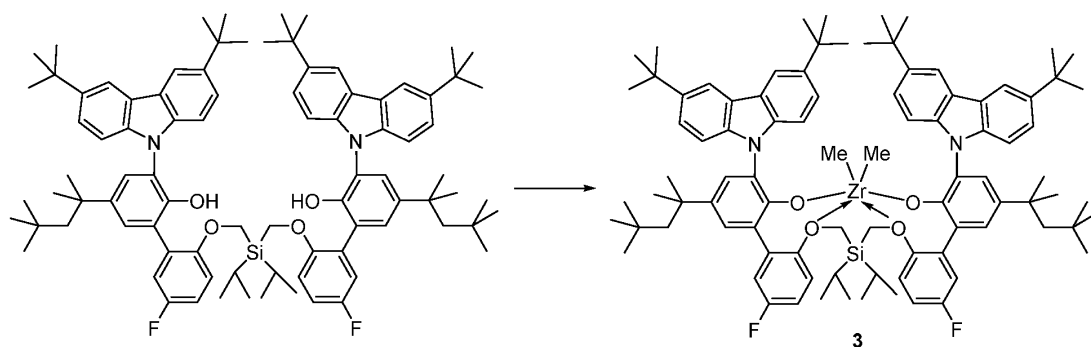
BPP-1	 1
BPP-2	 2
BPP-3	 3
BPP-4	 4
BPP-5	 5

BPP-6	 6
BPP-7	 7
BPP-8	 8
BPP-9	 9
BPP-10	 10
BPP-11	 11

27



[00114] Preparation of BPP 3 (Ligand disclosed in WO2018022975 A1)

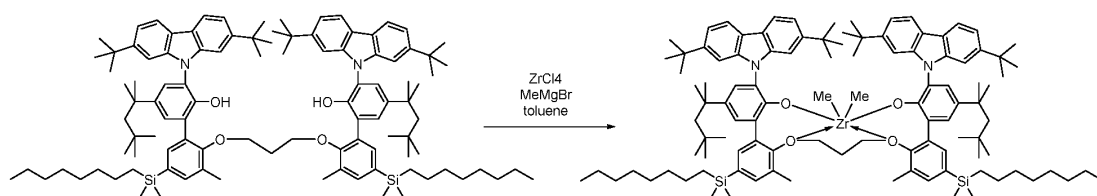


[00115] Synthesis of 6',6'''-(((diisopropylsilanediyl)bis(methylene))bis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-fluoro-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)dimethyl-zirconium (BPP-3): MeMgBr in diethyl ether (3.00 M, 5.33 mL, 16.0 mmol) was added to a -30 °C solution of ZrCl₄ (0.895 g, 3.84 mmol) in toluene (60 mL). After stirring for 3 minutes the solid ligand (5.00 g, 3.77 mmol) was added portionwise. The mixture was stirred for 8 h then the solvent was removed under reduced pressure overnight to afford a dark residue. Hexanes/toluene (10:1 70 mL) was added to the residue, 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 (2 x 15 mL). The combined extracts were concentrated to dryness under reduced pressure. Pentane (20 mL) was added to the tan solid, the heterogeneous mixture

was placed in the freezer ($-35\text{ }^{\circ}\text{C}$) for 18 h. The brown pentane layer was removed using a pipette. The remaining material was dried under vacuum, which provided BPP-3 (4.50 g, yield: 83 %) as a white powder:

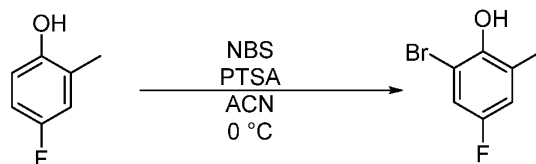
[00116] ^1H NMR (400 MHz, C_6D_6) δ 8.65 – 8.56 (m, 2H), 8.40 (dd, $J = 2.0, 0.7$ Hz, 2H), 7.66 – 7.55 (m, 8H), 7.45 (d, $J = 1.9$ Hz, 1H), 7.43 (d, $J = 1.9$ Hz, 1H), 7.27 (d, $J = 2.5$ Hz, 2H), 7.10 (d, $J = 3.2$ Hz, 1H), 7.08 (d, $J = 3.1$ Hz, 1H), 6.80 (ddd, $J = 9.0, 7.4, 3.2$ Hz, 2H), 5.21 (dd, $J = 9.1, 4.7$ Hz, 2H), 4.25 (d, $J = 13.9$ Hz, 2H), 3.23 (d, $J = 14.0$ Hz, 2H), 1.64 – 1.52 (m, 4H), 1.48 (s, 18H), 1.31 (s, 24H), 1.27 (s, 6H), 0.81 (s, 18H), 0.55 (t, $J = 7.3$ Hz, 12H), 0.31 (hept, $J = 7.5$ Hz, 2H), -0.84 (s, 6H); ^{19}F NMR (376 MHz, C_6D_6) δ -116.71 .

[00117] Synthesis of BPP-9:

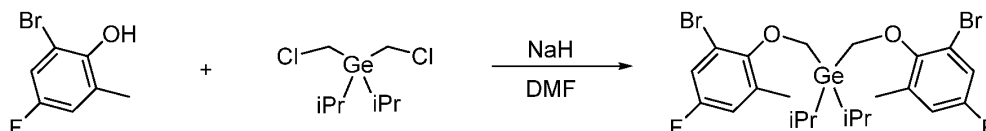


[00118] A 100 mL oven dried glass bottle was charged with ZrCl_4 (798 mg, 3.43 mmol), toluene (30 mL), and a stir bar. The solution was placed in the freezer and cooled to $-30\text{ }^{\circ}\text{C}$ for 20 min. The solution was taken out of the freezer, and was treated with MeMgBr (4.35 mL, 13.1 mmol, 3 M in Et_2O) and stirred for 15 minutes. To the cold suspension, the BPP-9 ligand (5.00 g, 3.26 mmol) was added as a solid. The reaction was stirred at room temperature for 3 h, and then filtered through a fritted plastic funnel. The filtrate was dried under vacuum. The resulting solid was washed with hexanes, and dried under vacuum, providing BPP-9 as an off-white powder (3.31 g, 62%):

[00119] ^1H NMR (400 MHz, Benzene- d_6) δ 8.19 (d, $J = 8.2$ Hz, 2H), 8.03 – 7.96 (m, 4H), 7.87 (d, $J = 2.5$ Hz, 2H), 7.81 – 7.76 (m, 2H), 7.64 (d, $J = 2.5$ Hz, 2H), 7.56 (d, $J = 1.7$ Hz, 2H), 7.51 (dd, $J = 8.2, 1.7$ Hz, 2H), 7.30 (dd, $J = 8.3, 1.7$ Hz, 2H), 7.06 – 7.01 (m, 2H), 3.57 (dt, $J = 9.9, 4.9$ Hz, 2H), 3.42 (dt, $J = 10.3, 5.2$ Hz, 2H), 1.79 (d, $J = 14.5$ Hz, 2H), 1.66 (d, $J = 14.4$ Hz, 2H), 1.60 (s, 18H), 1.46 (s, 6H), 1.42 (s, 6H), 1.37 – 1.22 (m, 50H), 0.94 – 0.91 (m, 24H), 0.62 – 0.56 (m, 4H), 0.11 (s, 6H), 0.08 (s, 6H), -0.64 (s, 6H).

[00120] Preparation of BPP-10

[00121] Synthesis of 2-bromo-4-fluoro-6-methyl-phenol: 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 °C with ice for 25 min (a precipitate formed). The cooled solution, was slowly treated with *N*-bromosuccinimide (70.55 g, 396.4 mmol) (over the course of approx. 5 min), and was allowed reach room temperature while stirring overnight. The reaction was analyzed by ^{19}F NMR spectroscopy and GC/MS to confirm complete conversion. 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 CH_2Cl_2 . The volatiles were removed under vacuum (1st fraction yield: 46 g, 56%). ^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). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -122.84.

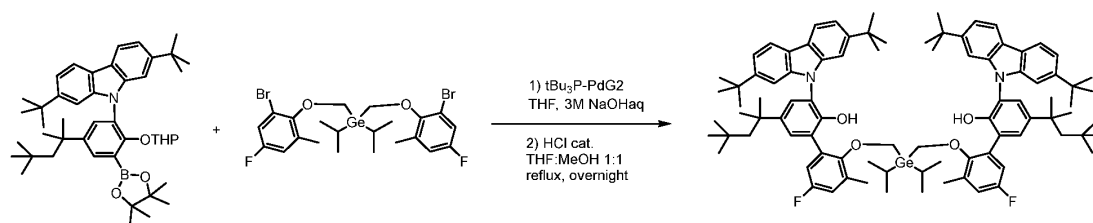
**[00122] Synthesis of bis((2-bromo-4-fluoro-6-**

methylphenoxy)methyl)diisopropylgermane: In the glove box, 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 h. 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 a pale yellow oil as product. All clean fractions (some fractions contained <10% of starting phenol) were combined, and the final product was left under vacuum overnight (Yield: 9 g, 62%):

[00123] ^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); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.03.

[00124] Synthesis of BPP-10 ligand

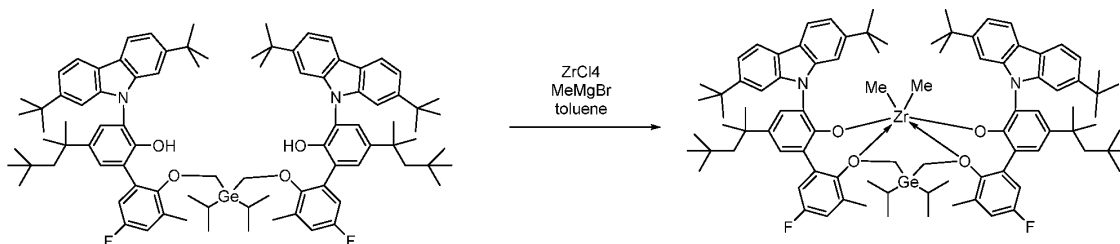


[00125] A 500 mL glass-bottle, equipped with a stir bar, was charged with 2,7-di-tert-butyl-9-(2-(((tetrahydro-2H-pyran-2-yl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(2,4,4-trimethylpentan-2-yl)phenyl)-9H-carbazole (Disclosed in WO2014105411 A1) (29.0 g, 41.9 mmol), bis((2-bromo-4-fluoro-6-methylphenoxy)methyl)diisopropylgermane (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) (tBu₃P-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 the BPP-10 ligand as an off-white solid (Yield: 6.5 g, 54%):

[00126] ^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

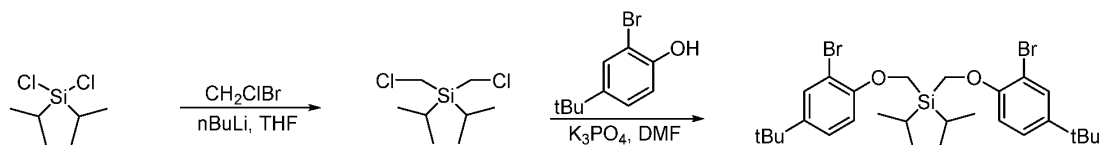
(s, 2H), 3.79 (s, 4H), 2.12 (s, 6H), 1.71 (s, 6H), 1.56 (s, 4H), 1.38 (s, 12H), 1.31 (s, 36H), 0.83 – 0.73 (m, 30H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.02.

[00127] Synthesis of BPP 10:



[00128] A 100 mL oven dried glass bottle was charged with ZrCl_4 (402 mg, 1.72 mmol), toluene (83 mL), and a stir bar. The solution was placed in the freezer and cooled to -30 C for 20 min. The solution was taken out of the freezer, and was treated with MeMgBr (2.4 mL, 7.1 mmol, 3 M in Et_2O) and stirred for 3 minutes. To the cold suspension, the BPP-10 ligand (2.3 g, 1.64 mmol) was added as a solid, and the residual powder was dissolved in cold toluene (3 mL) and added to the reaction. The reaction was stirred overnight at room temperature, and then filtered through a fritted plastic funnel. The filtrate was dried under vacuum, redissolved in toluene (40 mL), filtered again through a plug of CELITE, and dried again under vacuum. The resulting solid was washed with pentane (approx. 5 mL) and dried under vacuum, providing BPP-10 as an off-white powder (2.1 g, 84%):

[00129] ^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); ^{19}F NMR (376 MHz, Benzene-*d*₆) δ -116.24.

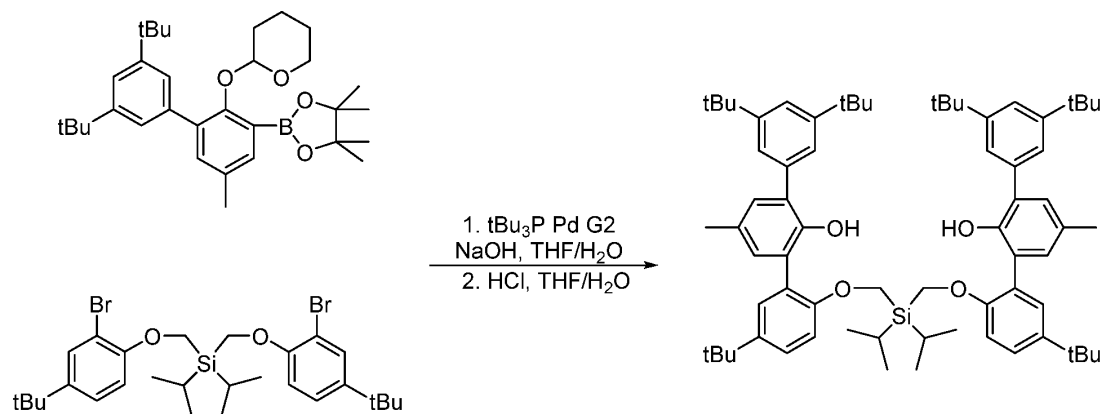
[00130] Synthesis of BPP-12**[00131] Preparation of bis((2-bromo-4-t-butylphenoxy)methyl)diisopropylsilane**

[00132] In a glovebox, diisopropyldichlorosilane (3.703 g, 20 mmol, 1.0 equiv) was dissolved in anhydrous THF (120 mL) in a 250 mL single-neck round-bottom flask. The flask was capped with a septum, sealed, taken out of glovebox, and cooled to $-78\text{ }^\circ\text{C}$ in a dry ice-acetone bath. Bromochloromethane (3.9 mL, 60 mmol, 3.0 equiv) was added. A solution of $n\text{-BuLi}$ (18.4 mL, 46 mmol, 2.3 equiv) in hexane was added to the cooled wall of the flask over a period of 3h using a syringe pump. The mixture was allowed to warm up to room temperature overnight (16h) and saturated NH_4Cl (30 mL) was added. The two layers were separated. The aqueous layer was extracted with ether (2 x 50 mL). The combined organic layer was dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was used for the next step without further purification.

[00133] In a glove box, a 40 mL vial was charged with bis(chloromethyl)diisopropylsilane (2.14 g, 10 mmol, 1.0 equiv), 4-*t*-butyl-2-bromophenol (6.21 g, 27 mmol, 2.7 equiv), K_3PO_4 (7.46 g, 35 mmol, 3.5 equiv), and DMF (10 mL). The reaction mixture was stirred at $80\text{ }^\circ\text{C}$ overnight. After cooling down to room temperature, the reaction mixture was purified by column chromatography using ether/hexane (0/100 $\rightarrow$ 30/70) as the eluent. Collected 4.4 g of a colorless oil, 73% overall yield after 2 steps.

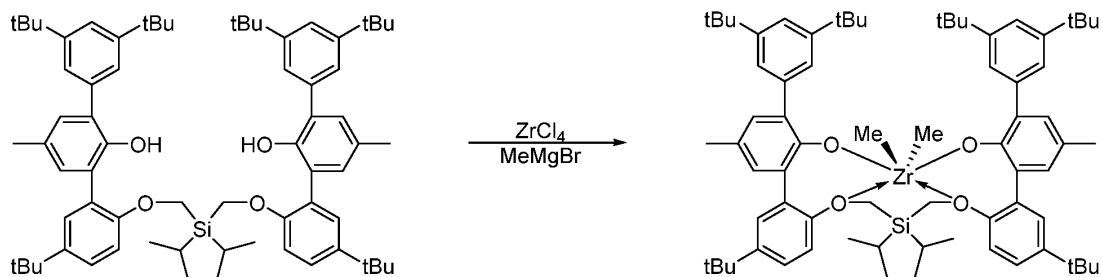
[00134] ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 2.4\text{ Hz}$, 2H), 7.26 (dd, $J = 8.6, 2.4\text{ Hz}$, 2H), 6.98 (d, $J = 8.6\text{ Hz}$, 2H), 3.93 (s, 4H), 1.45 – 1.33 (m, 2H), 1.28 (s, 18H), 1.20 (d, $J = 7.3\text{ Hz}$, 12H).

**[00135] Preparation of 6'',6'''''-
(((diisopropylsilanediyl)bis(methylene))bis(oxy))bis(3,3'',5-tri-tert-butyl-5'-methyl-
[1,1':3',1''-terphenyl]-2'-ol)**



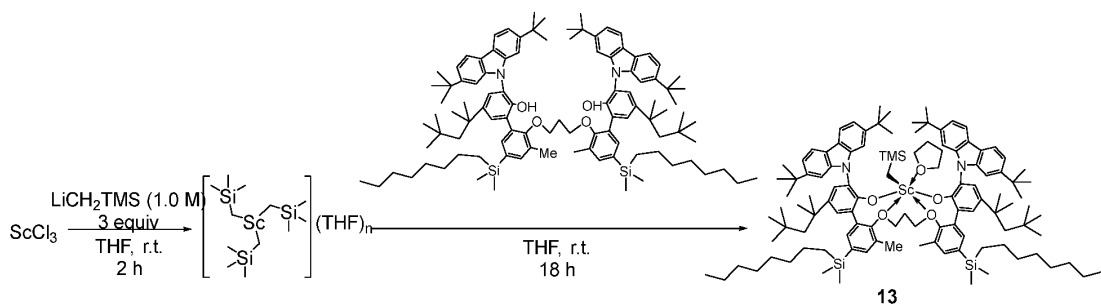
[00136] In a glove box, a 40 mL vial equipped with a stir bar was charged with bis((2-bromo-4-*t*-butylphenoxy)methyl)diisopropylsilane (1.20 g, 2.0 mmol, 1.0 equiv), 2-(3',5'-di-*tert*-butyl-5-methyl-2-((tetrahydro-2H-pyran-2-yl)oxy)-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.54 g, 5.0 mmol, 2.5 equiv), *t*Bu₃P Pd G2 (0.031 g, 0.06 mmol, 0.03 equiv), THF (3 mL), and NaOH 4 M solution (3.0 mL, 12.0 mmol, 6.0 equiv). The vial was heated under nitrogen at 55 °C for 2 hours. When completed, the top organic layer was extracted with ether and filtered through a short plug of silica gel. Solvents were removed under reduced pressure. The residue was dissolved in THF (10 mL) and MeOH (10 mL). Concentrated HCl (0.5 mL) was then added. The resulting mixture was heated at 75 °C for 2 hours then cooled to room temperature. Solvents were removed under reduced pressure. The residue was purified by reverse phase column chromatography using THF/MeCN (0/100 → 100/0) as the eluent. Collected 1.62 g of a white solid, 78% yield.

[00137] ¹H NMR (400 MHz, CDCl₃) δ 7.39 (t, *J* = 1.8 Hz, 2H), 7.36 (d, *J* = 1.8 Hz, 4H), 7.29 (d, *J* = 2.5 Hz, 2H), 7.22 (dd, *J* = 8.6, 2.6 Hz, 2H), 7.10 (d, *J* = 2.2 Hz, 2H), 6.94 (d, *J* = 2.3, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.37 (s, 2H), 3.61 (s, 4H), 2.32 (d, *J* = 0.9 Hz, 6H), 1.33 (s, 36H), 1.29 (s, 18H), 0.90 – 0.81 (m, 2H), 0.73 (d, *J* = 7.1 Hz, 12H).

[00138] Preparation of BPP-12

[00139] In a glovebox, an oven dried 40 mL vial with a stir bar was charged with ZrCl_4 (47 mg, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6.0 mL). The vial was cooled to $-30\text{ }^\circ\text{C}$ in freezer for at least 30 minutes. The vial was taken out of freezer. MeMgBr (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added to the stirring suspension. After 2 minutes, 6'',6''''-(((diisopropylsilanediyl)bis(methylene))bis(oxy))bis(3,3'',5-tri-tert-butyl-5'-methyl-[1,1':3',1''-terphenyl]-2'-ol) (206 mg, 0.2 mmol, 1.0 equiv) was added as solid. The resulting mixture was stirred at room temperature overnight. Solvents were removed under vacuum to yield a dark solid which was washed with hexanes (10 mL) then extracted with toluene (12 mL). After filtering, the toluene extract was dried under vacuum. Collected 170 mg of a white solid, 74% yield.

[00140] ^1H NMR (400 MHz, C_6D_6) δ 8.20 – 7.67 (m, 4H), 7.79 (t, $J = 1.8\text{ Hz}$, 2H), 7.56 (d, $J = 2.5\text{ Hz}$, 2H), 7.26 (d, $J = 2.4\text{ Hz}$, 2H), 7.21 (d, $J = 2.4\text{ Hz}$, 2H), 7.18 (d, $J = 2.4\text{ Hz}$, 2H), 5.67 (d, $J = 8.6\text{ Hz}$, 2H), 4.61 (d, $J = 13.5\text{ Hz}$, 2H), 3.46 (d, $J = 13.5\text{ Hz}$, 2H), 2.26 (s, 6H), 1.47 (s, 36H), 1.25 (s, 18H), 0.52 (dd, $J = 17.0, 7.5\text{ Hz}$, 12H), 0.30 – 0.18 (m, 2H), - 0.05 (s, 6H).

[00141] Synthesis of BPP-13

[00142] In a nitrogen glove box, an oven-dried vial was charged with ScCl_3 (0.016 g, 0.106 mmol), THF (ca. 50 mL), and a magnetic stir bar. The mixture was cooled at $-30\text{ }^\circ\text{C}$ and then

LiCH₂TMS (1.0 M in pentane, 0.35 mL, 0.35 mmol) was added dropwise and then the mixture was stirred at room temperature for 1.5 h. To this mixture, 1 equiv of ligand formula i (0.168 g, 0.106 mmol) in THF (ca. 10 mL) was slowly added and the reaction mixture was allowed to be stirred at room temperature for 18 h. Solvent was then removed in vacuo to afford BPP-19 as a white solid (0.154 g, 83%).

[00143] Example 2 –Polymerization Reactions with Metal-Ligand Complexes and Comparative Activators and hydrocarbyl-modified methylaluminoxanes having less than 25 mole% of the compound $AlR^{A1}R^{B1}R^{C1}$ based on total moles of aluminum

[00144] Metal-ligand complexes **2**, **4**, and **11** were tested in a batch reactor using MMAO-A2 or MMAO-comp 2 as the activator, and the data are summarized in Tables 1-2. The dry weight efficiencies are higher when the catalyst was activated with MMAO-A2 as opposed to MMAO-comp 2.

Table 1: Hydrocarbyl-Modified Methylaluminoxane Compositions

Name	Solvent	Methane (mol %)	Isobutane (mol %)	Aluminum (mol %)	Aluminum species as $AlR^{A1}R^{B1}R^{C1}$ (%)
MMAO-A1	Isopar E	98.6	0.4	7	15
MMAO-comp 1	Heptane	65.6	33.3	6.8	38
MMAO-A2	Isopar E			6.76	11
MMAO-comp 2	Heptane			6.97	29
MMAO-B	Toluene	99.6	0	7	20
MMAO-C	Toluene	99.7		6.8	24

* MMAO-A1 and A2 are modified with *n*-octyl substituents such that the methyl:*n*-octyl ratio is approximately 6:1. MMAO-B is modified with *n*-octyl substituents such that the methyl:*n*-octyl ratio is approximately 19:1. All the substituents in MMAO-C are methyl.

Table 2. Batch reactor polymerization data of Bis-phenylphenoxy Complexes using MMAO-comp 2 or MMAO-A2

BPP	H ₂ (mmol)	Activator	Al(R ₃) (%) ^[B]	Cat. (umol)	Eff. ^[A]	Mw (g/mol)	Density (g/ cc)	PDI
11	0	MMAO-comp 2	29	1.0	0.36	1,136,996	0.8709	3.07
11	0	MMAO-A2	11	0.75	0.70	933,892	0.8676	2.23
4	0	MMAO-comp 2	29	0.5	0.65	90,785	0.8731	2.44
4	0	MMAO-A2	11	0.2	1.78	81,478	0.8760	1.91

[00145] Polymerization conditions: 150 °C, 1342 g ISOPAR E; 177g 1-octene; 52g ethylene; a total pressure of 230 psi; All MMAO at 100 ratio Al:Catalyst Metal. ^[A]The catalyst efficiency (Eff.) is measured as 10⁶ g polymer /g metal in the catalyst). ^[B] Aluminum species as AlR^AR^BR^C.

Table 3. Batch reactor polymerization data of Bis-phenylphenoxy Complexes using MMAO-comp 2 or MMAO-A2

BPP	H ₂ (mmol)	Activator	Al(R ₃) (%) ^[B]	Cat (umol)	Eff. ^[A]	M _w (g/mol)	Density (g/cm ³)	PDI
2	0	MMAO-comp 2	29	1.0	0.55	317,498	0.8766	2.12
2	0	MMAO-A2	11	0.325	1.14	284,349	0.8769	2.12
4	0	MMAO-comp 2	29	0.55	0.34	69,773	0.878	1.99
4	0	MMAO-A2	11	0.168	1.47	70,575	0.8782	1.97

[00146] Polymerization conditions: 165 °C, 1345 g ISOPAR E; 175 g 1-octene; 50g ethylene; total pressure 237 psi; All MMAO at 100 ratio Al:Catalyst Metal. ^[A]The catalyst efficiency (Eff.) is measured as 10⁶ g polymer /g metal in the catalyst). ^[B] Aluminum species as AlR^AR^BR^C.

Table 4: Continuous Process Ethylene/1-Octene Copolymerization Reactions.

BPP	MMAO	Al(R ₃) (%) ^[D]	Al conc in reactor (ppm)	Eff. ^[C]	% Solids (%) ^[A]	H ₂ (mol %)	C2 conve rsion (%)	I ₂ (g/10 min)	I ₁₀ /I ₂	Density (g/cc)
1	MMAO-A1	15	2.0	27.0	14.5	0.06	80.7	1.7	12.0	0.8798
1	MMAO-comp 1	38	5.0	8.46	14.1	0.09	80.5	1.9	10.3	0.8840
2	MMAO-A1	15	2.0	7.76	14.1	0.21	80.9	1.8	7.8	0.8825
2	MMAO-comp 1	38	2.0	1.35	13.7	0.24	80.5	2.0	7.3	0.8852
3	MMAO-A1	15	2.0	40.4	15.0	0.05	80.8	1.9	9.9	0.8758
3	MMAO-comp 1	38	6.0	2.38	14.4	0.1	80.5	2.1	9.5	0.8773
4	MMAO-A1	15	2.0	55.4	14.8	0.0	80.1	11.5	9.5	0.8779
4	MMAO-comp 1	38		N/A						
5	MMAO-A1	15	0.97	38.2	15.2	0.0	80.9	140	N/D	0.8700
5 ¹	MMAO-comp 1	38	9.8	1.22	8.14	0.0	57.6	146	N/D	0.8756
5	MMAO-B	20	2.0	42.0	15.1	0.0	80.8	129	N/D	0.8716
5	MMAO-C	24	2.0	41.6	14.9	0.0	80.7	131	N/D	0.8712
6	MMAO-A1	15	2.0	12.3	13.7	0.37	81.0	2.2	5.9	0.8869
6	MMAO-comp 1	38	2.0	2.74	13.6	0.37	81.2	2.1	5.9	0.8890
6	MMAO-B	20	2.0	10.8	13.5	0.35	80.8	2.1	6.1	0.8867
6	MMAO-C	24	2.0	9.89	13.6	0.36	80.6	2.0	6.0	0.8848
7 ²	MMAO-A1	15	5.8	0.72	14.2	0.46	80.9	1.6	7.2	0.8788
7	MMAO-comp 1	38		N/A						
12	MMAO-A1	15	2.0	13.6	13.8	0.38	80.5	2.1	6.1	0.8865
12	MMAO-comp 1	38	2.0	4.78	13.8	0.36	80.7	1.9	5.9	0.8864

[00147] Polymerization at reactor temperature of 160 °C, feed flows of 3.4 kg/h of ethylene, 3.3 kg/h of 1-octene, 21 kg/h ISOPAR E, ^[A]% Solids is the concentration of polymer in the reactor. ^[B]H₂ (mol%) is defined as the mole fraction of hydrogen, relative to ethylene, fed into the reactor. ^[C]The efficiency (Eff.) is measured as 10⁶ g polymer /g metal in the catalyst component). Ethylene conversion is measured as the difference between the ethylene fed to the reactor relative to the amount exiting the reactor, expressed as a percentage. ¹Reactor temperature = 153 °C, 2.5 kg/h of ethylene, 3.3 kg/h of 1-octene, 21 kg/h ISOPAR E. ²Reactor temperature of 160 °C, 3.4 kg/h of ethylene, 2.4 kg/h of 1-octene, 22 kg/h ISOPAR E. N/D = not determined. ^[D] Aluminum species as AlR^{A1}R^{B1}R^{C1}. N/A = Unable to achieve steady state reaction under these reactor conditions.

Table 5: Continuous Process Ethylene/1-Octene Copolymerization Reactions.

BPP	MMAO	Al(R) ₃ (%) ^[D]	Al conc in reactor (ppm)	Eff. ^[C]	% Solids (%) ^[A]	H ₂ (mol %)	C2 conversion (%)	I ₂ (g/10min)	I ₁₀ /I ₂	Density (g/cc)
9	MMAO-A1	15	2.0	125	16.0	0.0	85.3	8.9	6.24	0.9375
9	MMAO-comp 1	38	2.0	31.5	16.2	0.0	85.9	8.3	6.21	0.9376
10	MMAO-A1	15	2.0	22.6	12.5	0.26	88.3	2.0	5.38	0.9390
10	MMAO-comp 1	38	5.4	1.47	15.9	0.35	84.8	3.2	5.91	0.9410

[00148] Polymerization at reactor temperature of 190 °C, 4.6 kg/h of ethylene, 2.0 kg/h of 1-octene, 21 kg/h ISOPAR E, ^[A]% Solids is the concentration of polymer in the reactor. ^[B]H₂ (mol%) is defined as the mole fraction of hydrogen, relative to ethylene, fed into the reactor. Ethylene conversion is measured as the difference between the ethylene fed to the reactor relative to the amount exiting the reactor, expressed as a percentage. ^[C]The efficiency (Eff.) is measured as 10⁶ g polymer /g metal in the catalyst). ^[D] Aluminum species as AlR^{A1}R^{B1}R^{C1}

Table 6. Batch reactor polymerization data of BPP-13

MMAO	Aluminum AlR ^{A1} R ^{B1} R ^{C1} (%)	Al:Sc ratio	Eff. ^[A]	T _m (°C)	Mn (g/mol)	PDI	Mw (g/mol)
MMAO-A1	15	20	0.73	132.59	100,988	1.99	173,471
MMAO-A1	15	50	0.68	132.77	104,529	1.96	177,162
MMAO-A1	15	100	0.56	132.72	100,966	2.00	166,684
MMAO-Comp 1	38	20	0.84	132.49	97,256	1.96	162,902

MMAO- Comp 1	38	50	0.69	131.79	113,401	1.95	189,574
MMAO- Comp 1	38	100	0.41	131.97	114,469	1.97	189,631

[00149] Polymerization conditions: 190 °C, 1250 g ISOPAR E; 65 g octene; 85 g ethylene; total pressure 415 psi; reaction time = 10 min. ^[A]Efficiency (Eff) is calculated based of the amount of ethylene uptake and is expressed as 10⁶ g ethylene uptake /g metal in the catalyst).

Equipment Standards

[00150] All solvents and reagents are obtained from commercial sources and used as received unless otherwise noted. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether are purified *via* passage through activated alumina and, in some cases, Q-5 reactant. Solvents used for experiments performed in a nitrogen-filled glovebox are further dried by storage over activated 4Å molecular sieves. Glassware for moisture-sensitive reactions is dried in an oven overnight prior to use. NMR spectra are recorded on Varian 400-MR and VNMR5-500 spectrometers. LC-MS analyses are performed using a Waters e2695 Separations Module coupled with a Waters 2424 ELS detector, a Waters 2998 PDA detector, and a Waters 3100 ESI mass detector. LC-MS separations are performed on an XBridge C18 3.5 µm 2.1x50 mm column using a 5:95 to 100:0 acetonitrile to water gradient with 0.1% formic acid as the ionizing agent. HRMS analyses are performed using an Agilent 1290 Infinity LC with a Zorbax Eclipse Plus C18 1.8µm 2.1x50 mm column coupled with an Agilent 6230 TOF Mass Spectrometer with electrospray ionization. ¹H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet and m = multiplet), integration, and assignment). Chemical shifts for ¹H NMR data are reported in ppm downfield from internal tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent as references. ¹³C NMR data are determined with ¹H decoupling, and the chemical shifts are reported downfield from tetramethylsilane (TMS, δ scale) in ppm versus the using residual carbons in the deuterated solvent as references.

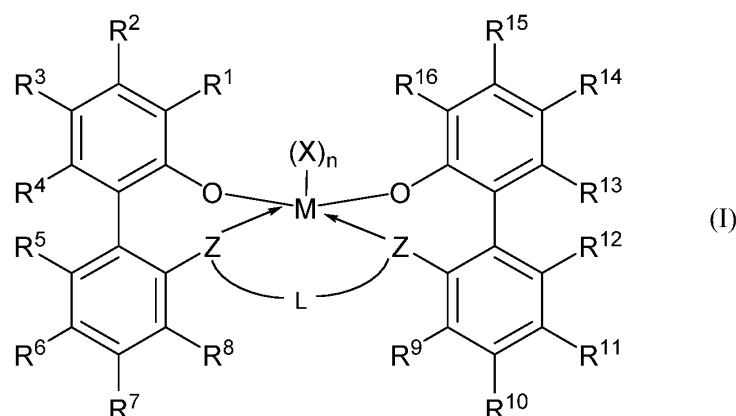
CLAIMS

1. A process of polymerizing olefin monomers, the process comprising reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system, wherein the catalyst system comprises:

hydrocarbyl-modified methylaluminoxane having less than 25 mole percent

trihydrocarbyl aluminum compounds $\text{AlR}^{\text{A1}}\text{R}^{\text{B1}}\text{R}^{\text{C1}}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A1} , R^{B1} , and R^{C1} are independently linear ($\text{C}_1\text{--C}_{40}$)alkyl, branched ($\text{C}_1\text{--C}_{40}$)alkyl, or ($\text{C}_6\text{--C}_{40}$)aryl; and

one or more metal–ligand complexes according to formula (I):



where:

M is titanium, zirconium, hafnium, scandium, yttrium, or an element of the lanthanide series of the periodic table;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from unsaturated

($\text{C}_2\text{--C}_{50}$)hydrocarbon, unsaturated ($\text{C}_2\text{--C}_{50}$)heterohydrocarbon, saturated

($\text{C}_2\text{--C}_{50}$)heterohydrocarbon, ($\text{C}_1\text{--C}_{50}$)hydrocarbyl, ($\text{C}_6\text{--C}_{50}$)aryl,

($\text{C}_6\text{--C}_{50}$)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl,

($\text{C}_4\text{--C}_{12}$)diene, halogen, $-\text{N}(\text{R}^{\text{N}})_2$, and $-\text{N}(\text{R}^{\text{N}})\text{COR}^{\text{C}}$;

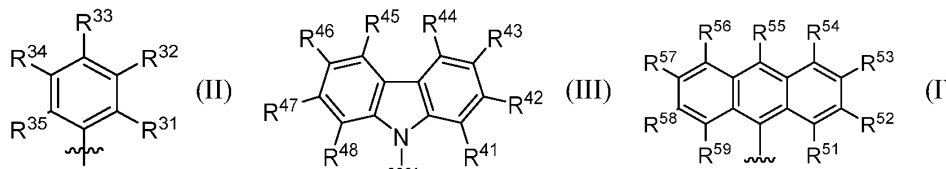
the metal–ligand complex is overall charge-neutral;

each Z is independently chosen from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^{\text{N}})-$, or $-\text{P}(\text{R}^{\text{P}})-$;

R^1 and R^{16} are independently selected from the group consisting of $-\text{H}$,

($\text{C}_1\text{--C}_{40}$)hydrocarbyl, ($\text{C}_1\text{--C}_{40}$)heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$,

$-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



where each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-\text{H}$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen;

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 selected from $-\text{H}$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, $(\text{C}_1-\text{C}_{40})$ 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; L is $(\text{C}_1-\text{C}_{40})$ hydrocarbylene or $(\text{C}_2-\text{C}_{40})$ heterohydrocarbylene; and each R^{C} , R^{P} , and R^{N} in formula (I) is independently a $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, or $-\text{H}$.

2. The polymerization process according to claim 1 or claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 20 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.
3. The polymerization process according to claim 1 or claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.
4. The polymerization process according to claim 1 or claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 10 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

5. The polymerization process according to any one of claim 1 to claim 4, where the hydrocarbyl-modified methylaluminoxane is modified methylaluminoxane.
6. The polymerization process according to any one of claims 1 to 5, wherein R^1 and R^{16} are identical.
7. The polymerization process according to any one of the preceding claims, wherein at least one of R^1 and R^{16} is a radical having formula (III).
8. The polymerization process according to claim 7, wherein R^{42} and R^{47} are (C_1-C_{20}) hydrocarbyl or $-Si[(C_1-C_{20})\text{hydrocarbyl}]_3$.
9. The polymerization process according to claim 7, wherein R^{43} and R^{46} are (C_1-C_{20}) hydrocarbyl or $-Si[(C_1-C_{20})\text{hydrocarbyl}]_3$.
10. The polymerization process according to any one of claims 1 to 5, wherein at least one of R^1 and R^{16} is a radical having formula (II).
11. The polymerization process according to claim 10, wherein R^{32} and R^{34} are (C_1-C_{12}) hydrocarbyl or $-Si[(C_1-C_{20})\text{hydrocarbyl}]_3$.
12. The polymerization process according to any one of claims 1 to 5, wherein at least one of R^1 and R^{16} is a radical having formula (IV).
13. The polymerization process according to claim 12, wherein at least two of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} are (C_1-C_{20}) hydrocarbyl or $-Si[(C_1-C_{20})\text{hydrocarbyl}]_3$.
14. The polymerization process according to any of the preceding claims, wherein:
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.
15. The polymerization process according to any of claims 1 to 13, wherein R^8 and R^9 are independently (C_1-C_4) alkyl.
16. The polymerization process according to any of the preceding claims, wherein R^3 and R^{14} are (C_1-C_{20}) alkyl.

17. The polymerization process according to any one of the preceding claims, wherein R^3 and R^{14} are methyl, R^6 and R^{11} are halogen.
18. The polymerization process according to any one of claims 1-14, wherein R^6 and R^{11} are *tert*-butyl.
19. The polymerization process according to any one of claims 1 to 14, wherein R^3 and R^{14} are *tert*-octyl or *n*-octyl.
20. The polymerization process according to any one of the preceding claims, wherein M is Zr or Sc.
21. The polymerization process according to any one of the preceding claims, wherein L is chosen from $-\text{CH}_2(\text{CH}_2)_m\text{CH}_2-$, where m is 1 to 3, $-\text{CH}_2\text{Si}(\text{R}^{\text{C}})(\text{R}^{\text{D}})\text{CH}_2-$, $-\text{CH}_2\text{Ge}(\text{R}^{\text{C}})(\text{R}^{\text{D}})\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)-$, bis(methylene)cyclohexan-1,2-diyl; $-\text{CH}_2\text{CH}(\text{R}^{\text{C}})\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{R}^{\text{C}})_2\text{CH}_2-$, where each R^{C} in L is $(\text{C}_1-\text{C}_{20})$ hydrocarbyl and R^{D} in L is $(\text{C}_1-\text{C}_{20})$ hydrocarbyl.
22. The polymerization process according to any one of the preceding claims, wherein the catalyst system does not contain a borate activator.
23. The polymerization process according to any one of the preceding claims, wherein the olefin monomer is $(\text{C}_3-\text{C}_{20})\alpha$ -olefin.
24. The polymerization process according to any claims 1 to 21, wherein the olefin monomer is not $(\text{C}_3-\text{C}_{20})\alpha$ -olefin.
25. The polymerization process according to any one of the preceding claims, wherein the olefin monomer is cyclic olefin.
26. The polymerization process according to any one of the preceding claims, wherein the polymerization process is a solution polymerization reaction.