

HETEROATOM-BRIDGED BIS-PHENYL-PHENOXY CATALYSTS AND ETHYLENE COPOLYMERS WITH IMPROVED FEATURES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 63/625,518, entitled “Performance of Heteroatom-Bridged Bis-Phenyl-Phenoxy Catalysts,” filed January 26, 2024, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to olefin polymerization catalyst systems and processes and, more specifically, to heteroatom-bridged bis-phenyl-phenoxy catalyst systems for olefin polymerization.

BACKGROUND

[0003] Olefin-based polymers such as polyethylene and/or polypropylene are produced via various catalyst systems. Selection of such catalyst systems used in the polymerization process of the olefin-based polymers is an important factor contributing to the characteristics and properties of such olefin-based polymers.

[0004] Polyethylene and polypropylene are manufactured for a wide variety of articles. The polyethylene and polypropylene polymerization process can be varied in a number of respects to produce a wide variety of resultant polyethylene resins having different physical properties that render the various resins suitable for use in different applications. The ethylene monomers and optionally one or more co-monomers are present in liquid diluents (such as solvents), such as an alkane or isoalkane, for example isobutane. Hydrogen may also be added to the reactor. The catalyst systems for producing polyethylene may typically comprise a chromium-based catalyst system, a Ziegler–Natta catalyst system, and/or a molecular (either metallocene or non-metallocene molecular) catalyst system. The reactants in the diluent and the catalyst system are circulated at an elevated polymerization temperature around the reactor, thereby producing polyethylene homopolymer or copolymer. Either periodically or continuously, part of the reaction mixture, including the polyethylene product dissolved in the diluent, together with unreacted ethylene and one or more optional co-monomers, is

removed from the reactor. The reaction mixture when removed from the reactor may be processed to remove the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor serially connected to the first reactor where a second polyethylene fraction may be produced.

SUMMARY

[0005] Despite previous research efforts in developing catalyst systems suitable for olefin polymerization, such as polyethylene or polypropylene polymerization, there is still a need to increase the efficiencies of catalyst systems to reduce their cost-in-use, particularly without compromising other critical properties such as native molecular weight, comonomer incorporation, and solubility in alkane solvents. Previously reported heteroatom-bridged bis-phenyl-phenoxy catalyst systems are primarily directed to metal–ligand complexes containing silicon or germanium bridges wherein two isopropyl groups are bonded to the silicon or germanium atoms of the respective silicon or germanium bridges. However, after systematic investigation of the structure-performance relationship of germanium- or silicon-bridged bis-phenyl-phenoxy catalyst systems, it has now been found that the substituents on the silicon and germanium bridge atoms can have a tremendous impact on important properties of the catalyst systems, including but not limited to, catalyst activity, native molecular weight, comonomer incorporation, and solubility in alkane solvents. In fact, it has now been found that the catalyst efficiency can be significantly improved, e.g., by up to 2-3 times in some cases, by changing the isopropyl substituents to certain alkyl groups. Moreover, the enhanced activity achieved by the germanium- or silicon-bridged bis-phenyl-phenoxy catalyst systems described herein is obtained without compromising other critical properties such as native molecular weight, comonomer incorporation, and solubility in alkane solvents. Indeed, the native molecular weight, comonomer incorporation, and solubility in alkane solvents were either improved or maintained with most of the catalyst systems described herein.

[0006] Therefore, the catalyst systems described herein, and the polymerizations processes incorporating the same, allow for improved olefin polymerization processes with high catalyst efficiencies. The high catalyst efficiencies achieved by the catalyst systems described herein allow for a reduced catalyst cost-in-use, and therefore improve the commercial

potential for heteroatom-bridged bis-phenyl-phenoxy catalysts. Moreover, the catalyst systems described herein are particularly useful for the development of new low cost-in-use catalysts.

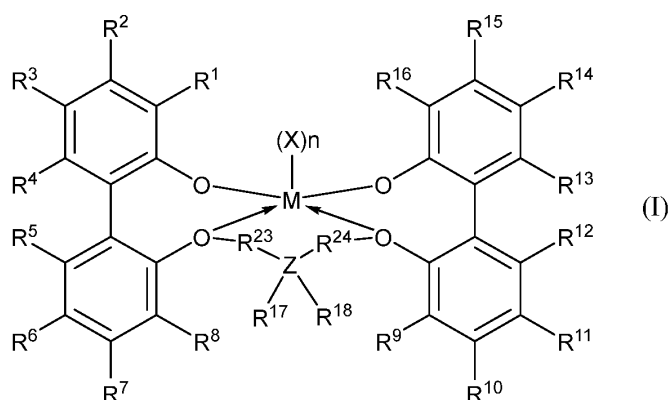
[0007] Additionally, it has been found that the catalyst systems described herein, and the polymerizations processes incorporating the same, may be used to produce ethylene/butene copolymers having a narrow short-chain branching distribution (SCBD) at high temperatures and high production rates. Existing catalyst systems used for ethylene/butene copolymerization are prone to produce ethylene/butene copolymers having broad SCBDs and increased high comonomer content (HCC) fractions when reactor configuration or process conditions deviate from the ideal case. In such circumstances, plants are forced to operate at reduced production rate and/or higher density target, causing reduced profit and/or inferior product performance.

[0008] Low density ethylene/ α -olefin copolymers such as ethylene/butene copolymers tend to block during storage and/or transportation. Specifically, for a polymer of a given density and melt index specification, a broader SCBD and higher HCC fraction can lead to pellet massing and poor materials handling. The HCC fraction indicates the weight fraction of a polymer sample made up by chains with high comonomer content and/or low molecular weight, and may be measured using thermal gradient interaction chromatography. In addition to poor solid handling performance, polymers with broader SCBD also often have higher oligomer and/or or BBB triads content that can negatively impact curing performance in a variety of applications. Accordingly, there is a need for improved catalyst systems and polymerization processes that produce copolymers with reduced HCC fractions and narrow SCBDs.

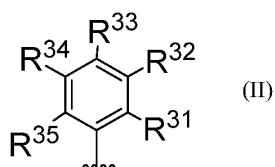
[0009] As indicated above, it has been surprisingly found that the catalyst systems described herein have excellent comonomer incorporation capabilities, a long half-life, and are able to produce ethylene/ α -olefin copolymers, such as ethylene/butene copolymers, with reduced HCC fractions, narrow SCBDs, low vinyl unsaturation, and low levels of BBB triads. This combination of features provides the copolymers with excellent curing response using peroxide as a curing agent, without sacrificing weatherability or durability typically seen in polymers with good curing achieved by high unsaturation levels. Moreover, the efficient comonomer incorporation exhibited by the catalyst systems described herein result in lower butene concentration post-reactor such that liquid-liquid and/or vapor-liquid equilibrium

issues can be avoided in the post-reactor heater, which may improve transition times between comonomer grades. The polymer stream would maintain one phase, thus allowing for efficient heat transfer in the post-reactor heater and higher production rates with minimum broadening of SCBD.

[0010] Embodiments of this disclosure include catalyst systems that include a metal–ligand complex according to formula (I):



[0011] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium; n is 1 or 2; when n is 1, X is a monodentate ligand or a bidentate ligand; when n is 2, each X is a monodentate ligand and is the same or different; the metal–ligand complex is overall charge-neutral; each Z is independently chosen from silicon or germanium; R¹ and R¹⁶ are radicals having formula (II):



[0012] In formula (II), each of R^{31–35} is independently chosen from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –OR^C, –SR^C, –CN, –CF₃, halogen, and –H.

[0013] In formula (I), each of R^{2–4}, R^{5–8}, R^{9–12}, and R^{13–15} is independently selected from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –N=CHR^C, –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)–, halogen, and –H; R¹⁷ and R¹⁸ are independently (C₅–C₄₀)hydrocarbyl; R²³ and R²⁴ are independently selected from –(CR^C)_m–,

where m is 1 or 2; and 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

[0014] The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, in which:

[0015] FIG. 1A graphically depicts thermal gradient interaction chromatography (TGIC) short chain branching distribution (SCBD) curves for a copolymer design wherein the melt index I_2 is approximately 0.26 dg/min, for an inventive example and a comparative example, according to one or more embodiments described in this disclosure;

[0016] FIG. 1B graphically depicts TGIC SCBD curves for another copolymer design wherein the melt index I_2 is approximately 5 dg/min, for an inventive example and a comparative example, according to one or more embodiments described in this disclosure;

[0017] FIG. 1C graphically depicts TGIC SCBD curves for another copolymer design wherein the melt index I_2 is approximately 1.2 dg/min, for an inventive example and a comparative example, according to one or more embodiments described in this disclosure;

[0018] FIG. 2 graphically depicts HCC value (wt%) versus density (g/cc) for the ethylene/1-butene copolymers produced in an ethylene/butene copolymerization study, according to one or more embodiments described in this disclosure;

[0019] FIG. 3 graphically depicts BBB Triads Content (BBB triads per 1000 carbon atoms) versus density (g/cc) for the ethylene/1-butene copolymers produced in the ethylene/butene copolymerization study, according to one or more embodiments described in this disclosure;

[0020] FIG. 4 graphically depicts Vinyl Content (vinyls per 1000 carbon atoms) versus density (g/cc) for the ethylene/1-butene copolymers produced in the ethylene/butene copolymerization study, according to one or more embodiments described in this disclosure; and

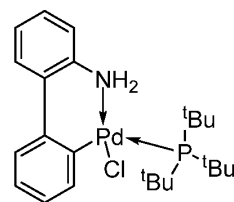
[0021] FIG. 5 depicts the extrapolation of the elution temperature for TGIC temperature calibration.

DETAILED DESCRIPTION

[0022] 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.

[0023] Common abbreviations are listed below:

[0024] **R, Z, M, X and n**: as defined above; **Me**: methyl; **Et**: ethyl; **Ph**: phenyl; **Bn**: benzyl; **i-Pr**: *iso*-propyl; **t-Bu**: *tert*-butyl; **t-Oct**: *tert*-octyl (2,4,4-trimethylpent-2-yl); **n-Oct**: *n*-octyl; **Ts**: toluene sulfonate; **THF**: tetrahydrofuran; **Et₂O**: diethyl ether; **MeOH**: methanol; **DMA**: dimethylacetamide; **DME**: dimethoxyethane; **CH₂Cl₂ or DCM**: dichloromethane; **CCl₄**: carbon tetrachloride; **EtOH**: ethanol; **CH₃CN**: acetonitrile; **EtOAc**: ethyl acetate; **C₆D₆**: deuterated benzene or benzene-*d*₆; **CDCl₃**: deuterated chloroform; **DMSO-*d*₆**: deuterated dimethylsulfoxide; **DBA**: dibenzylideneacetone; **PPh₃**:



triphenylphosphine; **tBu₃P**: tri-*t*-butylphosphine; **tBu₃P Pd G2**: ; **SiO₂**: silica gel; **Me₄Si**: tetramethylsilane; **NaOH**: sodium hydroxide; **HCl**: hydrochloric acid; **NaHCO₃**: sodium bicarbonate; **NaO*t*Bu**: sodium *tert*-butoxide; **K₃PO₄**: potassium phosphate tribasic; **brine**: saturated aqueous sodium chloride; **Na₂SO₄**: sodium sulfate; **MgSO₄**: magnesium sulfate; ***n*-BuLi**: *n*-butyllithium; **CuI**: copper(I) iodide; **Cs₂CO₃**: cesium carbonate; **HfCl₄**: hafnium(IV) chloride; **HfBn₄**: hafnium(IV) tetrabenzyl; **ZrCl₄**: zirconium(IV) chloride; **ZrBn₄**: zirconium(IV) tetrabenzyl; **N₂**: nitrogen gas; **PhMe**: toluene; **MAO**: methylaluminoxane; **MMAO**: modified methylaluminoxane; **PTFE**: polytetrafluoroethylene; **GC**: gas chromatography; **LC**: liquid chromatography; **NMR**: nuclear magnetic resonance; **HRMS**: high resolution mass spectrometry; **mmol**: millimoles; **mL**: milliliters; **M**: molar; **min**: minutes; **h**: hours; **d**: days; **equiv**: equivalents.

[0025] 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.). Use of the singular includes use of the plural and vice versa (e.g., a hexane solvent, includes

hexanes). A named R group will generally have the structure that is recognized in the art as corresponding to R groups having that name. These definitions are intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

[0026] The term “procatalyst” refers to a compound that has 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.

[0027] 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 version of a 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.

[0028] In some embodiments, each of the chemical groups (e.g., X, R, Z, etc.) of the metal-ligand complex of formula (I) may be unsubstituted, that is, can be defined without use of a substituent R^S, provided the above-mentioned conditions are satisfied. In other embodiments, at least one of the chemical groups of the metal ligand complex of formula (I) independently contain one or more of the substituents R^S. In most embodiments, there are not more than a total of 20 R^S, and in other embodiments, not more than a total of 10 R^S, and in some embodiments, not more than a total of 5 R^S in the metal ligand complex of formula (I). Where the compound contains two or more substituents R^S, each R^S independently is bonded to a same or different substituted chemical group. When two or more R^S are bonded to a same chemical group, they independently are bonded to a same or different carbon atom or

heteroatom in the same chemical group up to and including persubstitution of the chemical group.

[0029] The term “persubstitution” means each hydrogen atom (H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). The term “polysubstitution” means each of at least two, but not all, hydrogen atoms bonded to carbon atoms or heteroatoms of a corresponding unsubstituted compound or functional group are replaced by a substituent.

[0030] 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 mean the same thing.

[0031] The term “(C₁-C₄₀)hydrocarbyl” means a hydrocarbon radical of from 1 to 40 carbon atoms and the term “(C₁-C₄₀)hydrocarbylene” means a hydrocarbon diradical of from 1 to 40 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic, including bicyclic; 3 carbon atoms or more) or acyclic, and each hydrocarbon is unsubstituted or substituted by one or more R^S .

[0032] In this disclosure, a (C₁-C₄₀)hydrocarbyl may be an unsubstituted or substituted (C₁-C₄₀)alkyl, (C₃-C₄₀)cycloalkyl, (C₃-C₂₀)cycloalkyl-(C₁-C₂₀)alkylene, (C₆-C₄₀)aryl, or (C₆-C₂₀)aryl-(C₁-C₂₀)alkylene. Each of the aforementioned (C₁-C₄₀)hydrocarbyl groups has a maximum of 20 carbon atoms (i.e., (C₁-C₂₀)hydrocarbyl).

[0033] The terms “(C₁-C₄₀)alkyl” and “(C₁-C₁₈)alkyl” mean a saturated straight or branched hydrocarbon radical of from 1 to 40 carbon atoms or from 1 to 18 carbon atoms, respectively, that is unsubstituted or substituted by one or more R^S . Examples of unsubstituted (C₁-C₄₀)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” (with square brackets) 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, respectively.

Each (C₁–C₅)alkyl independently is methyl, trifluoromethyl, ethyl, 1-propyl, 2-propyl (also called 1-methylethyl and *iso*-propyl), or 1,1-dimethylethyl (also called *tert*-butyl).

[0034] The term “(C₆–C₄₀)aryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic aromatic hydrocarbon radical of from 6 to 40 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms, and the mono-, bi- or tricyclic radical comprises 1, 2 or 3 rings, respectively; wherein the 1 ring is aromatic and the 2 or 3 rings independently are fused or non-fused and at least one of the 2 or 3 rings is aromatic. Examples of unsubstituted (C₆–C₄₀)aryl are unsubstituted (C₆–C₂₀)aryl unsubstituted (C₆–C₁₈)aryl; 2-(C₁–C₅)alkyl-phenyl; 2,4-bis(C₁–C₅)alkyl-phenyl; phenyl; fluorenyl; tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; and phenanthrene. Examples of substituted (C₆–C₄₀)aryl are substituted (C₁–C₂₀)aryl; substituted (C₆–C₁₈)aryl; 2,4-bis[(C₂₀)alkyl]-phenyl; polyfluorophenyl; pentafluorophenyl; and fluoren-9-one-1-yl.

[0035] The term “(C₃–C₄₀)cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 40 carbon atoms that is unsubstituted or substituted by one or more R^S. Other cycloalkyl groups (e.g., (C₃–C₁₂)alkyl) are defined in an analogous manner as having from x to y carbon atoms and being either unsubstituted or substituted with one or more R^S. Examples of unsubstituted (C₃–C₄₀)cycloalkyl are unsubstituted (C₃–C₂₀)cycloalkyl, unsubstituted (C₃–C₁₀)cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C₃–C₄₀)cycloalkyl are substituted (C₃–C₂₀)cycloalkyl, substituted (C₃–C₁₀)cycloalkyl, cyclopentanone-2-yl, and 1-fluorocyclohexyl.

[0036] Examples of (C₁–C₄₀)hydrocarbylene include unsubstituted or substituted (C₆–C₄₀)arylene, (C₃–C₄₀)cycloalkylene, and (C₁–C₄₀)alkylene (e.g., (C₁–C₂₀)alkylene). In some embodiments, the diradicals are on the same carbon atom (e.g., –CH₂–) or on adjacent carbon atoms (i.e., 1,2- diradicals), or are spaced apart by one, two, or more than two intervening carbon atoms (e.g., respective 1,3-diradicals, 1,4-diradicals, etc.). Some diradicals include α,ω -diradical. The α,ω -diradical is a diradical that has maximum carbon backbone spacing between the radical carbons. Some examples of (C₂–C₂₀)alkylene α,ω -diradicals include ethan-1,2-diyl (i.e. –CH₂CH₂–), propan-1,3-diyl (i.e. –CH₂CH₂CH₂–), 2-

methylpropan-1,3-diyl (i.e. $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$). Some examples of $(\text{C}_6-\text{C}_{50})$ arylene α,ω -diradicals include phenyl-1,4-diyl, naphthalen-2,6-diyl, or naphthalen-3,7-diyl.

[0037] The term “ $(\text{C}_1-\text{C}_{40})$ alkylene” means a saturated straight chain or branched chain diradical (i.e., the radicals are not on ring atoms) of from 1 to 40 carbon atoms that is unsubstituted or substituted by one or more R^{S} . Examples of unsubstituted $(\text{C}_1-\text{C}_{50})$ alkylene are unsubstituted $(\text{C}_1-\text{C}_{20})$ alkylene, including unsubstituted $-\text{CH}_2\text{CH}_2-$, $-(\text{CH}_2)_3-$, $-(\text{CH}_2)_4-$, $-(\text{CH}_2)_5-$, $-(\text{CH}_2)_6-$, $-(\text{CH}_2)_7-$, $-(\text{CH}_2)_8-$, $-\text{CH}_2\text{C}^*\text{HCH}_3$, and $-(\text{CH}_2)_4\text{C}^*(\text{H})(\text{CH}_3)$, in which “C*” denotes a carbon atom from which a hydrogen atom is removed to form a secondary or tertiary alkyl radical. Examples of substituted $(\text{C}_1-\text{C}_{50})$ alkylene are substituted $(\text{C}_1-\text{C}_{20})$ alkylene, $-\text{CF}_2-$, $-\text{C}(\text{O})-$, and $-(\text{CH}_2)_{14}\text{C}(\text{CH}_3)_2(\text{CH}_2)_5-$ (i.e., a 6,6-dimethyl substituted normal-1,20-eicosylene). Since as mentioned previously two R^{S} may be taken together to form a $(\text{C}_1-\text{C}_{18})$ alkylene, examples of substituted $(\text{C}_1-\text{C}_{50})$ alkylene also include 1,2-bis(methylene)cyclopentane, 1,2-bis(methylene)cyclohexane, 2,3-bis(methylene)-7,7-dimethyl-bicyclo[2.2.1]heptane, and 2,3-bis(methylene)bicyclo[2.2.2]octane.

[0038] The term “ $(\text{C}_3-\text{C}_{40})$ cycloalkylene” means a cyclic diradical (i.e., the radicals are on ring atoms) of from 3 to 40 carbon atoms that is unsubstituted or substituted by one or more R^{S} .

[0039] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of heteroatoms include O, S, $\text{S}(\text{O})$, $\text{S}(\text{O})_2$, $\text{Si}(\text{R}^{\text{C}})_3$, $\text{P}(\text{R}^{\text{P}})$, $\text{N}(\text{R}^{\text{N}})$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $-\text{Ge}(\text{R}^{\text{C}})_2-$, or $-\text{Si}(\text{R}^{\text{C}})_2-$, where each R^{C} and each R^{P} is unsubstituted $(\text{C}_1-\text{C}_{18})$ hydrocarbyl or $-\text{H}$, and where each R^{N} is unsubstituted $(\text{C}_1-\text{C}_{18})$ hydrocarbyl. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms are replaced with a heteroatom. The term “ $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 50 carbon atoms, and the term “ $(\text{C}_1-\text{C}_{50})$ heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 50 carbon atoms. The heterohydrocarbon of the $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl or the $(\text{C}_1-\text{C}_{50})$ heterohydrocarbylene has one or more heteroatoms. The radical of the heterohydrocarbyl is on a carbon atom or a heteroatom, and diradicals of the heterohydrocarbyl may be on: (1) one or two carbon atom, (2) one or two heteroatoms, or (3) a carbon atom and a heteroatom. Each $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl and

(C₁–C₅₀)heterohydrocarbylene may be unsubstituted or substituted (by one or more R^S), aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic), or acyclic.

[0040] In some embodiments, the (C₁–C₄₀)heterohydrocarbyl independently is unsubstituted or substituted (C₁–C₄₀)heteroalkyl, (C₁–C₄₀)hydrocarbyl-O–, (C₁–C₄₀)hydrocarbyl-S–, (C₁–C₄₀)hydrocarbyl-S(O)–, (C₁–C₄₀)hydrocarbyl-S(O)₂–, (C₁–C₄₀)hydrocarbyl-Si(R^C)₂–, (C₁–C₄₀)hydrocarbyl-N(R^N)–, (C₁–C₄₀)hydrocarbyl-P(R^P)–, (C₂–C₄₀)heterocycloalkyl, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)alkylene, (C₃–C₂₀)cycloalkyl-(C₁–C₁₉)heteroalkylene, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)heteroalkylene, (C₁–C₄₀)heteroaryl, (C₁–C₁₉)heteroaryl-(C₁–C₂₀)alkylene, (C₆–C₂₀)aryl-(C₁–C₁₉)heteroalkylene, or (C₁–C₁₉)heteroaryl-(C₁–C₂₀)heteroalkylene.

[0041] The term “heteroaromatic hydrocarbon” means an aromatic hydrocarbon molecule or molecular framework in which one to four carbon atoms are replaced with heteroatoms. The term “(C₄–C₅₀)heteroaryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic heteroaromatic hydrocarbon radical of from 4 to 50 total carbon atoms, and the mono-, bi- or tricyclic radical comprises 1, 2 or 3 rings, respectively, wherein the 2 or 3 rings independently are fused or non-fused and at least one of the 2 or 3 rings is heteroaromatic. Other heteroaryl groups (e.g., (C_x–C_y)heteroaryl generally, such as (C₄–C₁₂)heteroaryl) are defined in an analogous manner as having from x to y carbon atoms (such as 4 to 12 carbon atoms) and being unsubstituted or substituted by one or more than one R^S. The monocyclic heteroaromatic hydrocarbon radical is a 5-membered or 6-membered ring. The 5-membered ring has from 1 to 4 carbon atoms and from 4 to 1 heteroatoms, each heteroatom being O, S, N, or P. Examples of 5-membered ring heteroaromatic hydrocarbon radical are pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; and tetrazol-5-yl. The 6-membered ring has 4 or 5 carbon atoms and 2 or 1 heteroatoms, the heteroatoms being N or P. Examples of 6-membered ring heteroaromatic hydrocarbon radical are pyridine-2-yl; pyrimidin-2-yl; and pyrazin-2-yl. The bicyclic heteroaromatic hydrocarbon radical can be a fused 5,6- or 6,6-ring system. Examples of the fused 5,6-ring system bicyclic heteroaromatic hydrocarbon radical are indol-1-yl; and benzimidazole-1-yl. Examples of the fused 6,6-ring system

bicyclic heteroaromatic hydrocarbon radical are quinolin-2-yl; and isoquinolin-1-yl. The tricyclic heteroaromatic hydrocarbon radical can be a fused 5,6,5-; 5,6,6-; 6,5,6-; or 6,6,6-ring system. An example of the fused 5,6,5-ring system is 1,7-dihydropyrrolo[3,2-f]indol-1-yl. An example of the fused 5,6,6-ring system is 1H-benzo[f] indol-1-yl. An example of the fused 6,5,6-ring system is 9H-carbazol-9-yl. An example of the fused 6,6,6-ring system is acrydin-9-yl.

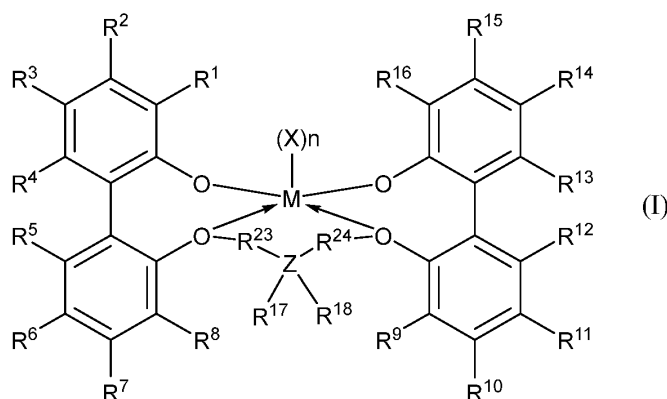
[0042] The aforementioned heteroalkyl may be saturated straight or branched chain radicals containing (C₁–C₅₀) carbon atoms, or fewer carbon atoms and one or more of the heteroatoms. Likewise, the heteroalkylene may be saturated straight or branched chain diradicals containing from 1 to 50 carbon atoms and one or more than one heteroatoms. The heteroatoms, as defined above, may include Si(R^C)₃, Ge(R^C)₃, Si(R^C)₂, Ge(R^C)₂, P(R^P)₂, P(R^P), N(R^N)₂, N(R^N), N, O, OR^C, S, SR^C, S(O), and S(O)₂, wherein each of the heteroalkyl and heteroalkylene groups are unsubstituted or substituted by one or more R^S.

[0043] Examples of unsubstituted (C₂–C₄₀)heterocycloalkyl are unsubstituted (C₂–C₂₀)heterocycloalkyl, unsubstituted (C₂–C₁₀)heterocycloalkyl, aziridin-1-yl, oxetan-2-yl, tetrahydrofuran-3-yl, pyrrolidin-1-yl, tetrahydrothiophen-S,S-dioxide-2-yl, morpholin-4-yl, 1,4- dioxan-2-yl, hexahydroazepin-4-yl, 3-oxa-cyclooctyl, 5-thio-cyclononyl, and 2-aza-cyclodecyl.

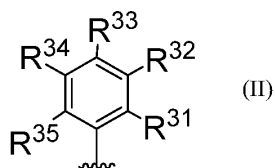
[0044] The term “halogen atom” or “halogen” means the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means anionic form of the halogen atom: fluoride (F[−]), chloride (Cl[−]), bromide (Br[−]), or iodide (I[−]).

[0045] 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 and/or triple bonds optionally may or may not be present in substituents R^S. The term “unsaturated” means containing one or more carbon–carbon double bonds, carbon–carbon triple bonds, or (in heteroatom-containing groups) one or more carbon–nitrogen, carbon–phosphorous, or carbon–silicon double bonds, not including any such double bonds that may be present in substituents R^S, if any, or in (hetero) aromatic rings, if any.

[0046] Embodiments of this disclosure include catalyst systems that include a metal–ligand complex according to formula (I):



[0047] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium; n is 1 or 2; when n is 1, X is a monodentate ligand or a bidentate ligand; when n is 2, each X is a monodentate ligand and is the same or different; the metal–ligand complex is overall charge-neutral; each Z is independently chosen from silicon or germanium; R¹ and R¹⁶ are radicals having formula (II):



[0048] In formula (II), each of R^{31–35} is independently chosen from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –OR^C, –SR^C, –CN, –CF₃, halogen, and –H.

[0049] In formula (I), each of R^{2–4}, R^{5–8}, R^{9–12}, and R^{13–15} is independently selected from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –N=CHR^C, –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)–, halogen, and –H; R¹⁷ and R¹⁸ are independently (C₅–C₄₀)hydrocarbyl; R²³ and R²⁴ are independently selected from –(CR^C)_m–, where m is 1 or 2; and each R^C, R^P, and R^N is independently a (C₁–C₃₀)hydrocarbyl, (C₁–C₃₀)heterohydrocarbyl, or –H.

[0050] It has been surprisingly found that when the R¹⁷ and R¹⁸ of formula (I) are independently (C₅–C₄₀)hydrocarbyl and R¹ and R¹⁶ are radicals having formula (II),

improved catalyst efficiency may be achieved without compromising other critical properties such as native molecular weight, comonomer incorporation, and solubility in alkane solvents. That is, when R^1 and R^{16} are radicals having formula (II), the catalyst efficiency impact of R^{17} and R^{18} being independently (C_5-C_{40}) hydrocarbyl is believed to be more significant than when R^1 and R^{16} are radicals having structure other than formula (II), particularly when M is zirconium.

[0051] In some embodiments of the metal–ligand complex of formula (I), R^{17} and R^{18} are independently (C_5-C_{20}) alkyl. In some embodiments, R^{17} and R^{18} are pentyl, hexyl, heptyl, octyl, or nonyl. In some embodiments, R^{17} and R^{18} are pentan-3-yl.

[0052] In some embodiments, R^{17} and R^{18} are independently (C_5-C_{20}) cycloalkyl. In some embodiments, R^{17} and R^{18} are cyclopentyl, cyclohexyl, cycloheptyl, or bicyclo[2.2.1]heptyl.

[0053] In some embodiments, R^{17} and R^{18} are connected to form a ring structure having at least 5 carbon atoms. In some embodiments, R^{17} and R^{18} are connected to form a ring structure having five carbon atoms, six carbon atoms, or seven carbon atoms.

[0054] In some embodiments of the metal–ligand complex of formula (I), R^6 and R^{11} are independently (C_2-C_{12}) alkyl. In some embodiments, R^6 and R^{11} are *tert*-butyl.

[0055] In some embodiments of the metal–ligand complex of formula (I), at least one of R^1 and R^{16} is a radical having formula (II), wherein R^{32} and R^{34} are *tert*-butyl.

[0056] In some embodiments of the metal–ligand complex of formula (I), R^3 and R^{14} are independently (C_1-C_{12}) alkyl. In some embodiments, R^3 and R^{14} are independently *tert*-octyl, *n*-octyl, or methyl.

[0057] In some embodiments of the metal–ligand complex of formula (I), R^8 and R^9 are $-H$.

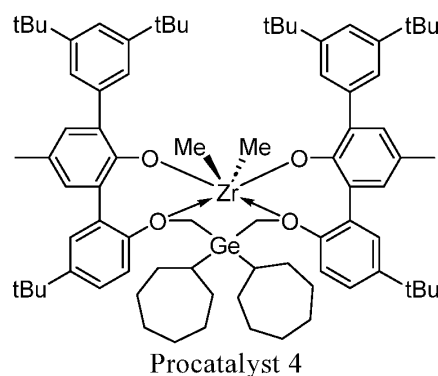
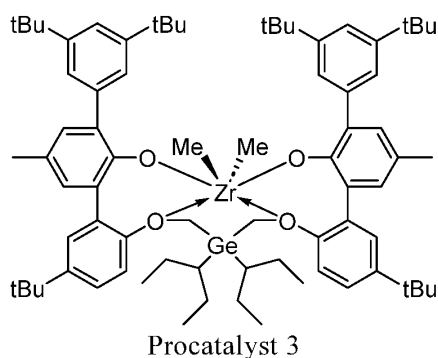
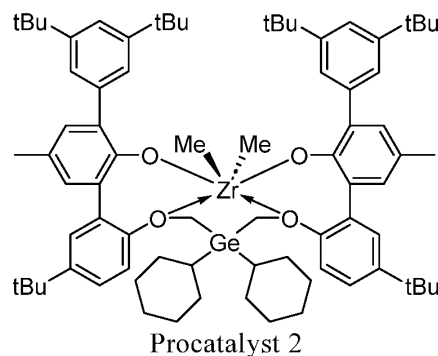
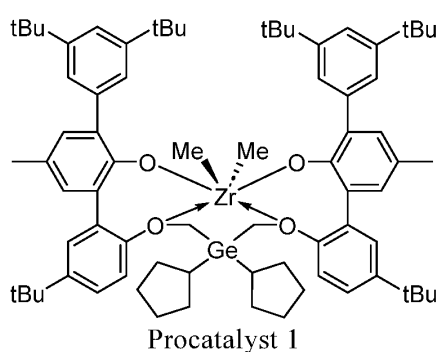
[0058] In some embodiments of the metal–ligand complex of formula (I), R^7 and R^{10} are halogen. In some embodiments of the metal–ligand complex of formula (I), R^5 and R^{12} are halogen. In some embodiments of the metal–ligand complex of formula (I), R^5 , R^7 , R^{10} , and R^{12} are halogen.

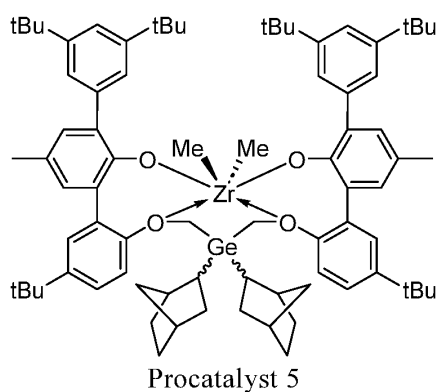
[0059] In some embodiments of the metal–ligand complex of formula (I), each X is a ligand independently chosen from (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-CH_2Si(R^C)_3-Q(OR^C)_Q$, $-Si(R^C)_3-Q(OR^C)_Q$, $-OSi(R^C)_3-Q(OR^C)_Q$, $-CH_2Ge(R^C)_3-Q(OR^C)_Q$, $-Ge(R^C)_3-Q(OR^C)_Q$, $-P(R^C)_{2-w}(OR^C)_w$, $-P(O)(R^C)_{2-w}(OR^C)_w$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^CSi(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-CN$, $-CF_3$, and halogen, wherein each R^C

is independently a substituted or unsubstituted (C_1 – C_{30})hydrocarbonyl, or a substituted or unsubstituted (C_1 – C_{30})heterohydrocarbonyl, each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2.

[0060] In some embodiments of the metal–ligand complex of formula (I), R^6 , R^7 , R^{10} , and R^{11} are not halogen. Without wishing to be bound by theory, it is believed that R^6 , R^7 , R^{10} , and R^{11} not being halogen may, in some embodiments, in combination with R^{17} and R^{18} being independently (C_5 – C_{40})hydrocarbonyl and R^1 and R^{16} being radicals having formula (II), result in improved catalyst efficiency without compromising other critical properties such as native molecular weight, and solubility in alkane solvents. Without wishing to be bound by theory, the presence of halogen in these positions is believed to be good for comonomer incorporation but detrimental for activity (resulting in increased cost-in-use), particularly when R^6 and R^{11} are halogen.

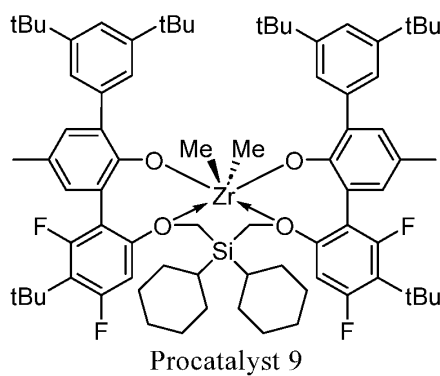
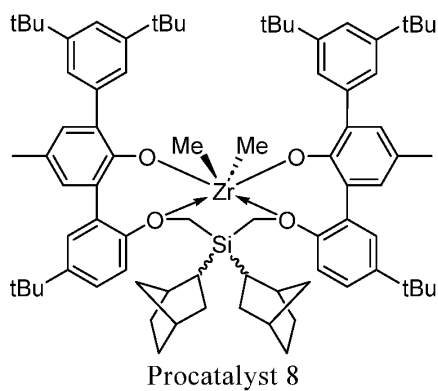
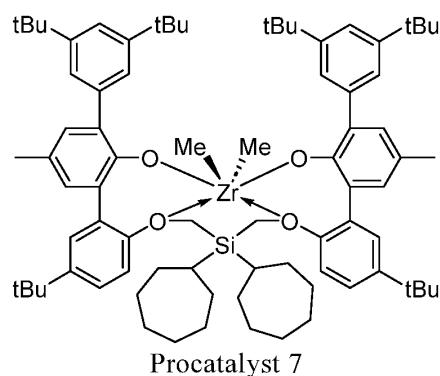
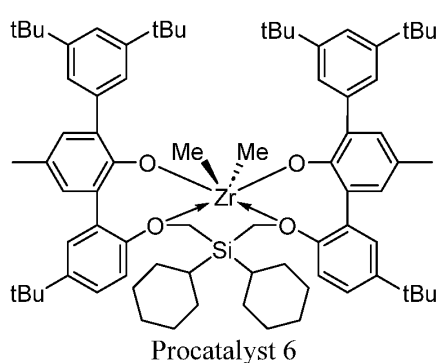
[0061] In specific embodiments of catalyst systems, the metal–ligand complex according to formula (I) may include, without limitation, a complex having the structure of any of Procatalysts 1–5:





[0062] Each of the metal–ligand complexes of Procatalysts 1–5 contains a germanium bridge that covalently connects one oxygen atom to another oxygen atom. Each substituent R^{17} and R^{18} of the metal–ligand complexes of Procatalysts 1–5 is independently (C_5-C_{40}) hydrocarbonyl.

[0063] In specific embodiments of catalyst systems, the metal–ligand complex according to formula (I) may include, without limitation, a complex having the structure of any of Procatalysts 6–9:



[0064] Each of the metal–ligand complexes of Procatalysts 6–9 contains a silicon bridge that covalently connects one oxygen atom to another oxygen atom. Each substituent R¹⁷ and R¹⁸ of the metal–ligand complexes of Procatalysts 6–9 is independently (C₅–C₄₀)hydrocarbyl.

[0065] Procatalyst Activation

[0066] The catalyst systems of this disclosure include a metal–ligand complex according to formula (I). The metal–ligand complex according to formula (I) may be in a catalytically active form or in a procatalyst form that is catalytically inactive or is at least substantially less catalytically active than the catalytically active form. The Procatalysts 1–9 are catalytically inactive forms of various metal–ligand complexes according to formula (I). The procatalyst system comprising the metal–ligand complex of formula (I) in a procatalyst form may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the metal–ligand complex to, or combining the metal–ligand complex with, an activating co-catalyst. Another example of a suitable activating technique includes bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. Subjecting a metal–ligand complex according to formula (I) in a procatalyst form to any of such activating techniques results in a catalytically activated form of the metal–ligand complex according to formula (I). In some embodiments, the catalytically activated form of the metal–ligand complex according to formula (I) may be the result of cleaving at least one X from the procatalyst form of the metal–ligand complex according to formula (I) by any of the foregoing activation techniques.

[0067] Co-Catalyst Component

[0068] In embodiments of the present disclosure, the catalyst system may include a co-catalyst component. 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 procatalyst according Formula (I) may be rendered catalytically active by contacting the procatalyst to, or combining the procatalyst with, one or more activating co-catalysts (also referred to herein as an “activators”). Additionally, the metal–ligand complex of formula (I) includes both a procatalyst form, which is neutral, and a catalytic form, which may be positively charged due

to the loss of a monoanionic ligand, such as benzyl or phenyl. Suitable activating co-catalysts for use herein include, but are not limited to: alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); modified alkyl aluminoxanes; hydrocarbyl-modified methylaluminoxanes; neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, hydrocarbyl-modified methylaluminoxane (e.g., MMAO-7), and isobutylalumoxane.

[0069] Lewis acid activators (co-catalysts) include Group 13 metal compounds containing from 1 to 3 (C₁–C₂₀)hydrocarbyl substituents as described herein. In one embodiment, Group 13 metal compounds are tri((C₁–C₂₀)hydrocarbyl)-substituted-aluminum, tri((C₁–C₂₀)hydrocarbyl)-boron compounds, tri((C₁–C₁₀)alkyl)aluminum, tri((C₆–C₁₈)aryl)boron compounds, and halogenated (including perhalogenated) derivatives thereof. In further embodiments, Group 13 metal compounds are tris(fluoro-substituted phenyl)boranes, tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tetrakis((C₁–C₂₀)hydrocarbyl) borate or a tri((C₁–C₂₀)hydrocarbyl)ammonium tetrakis((C₁–C₂₀)hydrocarbyl)borate (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borate). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁–C₂₀)hydrocarbyl)₄N⁺, a ((C₁–C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁–C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁–C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁–C₂₀)hydrocarbyl, when two or more are present, may be the same or different.

[0070] Combinations of neutral Lewis acid activators (co-catalysts) include mixtures comprising a combination of a tri((C₁–C₄)alkyl)aluminum and a halogenated tri((C₆–C₁₈)aryl)boron compound, especially a tris(pentafluorophenyl)borane. Other embodiments are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane. Ratios of numbers of moles of (metal–ligand complex) : (tris(pentafluoro-phenyl)borane): (alumoxane) [e.g.,

(Group 4 metal–ligand complex) : (tris(pentafluoro-phenylborane):(alumoxane)] are from 1:1:1 to 1:10:100, in other embodiments, from 1:1:1.5 to 1:5:30.

[0071] The catalyst system comprising the metal–ligand complex of formula (I) may be activated to form an active catalyst composition by combination with one or more co-catalysts, for example, a cation forming co-catalyst, a strong Lewis acid, or combinations thereof. Suitable activating co-catalysts include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to: modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl tetrakis(pentafluorophenyl)borate(1^-) amine (i.e. $[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$), and combinations of both.

[0072] In some embodiments, one or more of the foregoing activating co-catalysts are used in combination with each other. An especially preferred combination is a mixture of a tri((C_1 – C_4)hydrocarbyl)aluminum, tri((C_1 – C_4)hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound. The ratio of total number of moles of one or more metal–ligand complexes of formula (I) to total number of moles of one or more of the activating co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some other embodiments, at least 1:1000; and 10:1 or less, and in some other embodiments, 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, preferably the number of moles of the alumoxane that are employed is at least 100 times the number of moles of the metal–ligand complex of formula (I). When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, in some other embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal–ligand complexes of formula (I) from 0.5:1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal–ligand complexes of formula (I).

[0073] In one or more embodiments, the catalyst systems described herein comprise a metal–ligand complex according to formula (I) and a hydrocarbyl-modified methylaluminoxane. 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 may include 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 ETM as demonstrated in U.S. Patent No. 5,777,143. Modified methylaluminoxane compositions are generically disclosed and can be prepared as described in U.S. Patent Nos. 5,066,631 and 5,728,855, both of which are incorporated herein by reference in their entirety.

[0074] In some embodiments of the catalyst systems and processes described herein, the hydrocarbyl-modified methylaluminoxane may have 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 $AlR_1R_2R_3$, where R_1 , R_2 , and R_3 are independently (C_1-C_{40}) alkyl.

[0075] In some embodiments of the catalyst systems and processes described herein, the hydrocarbyl-modified methylaluminoxane has greater than 5 mole percent and less than 20 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.

[0076] In some embodiments, the trihydrocarbyl aluminum has a formula of $AlR_1R_2R_3$, where R_1 , R_2 , and R_3 are independently (C_1-C_{10}) alkyl. In one or more

embodiments, *RAI*, *RBI*, and *RCI* are independently methyl, ethyl, propyl, 2-propyl, butyl, *tert*-butyl, or octyl. In some embodiments, *RAI*, *RBI*, and *RCI* are the same. In other embodiments, at least one of *RAI*, *RBI*, and *RCI* is different from at least another of *RAI*, *RBI*, and *RCI*.

[0077] Polyolefins

[0078] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene and propylene. 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, ethylidene norbornene. 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.

[0079] 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 at least 50 percent by weight of units derived from ethylene. All individual values and subranges encompassed by “from at least 50 weight 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 percent by weight of units derived from ethylene; at least 70 percent by weight of units derived from ethylene; at least 80 percent by weight of units derived from ethylene; or from 50 to 100 percent by weight of units derived from ethylene; or from 80 to 100 percent by weight of units derived from ethylene.

[0080] In some embodiments, the ethylene-based polymers may comprise at least 50 percent by moles of 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 percent by moles of units derived from

ethylene; at least 96 percent by moles of units; at least 97 percent by moles of units derived from ethylene; or in the alternative, from 90 to 100 percent by moles of units derived from ethylene; from 90 to 99.5 percent by moles of units derived from ethylene; or from 97 to 99.5 percent by moles of units derived from ethylene.

[0081] In some embodiments of the ethylene-based polymer, the amount of additional α -olefin is less than 50%; other embodiments include at least 1 mole percent (mol%) to 20 mol%; and in further embodiments the amount of additional α -olefin includes at least 5 mol% to 10 mol%. In some embodiments, the additional α -olefin is 1-octene.

[0082] In some embodiments, the additional α -olefin co-monomers include 1-butene and the ethylene-based polymer is an ethylene/1-butene interpolymer, e.g., an ethylene/1-butene copolymer, wherein the ethylene-based polymer comprises from 20 wt% to 40 wt% units derived from 1-butene, based on a total weight of the ethylene-based polymer. In some embodiments, the ethylene-based polymer comprises from 22 wt% to 40 wt% units derived from 1-butene, from 22 wt% to 38 wt% units derived from 1-butene, from 24 wt% to 38 wt% units derived from 1-butene, from 24 wt% to 36 wt% units derived from 1-butene, from 26 wt% to 36 wt% units derived from 1-butene, from 26 wt% to 34 wt% units derived from 1-butene, from 28 wt% to 34 wt% units derived from 1-butene, from 28 wt% to 33 wt% units derived from 1-butene, or from 29 wt% to 33 wt% units derived from 1-butene, based on a total weight of the ethylene-based polymer.

[0083] 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, gas phase polymerization processes, slurry phase polymerization processes, and combinations thereof using one or more conventional reactors such as loop reactors, isothermal reactors, fluidized bed gas phase reactors, stirred tank reactors, continuously stirred-tank reactors, batch reactors, and combinations thereof in parallel or in series.

[0084] 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. 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.

[0085] In some embodiments, the polymerization process for producing an ethylene-based polymer includes polymerizing ethylene and at least one additional α -olefin in the presence of a catalyst system. In one or more embodiments, the catalyst system may include the metal–ligand complex according to formula (I) in its catalytically active form without a co-catalyst or an additional catalyst. In further embodiments, the catalyst system may include the metal–ligand complex according to formula (I) in its procatalyst form, its catalytically active form, or a combination of both forms, in combination with at least one co-catalyst. In further embodiments, the catalyst system may include the metal–ligand complex according to formula (I) in its procatalyst form in combination with at least one co-catalyst and at least one additional catalyst. In further embodiments, the catalyst system may include a first catalyst and at least one additional catalyst, and, optionally, at least one co-catalyst, where the first catalyst is a metal–ligand complex according to formula (I) in its catalytically active form.

[0086] 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.

[0087] In some embodiments, a polymerization process for producing an ethylene-based polymer may include polymerizing ethylene and optionally a $(\text{C}_3\text{--C}_{12})\alpha$ -olefin in the presence of a catalyst system, wherein the catalyst system incorporates at least one metal–ligand complex of formula (I). In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.850 g/cm^3 to 0.970 g/cm^3 measured according to ASTM D792 (incorporated herein by reference in its entirety); a melt flow ratio (I_{10}/I_2) from 5-15, where melt index I_2 is measured according to ASTM D1238 (incorporated herein by reference in its entirety) at $190\text{ }^\circ\text{C}$ and 2.16 kg load, and melt index I_{10} is measured according to ASTM D1238 at $190\text{ }^\circ\text{C}$ and 10 kg load; and a molecular weight distribution (MWD) from 1 to 5, where MWD is a ratio of weight average molecular weight to number average molecular weight.

[0088] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.850 g/cm^3 to 0.970 g/cm^3 , from 0.880 g/cm^3 to 0.920 g/cm^3 , from 0.880 g/cm^3 to 0.910 g/cm^3 , or from 0.880 g/cm^3 to 0.900 g/cm^3 , measured according to ASTM D792. In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.850 g/cm^3 to 0.880 g/cm^3 , from 0.854 g/cm^3 to 0.880 g/cm^3 , from 0.854 g/cm^3 to 0.875 g/cm^3 , from 0.856 g/cm^3 to 0.875 g/cm^3 , from 0.856 g/cm^3 to 0.872 g/cm^3 , from 0.858 g/cm^3 to 0.872 g/cm^3 , from 0.858 g/cm^3 to 0.870 g/cm^3 , from 0.858 g/cm^3 to 0.868 g/cm^3 , from 0.860 g/cm^3 to 0.868 g/cm^3 , or from 0.860 g/cm^3 to 0.866 g/cm^3 , measured according to ASTM D792.

[0089] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a weight average molecular weight M_w from 50 kg/mol to 200 kg/mol, such as, for example, from 50 kg/mol to 190 kg/mol, from 55 kg/mol to 190 kg/mol, from 55 kg/mol to 180 kg/mol, from 60 kg/mol to 180 kg/mol, from 60 kg/mol to 170 kg/mol, from 65 kg/mol to 170 kg/mol, from 65 kg/mol to 160 kg/mol, from 70 kg/mol to 160 kg/mol, or from 70 kg/mol to 150 kg/mol. In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.854 g/cm³ to 0.875 g/cm³ and a weight average molecular weight from 50 kg/mol to 200 kg/mol. In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.854 g/cm³ to 0.875 g/cm³ and a weight average molecular weight from 70 kg/mol to 150 kg/mol.

[0090] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a melt index I_2 from 0.1 dg/min to 30 dg/min, from 0.1 dg/min to 25 dg/min, from 0.1 dg/min to 30 dg/min, from 0.1 dg/min to 20 dg/min, from 0.1 dg/min to 15 dg/min, from 0.1 dg/min to 10 dg/min, from 0.2 dg/min to 10 dg/min, from 0.1 dg/min to 9 dg/min, from 0.2 dg/min to 9 dg/min, from 0.1 dg/min to 8 dg/min, from 0.2 dg/min to 8 dg/min, from 0.1 dg/min to 7 dg/min, from 0.2 dg/min to 7 dg/min, from 0.1 dg/min to 6 dg/min, from 0.15 dg/min to 6 dg/min, or from 0.2 dg/min to 6 dg/min, measured in accordance with ASTM D1238. In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.854 g/cm³ to 0.875 g/cm³ and a melt index I_2 from 0.1 to 30 dg/min. In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a density from 0.854 g/cm³ to 0.875 g/cm³ and a melt index I_2 from 0.1 to 10 dg/min.

[0091] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a melt flow ratio (I_{10}/I_2) from 5 to 15, from 5 to 10, or from 5 to 9.

[0092] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a molecular weight distribution (MWD) from 1 to 10, from 1 to 7, from 1 to 6, from 1 to 5, from 1 to 4, from 1 to 3.5, from 1.5 to 3, or from 1.5 to 2.5.

[0093] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have an HCC value of less than or equal to 3.0 wt%, less than or equal to 2.8 wt%, less than or equal to 2.4 wt%, less than or equal to 2.2 wt%, less than or equal to 2.0 wt%, less than or equal to 1.8 wt%, less than or equal to 1.6 wt%, less than or equal to 1.4 wt%, or less than or equal to 1.2 wt%, measured in accordance with the HCC Measurement Method described herein.

[0094] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a BBB triads content of less than or equal to 0.0075 BBB triads per 1000 carbons, or less than or equal to 0.007 BBB triads per 1000 carbons, measured in accordance with the BBB Triads Measurement Method described herein.

[0095] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a low vinyl unsaturation as demonstrated by having less than or equal to 0.01 vinyls per 1000 carbons. In some embodiments, the polymer resulting from polymerization processes and catalyst systems of the present disclosure may have less than or equal to 0.009 vinyls per 1000 carbons, or less than or equal to 0.008 vinyls per 1000 carbons, measured in accordance with the Vinyl Content Measurement Method described herein.

[0096] In some embodiments, the ethylene-based polymers of the present disclosure, including those resulting from the polymerization processes and catalyst systems described herein, may have a total unsaturation of less than or equal to 0.1 unsaturations per 1000 carbons, less than or equal to 0.09 unsaturations per 1000 carbons, less than or equal to 0.08 unsaturations per 1000 carbons, or less than or equal to 0.075 unsaturations per 1000 carbons, measured in accordance with the Total Unsaturation Measurement Method described herein.

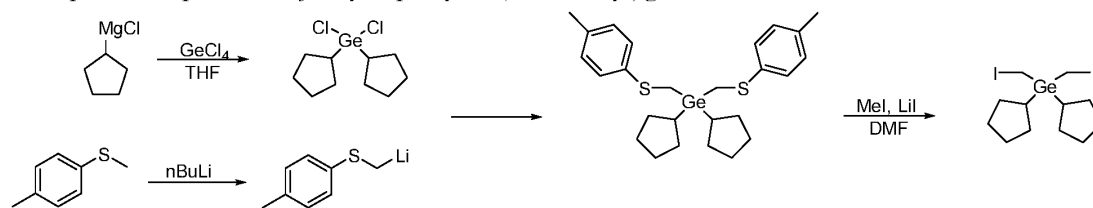
[0097] Embodiments of the catalyst systems described herein allow for improved olefin polymerization processes with high catalyst efficiencies. The high catalyst efficiencies achieved by the catalyst systems described herein allow for a reduced catalyst cost-in-use, which improves the commercial potential for heteroatom-bridged bis-phenyl-phenoxy catalysts. Moreover, the catalyst systems described herein demonstrate enhanced catalyst activity without compromising other critical properties such as native molecular weight, comonomer incorporation, and solubility in alkane solvents. Indeed, the native molecular weight, comonomer incorporation, and solubility in alkane solvents were either improved or maintained with most of the catalyst systems described herein.

[0098] Additionally, the catalyst systems described herein are able to produce ethylene/ α -olefin copolymers, such as ethylene/butene copolymers, with reduced HCC fractions, narrow SCBDs, low vinyl unsaturation, and low levels of BBB triads. This combination of features provides the copolymers with excellent curing response using peroxide as a curing agent, without sacrificing weatherability or durability typically seen in polymers with good curing achieved by high unsaturation levels.

[0099] One or more features of the present disclosure are illustrated in view of the examples as follows:

EXAMPLES

Example 1: Preparation of dicyclopentylbis(iodomethyl)germane



[0100] In a glove box, a 40 mL vial under nitrogen was charged with GeCl_4 (2.16 g, 10 mmol, 1.0 equiv) and dried THF (20 mL), and then cooled down to $-30\text{ }^\circ\text{C}$. Cyclopentylmagnesium chloride solution in diethyl ether (2 M, 10.5 mL, 21 mmol, 2.1 equiv) was added dropwise to the pre-cooled solution. The reaction was kept for 30 mins at $-30\text{ }^\circ\text{C}$ then slowly warmed up to room temperature. The reaction mixture was filtered to remove the precipitate (rinsed with hexane). The filtrate was concentrated, diluted with ether, and then

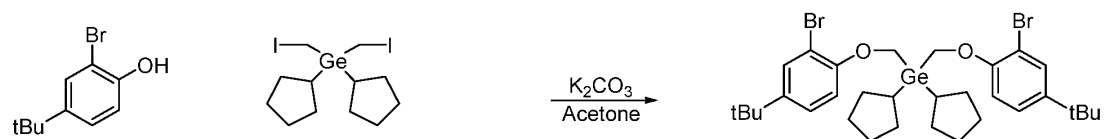
filtered. The process was repeated several times to remove Mg salts. The product was used for the next step without further purification.

[0101] A n-BuLi solution in hexanes (2.5 M, 8.4 mL, 21 mmol, 2.1 equiv) was added dropwise to a solution of methyl p-tolyl thioether (3.18 g, 23 mmol, 2.3 equiv) in THF (20 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 hour then slowly warmed up to room temperature for 2 hours. The resulting solution was added dropwise to a pre-cooled solution of dichlorodicyclopentylgermane prepared previously in THF (10 mL) at -10 °C to 0 °C. After 30 mins, MeOH (2 mL) was added to quench the reaction, diluted with ether (250 mL), and washed with brine. The organic layer was dried over MgSO₄, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 → 50/50) as the eluent. A yield of 2.6 g of a colorless oil was collected, providing a 53% yield.

[0102] In a glove box, an 8 mL arc sphere was charged with dicyclopentylbis((p-tolylthio)methyl)germane (0.973 g, 2.0 mmol, 1.0 equiv), LiI (0.268 g, 2.0 mmol, 1.0 equiv), MeI (3.0 mL, 48.0 mmol, 24.0 equiv), and DMF (2 mL), and then sealed and taken out of glove box. The reaction mixture was stirred at 120 °C for 24 hours. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel (rinsed with DCM). Solvents were removed under reduced pressure and the residue was purified by column chromatography using pentane/ether (100/0 → 80/20) as the eluent affording a light tan oil. A yield of 0.34 g was collected, providing a 34% yield.

[0103] ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 4H), 2.00 – 1.89 (m, 4H), 1.71 – 1.60 (m, 4H), 1.58 – 1.43 (m, 10H).

Example 2: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclopentylgermane

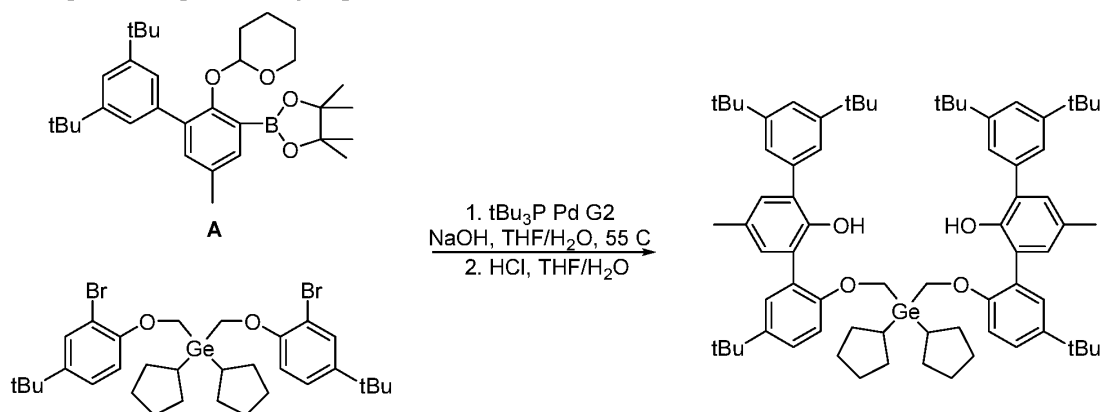


[0104] In a glove box, a 40 mL vial was charged with dicyclopentylbis(iodomethyl)germane (0.34 g, 0.69 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (0.474 g, 2.1 mmol, 3.0 equiv), K₂CO₃ (0.381 g, 2.76 mmol, 4.0 equiv), and acetone (2 mL). The reaction mixture was stirred at 65 °C overnight. After cooling down to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified

by column chromatography using ether/hexane (0/100 → 30/70) as the eluent. A yield of 0.44 g was collected, providing a 92% yield.

[0105] ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 2.4 Hz, 2H), 7.24 – 7.22 (m, 2H), 6.98 (dd, J = 8.7, 2.1 Hz, 2H), 4.11 (s, 4H), 2.01 – 1.92 (m, 4H), 1.68 – 1.58 (m, 10H), 1.54 – 1.48 (m, 4H), 1.27 (s, 18H).

Example 3: Preparation of Ligand 1



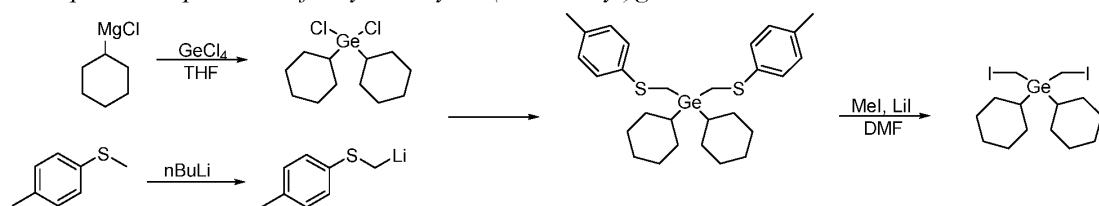
[0106] In a glove box, a 40 mL vial equipped with stir bars was charged with compound A (0.962 g, 1.9 mmol, 3.0 equiv, purchased from Boulder Scientific), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclopentylgermane (0.44 g, 0.63 mmol, 1.0 equiv), tBu_3P Pd G2 (0.01 g, 0.02 mmol, 0.03 equiv), THF (2 mL), and aqueous NaOH solution (4 M, 0.95 mL, 3.8 mmol, 6.0 equiv). The vial was heated under nitrogen at 55 °C overnight. 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. A yield of 0.51 g of a white solid was collected, providing a 72% yield.

[0107] ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, J = 1.8 Hz, 2H), 7.36 (d, J = 1.8 Hz, 4H), 7.31 (d, J = 2.6 Hz, 2H), 7.22 (dd, J = 8.6, 2.6 Hz, 2H), 7.11 (d, J = 2.3 Hz, 2H), 6.95 (d, J = 2.2, 2H), 6.71 (d, J = 8.6 Hz, 2H), 5.54 (s, 2H), 3.80 (s, 4H), 2.33 (s, 6H), 1.48 – 1.41 (m, 4H), 1.33 (s, 36H), 1.30 (s, 18H), 1.27 – 1.09 (m, 10H), 1.07 – 0.98 (m, 6H).

Example 4: Preparation of Procatalyst 1

[0108] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to $-30\text{ }^\circ\text{C}$ in a freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 1 (0.226 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was washed with hexanes (10 mL) then filtered. The remaining solids were extracted with toluene (12 mL). The toluene extract was dried under vacuum to afford a white solid. A yield of 0.21 g of the white solid was collected, providing a 84% yield.

[0109] ^1H NMR (400 MHz, C_6D_6) δ 8.14 (br s, 2H), 7.79 (t, $J = 1.9$ Hz, 2H), 7.56 (d, $J = 2.5$ Hz, 2H), 7.28 – 7.17 (m, 6H), 5.68 (d, $J = 8.6$ Hz, 2H), 4.82 (d, $J = 11.5$ Hz, 2H), 3.66 (d, $J = 11.5$ Hz, 2H), 2.27 (s, 6H), 1.62 – 1.18 (m, 66H), 0.83 – 0.68 (m, 4H), 0.55 – 0.43 (m, 2H), -0.04 (s, 6H).

Example 5: Preparation of dicyclohexylbis(iodomethyl)germane

[0110] In a glove box, a 40 mL vial under nitrogen was charged with GeCl_4 (2.16 g, 10 mmol, 1.0 equiv) and dried toluene (20 mL), and then cooled down to $-30\text{ }^\circ\text{C}$. Cyclohexylmagnesium chloride solution in diethyl ether (2 M, 10.5 mL, 21 mmol, 2.1 equiv) was added dropwise to the pre-cooled solution. The reaction was kept for 30 mins at $-30\text{ }^\circ\text{C}$ then slowly warmed up to room temperature. The reaction mixture was filtered to remove the

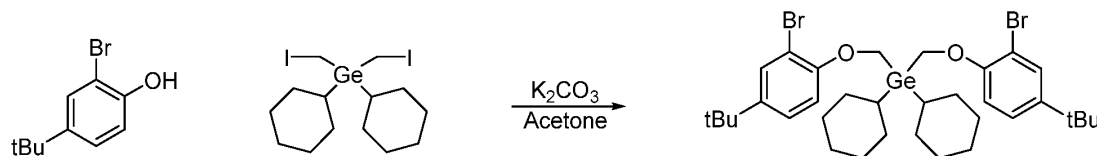
precipitate (rinsed with hexane). The filtrate was concentrated, diluted with ether, and then filtered. The process was repeated several times to remove Mg salts. The product was used for the next step without further purification.

[0111] A n-BuLi solution in hexanes (2.5 M, 8.4 mL, 21 mmol, 2.1 equiv) was added dropwise to a solution of methyl p-tolyl thioether (3.46 g, 25 mmol, 2.5 equiv) in THF (20 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 hour then slowly warmed up to room temperature for 2 hours. The resulting solution was added dropwise to a pre-cooled solution of dichlorodicyclohexylgermane prepared previously in THF (10 mL) at -10 to 0 °C. After 30 mins, MeOH (2 mL) was added to quench the reaction, diluted with ether (250 mL), and washed with brine. The organic layer was dried over MgSO₄, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 -> 50/50) as the eluent. A yield of 3.67 g of a colorless oil was collected, providing a 71% yield.

[0112] In a glove box, an 8 mL arc sphere was charged with dicyclohexylbis((p-tolylthio)methyl)germane (1.03 g, 2.0 mmol, 1.0 equiv), LiI (0.268 g, 2.0 mmol, 1.0 equiv), MeI (3.0 mL, 48.0 mmol, 24.0 equiv), and DMF (2 mL), then sealed and taken out of glove box. The reaction mixture was stirred at 120 °C for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel (rinsed with DCM). Solvents were removed under reduced pressure and the residue was purified by column chromatography using pentane/ether (100/0 -> 80/20) as the eluent, affording a light tan oil. A yield of 0.47 g was collected, providing a 45% yield.

[0113] ¹H NMR (400 MHz, CDCl₃) δ 2.22 (s, 4H), 1.84 – 1.68 (m, 10H), 1.51 – 1.38 (m, 6H), 1.32 – 1.22 (m, 6H).

Example 6: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclohexylgermane

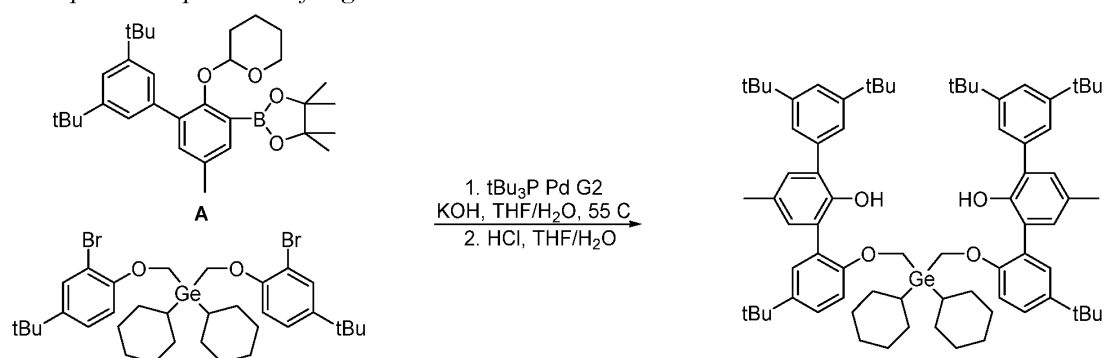


[0114] In a glove box, a 40 mL vial was charged with dicyclohexylbis(iodomethyl)germane (0.5 g, 0.96 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (0.77 g, 3.36 mmol, 3.5 equiv), K₂CO₃ (0.66 g, 4.8 mmol, 5.0 equiv), and acetone (2 mL). The reaction mixture was stirred

at 65 °C overnight. After cooling down to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 -> 30/70) as the eluent. A yield of 0.69 g was collected, providing a 99% yield.

[0115] ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 2.3 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.97 (d, J = 8.6 Hz, 2H), 4.10 (s, 4H), 1.94 – 1.85 (m, 4H), 1.76 – 1.66 (m, 6H), 1.60 – 1.50 (m, 6H), 1.33 – 1.23 (m, 6H), 1.27 (s, 18H).

Example 7: Preparation of Ligand 2



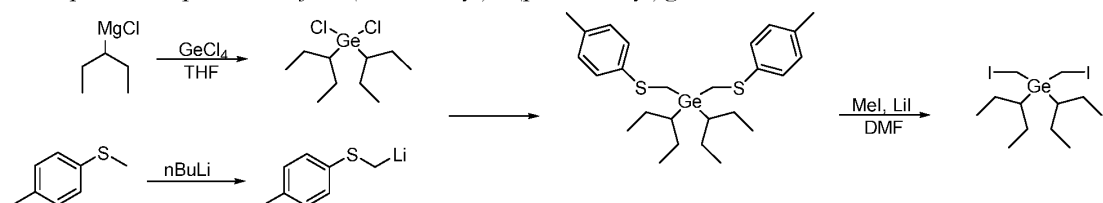
[0116] In a glove box, a 40 mL vial equipped with stir bars was charged with compound A (1.45 g, 2.86 mmol, 3.0 equiv, purchased from Boulder Scientific), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclohexylgermane (0.69 g, 0.95 mmol, 1.0 equiv), $\text{tBu}_3\text{P Pd G2}$ (0.01 g, 0.02 mmol, 0.02 equiv), THF (2 mL), and aqueous NaOH solution (4 M, 1.43 mL, 5.72 mmol, 6.0 equiv). The vial was heated under nitrogen at 55 °C overnight. 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. A yield of 0.65 g of a white solid was collected, providing a 59% yield.

[0117] ^1H NMR (400 MHz, CDCl_3) δ 7.40 (t, J = 1.8 Hz, 2H), 7.35 (d, J = 1.8 Hz, 4H), 7.33 (d, J = 2.5 Hz, 2H), 7.21 (dd, J = 8.6, 2.6 Hz, 2H), 7.11 (d, J = 2.3 Hz, 2H), 6.97 (d, J = 2.3 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 5.54 (s, 2H), 3.76 (br s, 4H), 2.34 (s, 6H), 1.38 – 1.25 (m, 64H), 1.00 – 0.78 (m, 12H).

Example 8: Preparation of Procatalyst 2

[0118] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to $-30\text{ }^\circ\text{C}$ in a freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 2 (0.231 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to $\sim 2\text{--}3\text{ mL}$ and kept at $-30\text{ }^\circ\text{C}$ for one day. The top solution was decanted and the remaining solid was dried under vacuum affording a white solid. A yield of 0.18 g of the white solid was collected, providing a 74% yield.

[0119] ^1H NMR (400 MHz, C_6D_6) δ 8.16 (br s, 2H), 7.80 (t, $J = 1.9\text{ Hz}$, 2H), 7.58 (d, $J = 2.5\text{ Hz}$, 2H), 7.30 – 7.24 (m, 4H), 7.19 (dd, $J = 8.6, 2.5\text{ Hz}$, 2H), 5.69 (d, $J = 8.6\text{ Hz}$, 2H), 4.82 (d, $J = 11.6\text{ Hz}$, 2H), 3.70 (d, $J = 11.6\text{ Hz}$, 2H), 2.32 (s, 6H), 1.63 – 1.35 (m, 40H), 1.30 – 1.21 (m, 20H), 1.19 – 0.95 (m, 10H), 0.73 – 0.53 (m, 4H).

Example 9: Preparation of bis(iodomethyl)di(pentan-3-yl)germane

[0120] In a glove box, a 40 mL vial under nitrogen was charged with CuCl (0.7 g, 7.0 mmol, 1.0 equiv), GeCl_4 (1.51 g, 7.0 mmol, 1.0 equiv), and dried THF (15 mL), and then cooled down to $-30\text{ }^\circ\text{C}$. 3-Pentylmagnesium bromide solution in diethyl ether (1 M, 14.0 mL, 14.0 mmol, 2.0 equiv) was added dropwise to the pre-cooled solution. The reaction was kept for

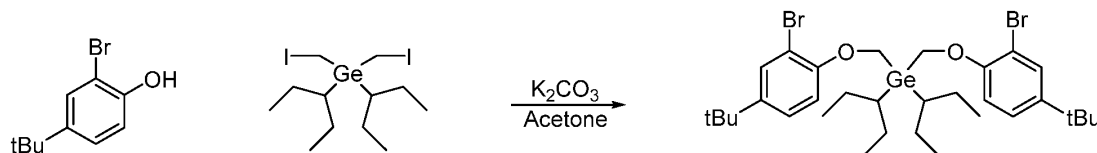
30 mins at $-30\text{ }^{\circ}\text{C}$ then slowly warmed up to room temperature. The reaction mixture was filtered to remove the precipitate (rinsed with hexane). The filtrate was concentrated, diluted with ether, and then filtered. The process was repeated several times to remove Mg salts. The product was used for the next step without further purification.

[0121] A n-BuLi solution in hexanes (2.5 M, 12.6 mL, 31.5 mmol, 2.1 equiv) was added dropwise to a solution of methyl p-tolyl thioether (4.77 g, 34.5 mmol, 2.3 equiv) in THF (20 mL) at $0\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at the same temperature for 1 hour then slowly warmed up to room temperature for 2 hours. The resulting solution was added dropwise to a pre-cooled solution of dichlorodi(pentan-3-yl)germane (3.87 g, 15.0 mmol, 1.0 equiv) in THF (15 mL) at $-10\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$. After 30 mins, MeOH (2 mL) was added to quench the reaction, diluted with ether (250 mL), and washed with brine. The organic layer was dried over MgSO_4 , filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 $\rightarrow$ 50/50) as the eluent. A yield of 2.3 g of a colorless oil was collected, providing a 31% yield.

[0122] In a glove box, an 8 mL arc sphere was charged with di(pentan-3-yl)bis((p-tolylthio)methyl)germane (0.98 g, 2.0 mmol, 1.0 equiv), LiI (0.268 g, 2.0 mmol, 1.0 equiv), MeI (3.0 mL, 48.0 mmol, 24.0 equiv), and DMF (2 mL), and then sealed and taken out of glove box. The reaction mixture was stirred at $120\text{ }^{\circ}\text{C}$ for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel (rinsed with DCM). Solvents were removed under reduced pressure and the residue was purified by column chromatography using pentane/ether (100/0 $\rightarrow$ 80/20) as the eluent affording a light tan oil. A yield of 0.56 g was collected, providing a 56% yield.

[0123] ^1H NMR (400 MHz, CDCl_3) δ 2.34 (s, 4H), 1.71 – 1.56 (m, 8H), 1.33 – 1.22 (m, 2H), 0.97 (t, $J = 7.4\text{ Hz}$, 12H).

Example 10: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclohexylgermane

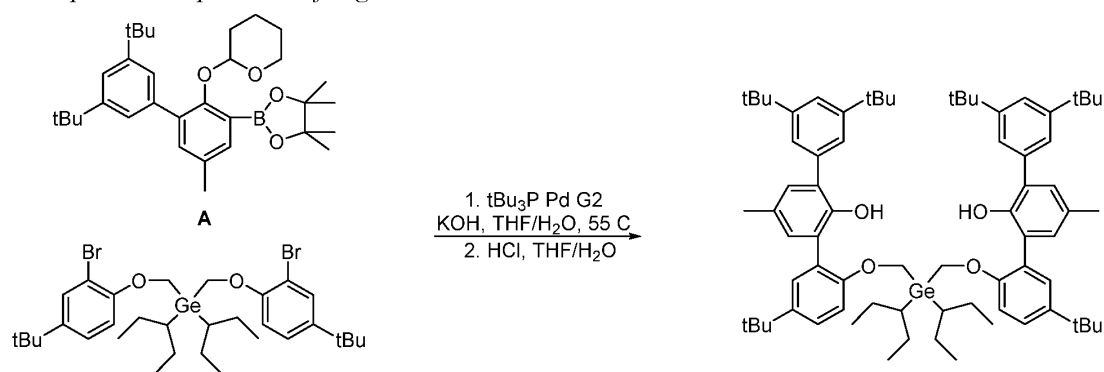


[0124] In a glove box, a 40 mL vial was charged with bis(iodomethyl)di(pentan-3-yl)germane (0.56 g, 1.1 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (1.03 g, 4.5 mmol,

4.0 equiv), K_2CO_3 (0.94 g, 6.8 mmol, 6.0 equiv), and acetone (2 mL). The reaction mixture was stirred at 65 °C overnight. After cooling down to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 → 30/70) as the eluent. A yield of 0.78 g was collected, providing a 99% yield.

[0125] ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 2.3 Hz, 2H), 7.26 – 7.23 (m, 2H), 6.98 (d, J = 8.6 Hz, 2H), 4.13 (s, 4H), 1.81 – 1.60 (m, 8H), 1.53 – 1.45 (m, 2H), 1.27 (s, 18H), 0.97 (t, J = 7.4 Hz, 12H).

Example 11: Preparation of Ligand 3

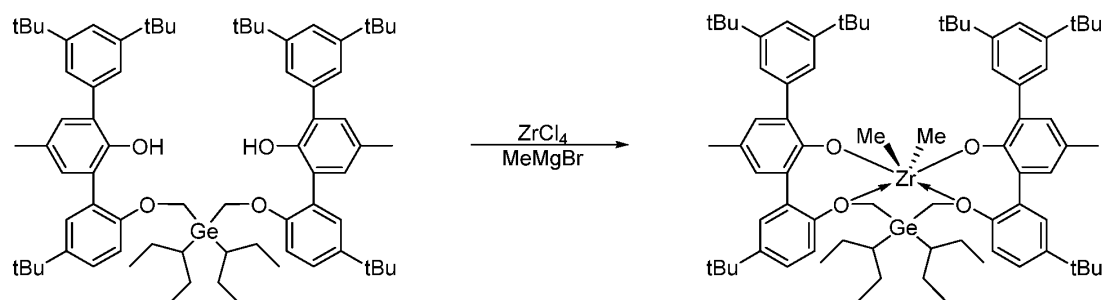


[0126] In a glove box, a 40 mL vial equipped with stir bars was charged with compound **A** (1.70 g, 3.35 mmol, 3.0 equiv, purchased from Boulder Scientific), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclohexylgermane (0.78 g, 1.1 mmol, 1.0 equiv), $\text{tBu}_3\text{P Pd G2}$ (0.017 g, 0.03 mmol, 0.03 equiv), THF (3 mL), and aqueous NaOH solution (4 M, 1.70 mL, 6.7 mmol, 6.0 equiv). The vial was heated under nitrogen at 55 °C overnight. 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. A yield of 0.86 g of a white solid was collected, providing a 68% yield.

[0127] ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.38 (m, 2H), 7.36 (d, J = 1.8 Hz, 4H), 7.29 (d, J = 2.5 Hz, 2H), 7.19 (dd, J = 8.7, 2.5 Hz, 2H), 7.12 (d, J = 2.3 Hz, 2H), 6.98 – 6.92 (m, 2H),

6.66 (d, $J = 8.6$ Hz, 2H), 5.47 (s, 2H), 3.78 (br s, 4H), 2.33 (s, 6H), 1.36 – 1.27 (m, 54H), 1.26 – 1.11 (m, 8H), 0.95 – 0.86 (m, 2H), 0.59 (t, $J = 7.3$ Hz, 12H).

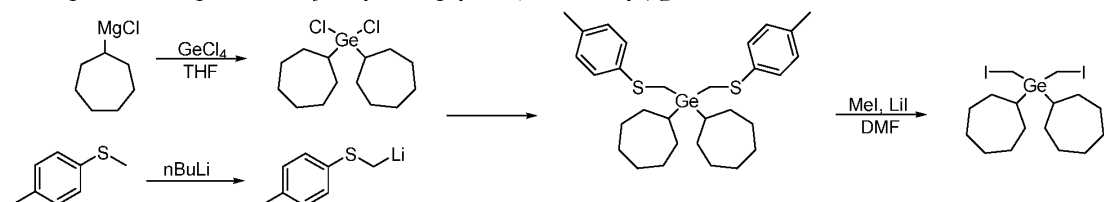
Example 12: Preparation of Procatalyst 3



[0128] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to -30 °C in a freezer. The vial was removed from the freezer then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 3 (0.226 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was washed with hexanes (10 mL) then filtered. The remaining solids were extracted with toluene (12 mL). The toluene extract was dried under vacuum to afford a white solid. A yield of 0.19 g of the white solid was collected, providing a 76% yield.

[0129] ^1H NMR (400 MHz, C_6D_6) δ 8.14 (br s, 2H), 7.78 (t, $J = 1.8$ Hz, 2H), 7.57 (d, $J = 2.4$ Hz, 2H), 7.29 – 7.23 (m, 4H), 7.20 – 7.17 (m, 2H), 5.71 (d, $J = 8.6$ Hz, 2H), 4.88 (d, $J = 11.6$ Hz, 2H), 3.80 (d, $J = 11.6$ Hz, 2H), 2.28 (s, 6H), 1.64 – 1.35 (m, 36H), 1.24 (s, 18H), 1.18 – 0.94 (m, 12H), 0.69 – 0.56 (m, 12H), 0.55 – 0.46 (m, 2H), -0.06 (s, 6H).

Example 13: Preparation of dicycloheptylbis(iodomethyl)germane



[0130] In a glove box, a 40 mL vial under nitrogen was charged with CuCl (0.7 g, 7.0 mmol, 1.0 equiv), GeCl_4 (1.51 g, 7.0 mmol, 1.0 equiv) and dried THF (15 mL), and then cooled down to -30 °C. Cycloheptylmagnesium bromide solution in diethyl ether (2 M, 7.0 mL, 14.0

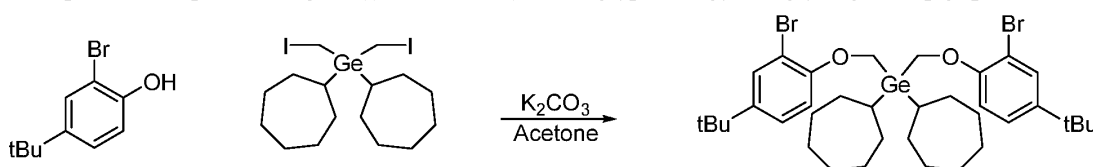
mmol, 2.0 equiv) was added dropwise to the pre-cooled solution. The reaction was kept for 30 mins at $-30\text{ }^{\circ}\text{C}$ then slowly warmed up to room temperature. The reaction mixture was filtered to remove the precipitate (rinsed with hexane). The filtrate was concentrated, diluted with ether, and then filtered. The process was repeated several times to remove Mg salts. The product was used for the next step without further purification.

[0131] A n-BuLi solution in hexanes (2.5 M, 12.6 mL, 31.5 mmol, 2.1 equiv) was added dropwise to a solution of methyl p-tolyl thioether (4.77 g, 34.5 mmol, 2.3 equiv) in THF (20 mL) at $0\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at the same temperature for 1 hour then slowly warmed up to room temperature for 2 hours. The reaction mixture was cooled back down to $0\text{ }^{\circ}\text{C}$ and a solution of dichlorodicycloheptylgermane (3.87 g, 15.0 mmol, 1.0 equiv) prepared above was added dropwise. After 30 mins, MeOH (2 mL) was added to quench the reaction, diluted with ether (250 mL), and washed with brine. The organic layer was dried over MgSO_4 , filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 $\rightarrow$ 50/50) as the eluent. A yield of 2.6 g of a colorless oil was collected, providing a 35% yield.

[0132] In a glove box, an 8 mL arc sphere was charged with dicycloheptylbis((p-tolylthio)methyl)germane (1.08 g, 2.0 mmol, 1.0 equiv), LiI (0.268 g, 2.0 mmol, 1.0 equiv), MeI (3.0 mL, 48.0 mmol, 24.0 equiv), and DMF (2 mL), and then sealed and taken out of glove box. The reaction mixture was stirred at $120\text{ }^{\circ}\text{C}$ for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel (rinsed with DCM). Solvents were removed under reduced pressure and the residue was purified by column chromatography using pentane/ether (100/0 - 80/20) as the eluent affording a light tan oil. A yield of 0.52 g was collected, providing a 47% yield.

[0133] ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 4H), 1.91 – 1.82 (m, 4H), 1.81 – 1.71 (m, 4H), 1.68 – 1.57 (m, 4H), 1.54 – 1.40 (m, 12H), 1.35 – 1.22 (m, 2H).

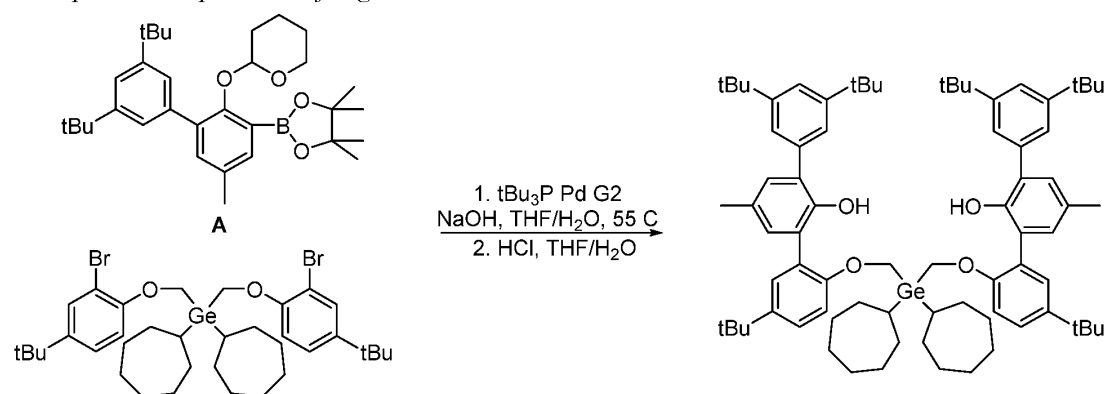
Example 14: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicycloheptylgermane



[0134] In a glove box, a 40 mL vial was charged with dicycloheptylbis(iodomethyl)germane (0.52 g, 0.95 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (0.65 g, 2.84 mmol, 3.0 equiv), K_2CO_3 (0.52 g, 3.8 mmol, 4.0 equiv), and acetone (2 mL). The reaction mixture was stirred at 65 °C overnight. After cooling down to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 → 30/70) as the eluent. A yield of 0.61 g was collected, providing a 86% yield.

[0135] 1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 2.4 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.98 (d, J = 8.7 Hz, 2H), 4.10 (s, 4H), 2.03 – 1.93 (m, 4H), 1.80 – 1.69 (m, 4H), 1.66 – 1.57 (m, 10H), 1.54 – 1.40 (m, 8H), 1.28 (s, 18H).

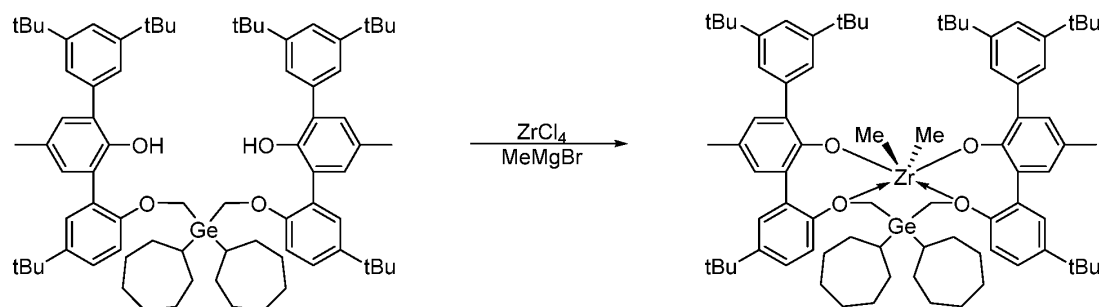
Example 15: Preparation of Ligand 4



[0136] In a glove box, a 40 mL vial equipped with stir bars was charged with compound **A** (1.23 g, 2.43 mmol, 3.0 equiv, purchased from Boulder Scientific), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicycloheptylgermane (0.61 g, 0.81 mmol, 1.0 equiv), tBu_3P Pd G2 (0.012 g, 0.02 mmol, 0.03 equiv), THF (3 mL), and aqueous NaOH solution (4 M, 1.22 mL, 4.9 mmol, 6.0 equiv). The vial was heated under nitrogen at 55 °C overnight. 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. A yield of 0.71 g of a white solid was collected, providing a 74% yield.

[0137] ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, $J = 1.7$ Hz, 2H), 7.34 (d, $J = 1.8$ Hz, 4H), 7.33 (d, $J = 2.5$ Hz, 2H), 7.22 (dd, $J = 8.6, 2.5$ Hz, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 6.97 (d, $J = 2.2$ Hz, 2H), 6.71 – 6.63 (m, 2H), 5.55 (s, 2H), 3.77 (br s, 4H), 2.34 (s, 6H), 1.49 – 1.40 (m, 4H), 1.38 – 1.26 (m, 60H), 1.23 – 1.12 (m, 6H), 1.08 – 0.94 (m, 10H).

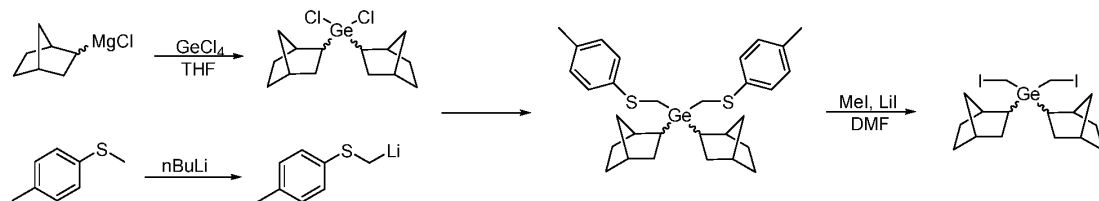
Example 16: Preparation of Procatalyst 4



[0138] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to -30 °C in a freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 4 (0.237 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to ~ 2 -3 mL and kept at -30 °C for one day. The top solution was decanted and the remaining solid was dried under vacuum affording a white solid. A yield of 0.22 g of the white solid was collected, providing a 84% yield.

[0139] ^1H NMR (400 MHz, C_6D_6) δ 8.15 (br s, 2H), 7.80 (t, $J = 1.8$ Hz, 2H), 7.59 (d, $J = 2.5$ Hz, 2H), 7.32 – 7.23 (m, 4H), 7.19 (dd, $J = 8.6, 2.5$ Hz, 2H), 5.69 (d, $J = 8.6$ Hz, 2H), 4.84 (d, $J = 11.5$ Hz, 2H), 3.75 (d, $J = 11.6$ Hz, 2H), 2.32 (s, 6H), 1.64 – 1.11 (m, 66H), 1.08 – 0.96 (m, 2H), 0.93 – 0.84 (m, 4H), 0.74 – 0.63 (m, 2H), -0.05 (s, 6H).

Example 17: Preparation of dinorbornylbis(iodomethyl)germane

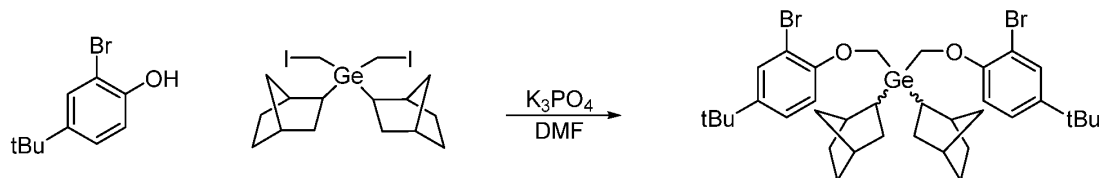


[0140] In a glove box, a 150 mL bottle was charged with CuCl (0.76 g, 7.7 mmol, 0.5 equiv), GeCl₄ (3.3 g, 15.4 mmol, 1.0 equiv) and dried THF (15 mL), and then cooled down to -30 °C. 2-Norbornylmagnesium chloride solution in diethyl ether (0.77 M, 44.0 mL, 33.9 mmol, 2.2 equiv) was added dropwise to the pre-cooled solution. The reaction was kept for 30 mins at -30 °C then slowly warmed up to room temperature. The reaction mixture was filtered to remove the precipitate (rinsed with hexane). The filtrate was concentrated, diluted with ether, and then filtered. The process was repeated several times to remove Mg salts. The product was used for the next step without further purification.

[0141] A n-BuLi solution in hexanes (2.5 M, 12.6 mL, 31.5 mmol, 2.1 equiv) was added dropwise to a solution of methyl p-tolyl thioether (4.77 g, 34.5 mmol, 2.3 equiv) in THF (20 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 hour then slowly warm up to room temperature for 2 hours. The reaction mixture was cooled back down to 0 °C and a solution of dichlorodinorbornylgermane (3.87 g, 15.0 mmol, 1.0 equiv) prepared above was added dropwise. After 30 mins, MeOH (2 mL) was added to quench the reaction, diluted with ether (250 mL), and washed with brine. The organic layer was dried over MgSO₄, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 -> 50/50) as the eluent. A yield of 4.8 g of a colorless oil was collected, providing a 59% yield.

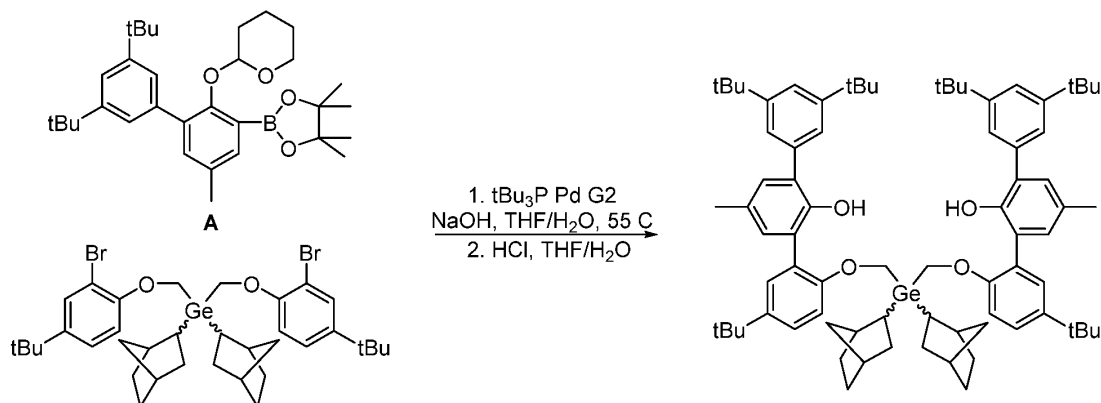
[0142] In a glove box, an 8 mL ARC sphere was charged with dinorbornylbis((p-tolylthio)methyl)germane (1.61 g, 3.0 mmol, 1.0 equiv), LiI (0.40 g, 3.0 mmol, 1.0 equiv), MeI (3.74 mL, 60.0 mmol, 20.0 equiv), and DMF (3 mL), and then sealed and taken out of glove box. The reaction mixture was stirred at 120 °C for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel (rinsed with DCM). Solvents were removed under reduced pressure and the residue was purified by column chromatography using pentane/ether (100/0 -> 80/20) as the eluent affording a light tan oil. A yield of 1.02 g was collected, providing a 62% yield.

[0143] ¹H NMR (400 MHz, CDCl₃) δ 2.36 – 2.23 (m, 4H), 1.94 – 1.46 (m, 10H), 1.37 – 1.17 (m, 12H).

Example 18: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dinorbornylgermane

[0144] In a glove box, a 40 mL vial was charged with dinorbornylbis(iodomethyl)germane (1.02 g, 1.87 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (1.5 g, 6.55 mmol, 3.5 equiv), K_3PO_4 (1.79 g, 8.4 mmol, 4.5 equiv), and DMF (3 mL). The reaction mixture was stirred at 80 °C overnight. After cooling down to room temperature, the reaction mixture was diluted with ether (15 mL) then filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using ether/hexane (0/100 → 30/70) as the eluent. A yield of 1.0 g was collected, providing a 71% yield.

[0145] 1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $J = 2.5$, 2H), 7.26 – 7.22 (m, 2H), 7.01 – 6.94 (m, 2H), 4.15 – 4.06 (m, 4H), 2.50 – 2.42 (m, 2H), 2.33 – 2.25 (m, 2H), 1.94 – 1.70 (m, 2H), 1.64 – 1.46 (m, 8H), 1.44 – 1.109 (m, 30H).

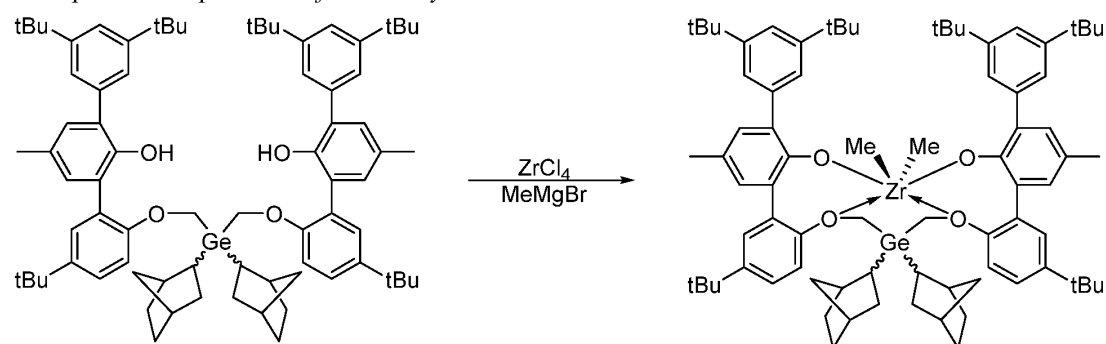
Example 19: Preparation of Ligand 5

[0146] In a glove box, a 40 mL vial equipped with stir bars was charged with compound A (2.03 g, 4.0 mmol, 3.0 equiv, purchased from Boulder Scientific), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dinorbornylgermane (1.0 g, 1.34 mmol, 1.0 equiv), tBu_3P Pd G2 (0.021 g, 0.04 mmol, 0.03 equiv), THF (3 mL), and aqueous NaOH solution (4 M, 2.0 mL, 8.0 mmol, 6.0 equiv). The vial was heated under nitrogen at 55 °C overnight. 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. A yield of 1.12 g of a white solid was collected, providing a 71% yield.

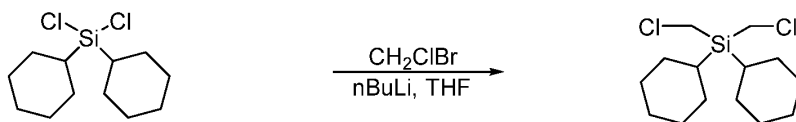
[0147] ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.34 (m, 6H), 7.34 – 7.29 (m, 2H), 7.13 – 7.09 (m, 2H), 6.99 – 6.93 (m, 2H), 6.77 – 6.65 (m, 2H), 5.54 – 5.47 (m, 2H), 3.85 – 3.67 (m, 4H), 2.34 (s, 6H), 2.01 – 1.79 (m, 4H), 1.35 – 1.28 (m, 54H), 1.27 – 1.13 (m, 8H), 1.10 – 0.99 (m, 2H), 0.91 – 0.75 (m, 8H).

Example 20: Preparation of Procatalyst 5

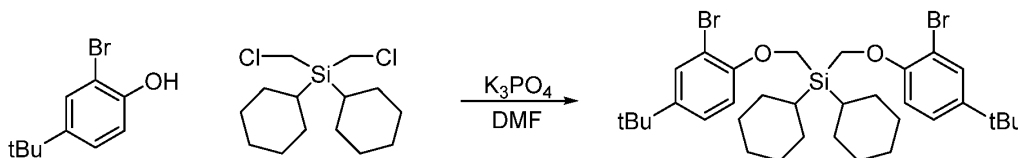


[0148] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to -30 °C in a freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 5 (0.236 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to ~2-3 mL and kept at -30 °C for one day. The top solution was decanted and the remaining solid was dried under vacuum affording a white solid. A yield of 0.21 g of the white solid was collected, providing a 81% yield.

[0149] ^1H NMR (400 MHz, C_6D_6) δ 8.12 (br s, 2H), 7.82 – 7.75 (m, 2H), 7.70 – 7.50 (m, 4H), 7.31 – 7.18 (m, 6H), 5.83 – 5.65 (m, 2H), 4.88 – 4.70 (m, 2H), 3.78 – 3.51 (m, 2H), 2.34 – 2.23 (m, 6H), 2.09 – 1.94 (m, 2H), 1.84 – 1.69 (m, 2H), 1.64 – 1.32 (m, 36H), 1.29 – 1.20 (m, 20H), 1.13 – 0.82 (m, 14H), 0.69 – 0.45 (m, 2H), -0.01 – -0.14 (m, 6H).

Example 21: Preparation of bis(chloromethyl)dicyclohexylsilane

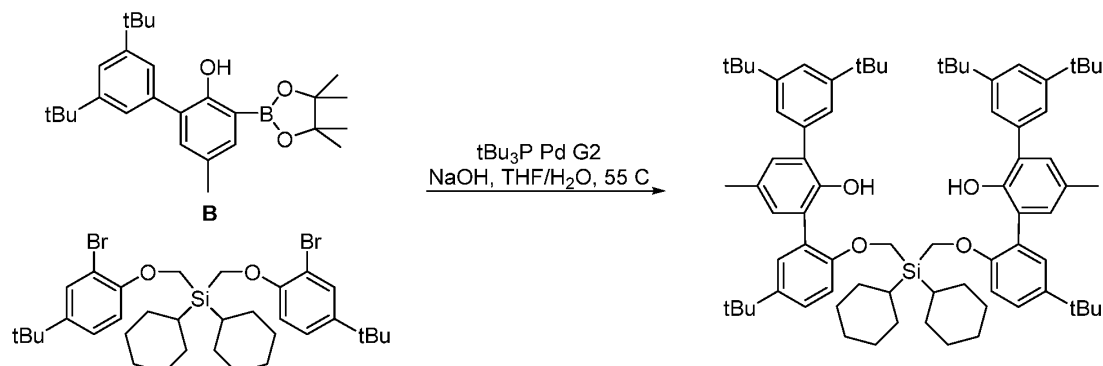
[0150] In a glove box, a 100 mL round-bottom flask (RBF) was charged with dichlorodicyclohexylsilane (5.33 g, 20.0 mmol, 1.0 equiv) and THF (30 mL). The flask was sealed and taken out of glove box. Bromochloromethane (5.2 mL, 80.0 mmol, 4.0 equiv) was added and the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ in a dry ice-acetone bath. Then a solution of $n\text{-BuLi}$ in hexane (2.5 M, 18.5 mL, 46.2 mmol, 2.3 equiv) was added to the cooled wall of the flask over a period of 2 hours using a syringe pump. The mixture was allowed to warm up to room temperature overnight. Then saturated aqueous NH_4Cl (30 mL) was added. The two layers were separated. The aqueous layer was extracted with ether (2 x 60 mL). The combined organic layer was dried over MgSO_4 , filtered through a short pad of silica gel, concentrated under reduced pressure, and then dried under vacuum. The crude product was used for the next step without further purification.

Example 22: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclohexylsilane

[0151] In a glove box, a 40 mL vial was charged with bis(chloromethyl)dicyclohexylsilane (1.47 g, 5.0 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (3.44 g, 15.0 mmol, 3.0 equiv), K_3PO_4 (4.26 g, 20.0 mmol, 4.0 equiv), and DMF (6 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. A yield of 2.8 g of a colorless oil was collected, providing a 82% yield.

[0152] ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 2.4\text{ Hz}$, 2H), 7.44 (d, $J = 2.3\text{ Hz}$, 2H), 6.96 (dd, $J = 8.6, 5.2\text{ Hz}$, 2H), 3.89 (s, 4H), 1.90 – 1.81 (m, 6H), 1.78 – 1.66 (m, 8H), 1.51 – 1.39 (m, 6H), 1.28 (s, 18H), 1.17 – 1.22 (m, 2H).

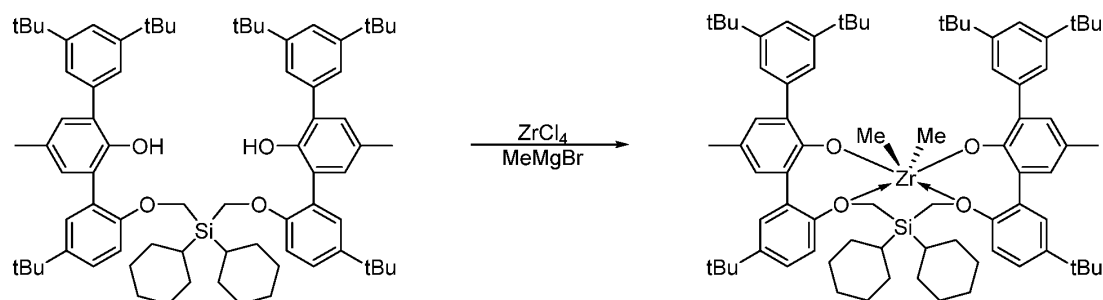
Example 23: Preparation of Ligand 6



[0153] In a glove box, a 40 mL vial equipped with stir bar was charged with compound **B** (1.9 g, 4.5 mmol, 3.0 equiv), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicyclohexylsilane (1.02 g, 1.5 mmol, 1.0 equiv), $t\text{Bu}_3\text{P Pd G2}$ (0.023 g, 0.05 mmol, 0.03 equiv), THF (3 mL), and aqueous NaOH solution (2.25 mL, 9.0 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 purified by reverse phase column chromatography using THF/MeCN (0/100 $\rightarrow$ 100/0) as the eluent. A yield of 1.2 g was collected, providing a 72% yield.

[0154] $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (t, $J = 1.8$ Hz, 2H), 7.35 (d, $J = 1.8$ Hz, 4H), 7.33 (d, $J = 2.5$ Hz, 2H), 7.20 (dd, $J = 8.6, 2.5$ Hz, 2H), 7.10 (d, $J = 2.2$ Hz, 2H), 6.97 (d, $J = 2.3$, 2H), 6.62 (d, $J = 8.7$ Hz, 2H), 5.48 (s, 2H), 3.56 (br s, 4H), 2.34 (s, 6H), 1.50 – 1.40 (m, 2H), 1.32 (s, 36H), 1.31 (s, 18H), 1.38 – 1.24 (m, 10H), 0.89 – 0.75 (m, 10H).

Example 24: Preparation of Procatalyst 6

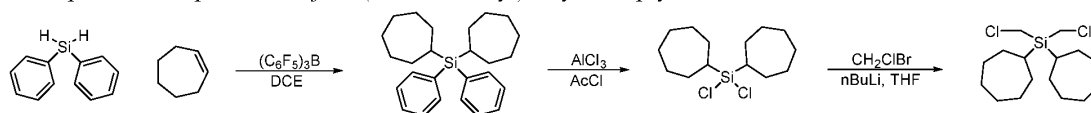


[0155] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to -30 °C in a freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3

equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 6 (0.22 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to ~ 2-3 mL and kept at $-30\text{ }^{\circ}\text{C}$ for one day. The top solution was decanted and the remaining solid was dried under vacuum affording a white solid. A yield of 0.17 g of the white solid was collected, providing a 69% yield.

[0156] ^1H NMR (400 MHz, C_6D_6) δ 8.16 (br s, 2H), 7.80 (t, $J = 1.9$ Hz, 2H), 7.59 (d, $J = 2.5$ Hz, 2H), 7.59 (br s, 2H), 7.26 (br s, 4H), 7.22 – 7.17 (m, 2H), 5.67 (d, $J = 8.6$ Hz, 2H), 4.62 (d, $J = 13.5$ Hz, 2H), 3.48 (d, $J = 13.5$ Hz, 2H), 2.31 (s, 6H), 1.67 – 1.34 (m, 44H), 1.31 – 1.17 (m, 28H), 1.13 – 0.92 (m, 10H), 0.77 – 0.49 (m, 6H), 0.27 – 0.16 (m, 2H), - 0.05 (s, 6H).

Example 25: Preparation of bis(chloromethyl)dicycloheptylsilane



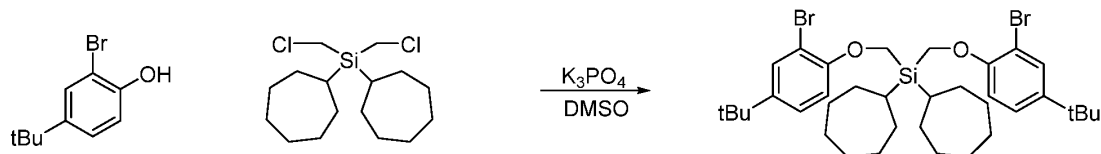
[0157] In a glove box, a 40 mL vial was charged with $(\text{C}_6\text{F}_5)_3\text{B}$ (0.07 g, 0.14 mmol, 0.07 equiv), Ph_2SiH_2 (0.37 g, 2.0 mmol, 1.0 equiv), cycloheptene (1.16 g, 12.0 mmol, 6.0 equiv), and 1,2-dichloroethane (2 mL). The resulting mixture was heated at $70\text{ }^{\circ}\text{C}$ overnight. The volatiles were removed under vacuum. The crude product was used for the next step without further purification.

[0158] In a glove box, a 40 mL vial was charged with AlCl_3 (0.67 g, 5.0 mmol, 2.5 equiv), dicycloheptyldiphenylsilane (0.75 g, 2.0 mmol, 1.0 equiv), and hexane (5 mL). A solution of AcCl (0.39 g, 5.0 mmol, 2.5 equiv) in hexane was added dropwise at room temperature. The mixture was stirred for 3 hours. The top layer was decanted, and the volatiles were removed under vacuum. The crude product was used for the next step without further purification.

[0159] In a glove box, a 100 mL RBF was charged with dichlorodicycloheptylsilane (2.55 g, 8.7 mmol, 1.0 equiv) and THF (20 mL). The flask was sealed and taken out of glove box. Bromochloromethane (2.26 mL, 35.0 mmol, 4.0 equiv) was added and the reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice-acetone bath. Then a solution of $n\text{-BuLi}$ in hexane (2.5 M, 7.65 mL, 19.1 mmol, 2.2 equiv) was added to the cooled wall of the flask over a period of 2

hours using a syringe pump. The mixture was allowed to warm up to room temperature overnight. Then saturated aqueous NH_4Cl (30 mL) was added. The two layers were separated. The aqueous layer was extracted with ether (2 x 60 mL). The combined organic layer was dried over MgSO_4 , filtered through a short pad of silica gel, concentrated under reduced pressure, and then dried under vacuum. The crude product was used for the next step without further purification.

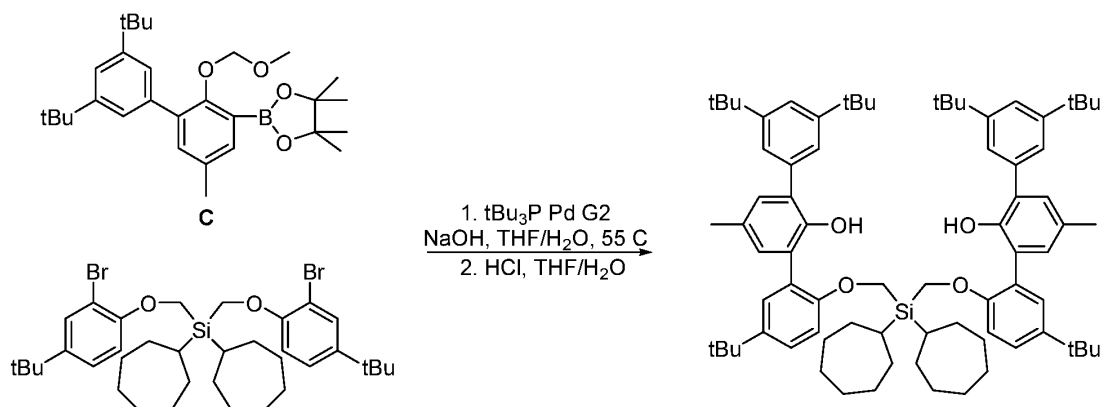
Example 26: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicycloheptylsilane



[0160] In a glove box, a 40 mL vial was charged with bis(chloromethyl)dicycloheptylsilane (0.64 g, 2.0 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (1.38 g, 6.0 mmol, 3.0 equiv), K_3PO_4 (1.7 g, 8.0 mmol, 4.0 equiv), and DMF (6 mL). The reaction mixture was stirred at 80 °C overnight. After cooling down to room temperature, the reaction mixture was purified by column chromatography using ether/hexane (0/100 → 30/70) as the eluent. A yield of 1.12 g of a colorless oil was collected, providing a 79% yield.

[0161] ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 2.4 Hz, 2H), 7.26 (dd, J = 8.6, 2.2 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 3.89 (s, 4H), 1.99 – 1.85 (m, 4H), 1.81 – 1.71 (m, 6H), 1.65 – 1.57 (m, 4H), 1.52 – 1.38 (m, 10H), 1.28 (s, 18H).

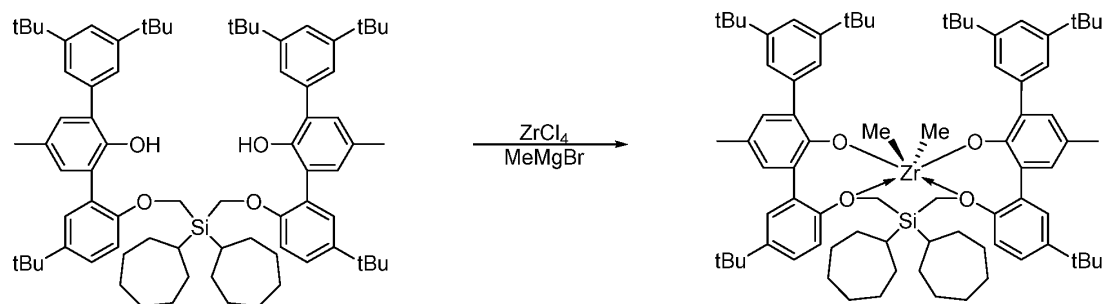
Example 27: Preparation of Ligand 7



[0162] In a glove box, a 40 mL vial equipped with stir bar was charged with compound **C** (1.66 g, 3.6 mmol, 3.0 equiv), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dicycloheptylsilane (0.84 g, 1.2 mmol, 1.0 equiv), $t\text{Bu}_3\text{P Pd G2}$ (0.018 g, 0.04 mmol, 0.03 equiv), THF (4 mL), and aqueous NaOH solution (1.8 mL, 7.1 mmol, 6.0 equiv). The vial was heated under nitrogen at 60 °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 (0.3 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 $\rightarrow$ 100/0) as the eluent. A yield of 1.00 g was collected, providing a 74% yield.

[0163] ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, J = 1.9 Hz, 2H), 7.34 (d, J = 1.9 Hz, 4H), 7.33 (d, J = 2.5 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.10 (d, J = 2.2 Hz, 2H), 6.97 (d, J = 2.2 Hz, 2H), 6.65 (d, J = 8.5 Hz, 2H), 5.49 (s, 2H), 3.57 (br s, 4H), 2.34 (s, 6H), 1.42 – 1.22 (m, 64H), 1.23 – 1.10 (m, 6H), 1.06 – 0.89 (m, 6H), 0.76 – 0.65 (m, 2H).

Example 28: Preparation of Procatalyst 7

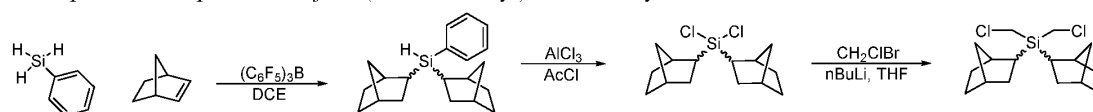


[0164] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to -30 °C in a freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand **7** (0.228 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to $\sim$ 2-3 mL and kept at -30 °C for one day. The top solution was decanted and

the remaining solid was dried under vacuum affording a white solid. A yield of 0.18 g of the white solid was collected, providing a 71% yield.

[0165] ^1H NMR (400 MHz, C_6D_6) δ 8.15 (br s, 2H), 7.79 (t, $J = 1.8$ Hz, 2H), 7.59 (d, $J = 2.5$ Hz, 2H), 7.59 (br s, 2H), 7.31 – 7.23 (m, 4H), 7.20 – 7.15 (m, 2H), 5.68 (d, $J = 8.6$ Hz, 2H), 4.64 (d, $J = 13.6$ Hz, 2H), 3.56 (d, $J = 13.4$ Hz, 2H), 2.31 (s, 6H), 1.73 – 1.04 (m, 70H), 1.02 – 0.73 (m, 6H), 0.39 – 0.28 (m, 2H), -0.06 (s, 6H).

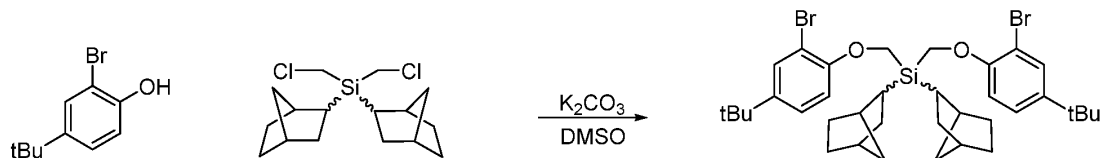
Example 29: Preparation of bis(chloromethyl)dinorbornylsilane



[0166] In a glove box, a 40 mL vial was charged with $(\text{C}_6\text{F}_5)_3\text{B}$ (0.23 g, 0.45 mmol, 0.15 equiv), PhSiH_3 (0.325 g, 3.0 mmol, 1.0 equiv), norbornene (1.70 g, 18.0 mmol, 6.0 equiv), and 1,2-dichloroethane (3 mL). The resulting mixture was heated at 85 °C overnight. The volatiles were removed under vacuum. The crude product was used for the next step without further purification.

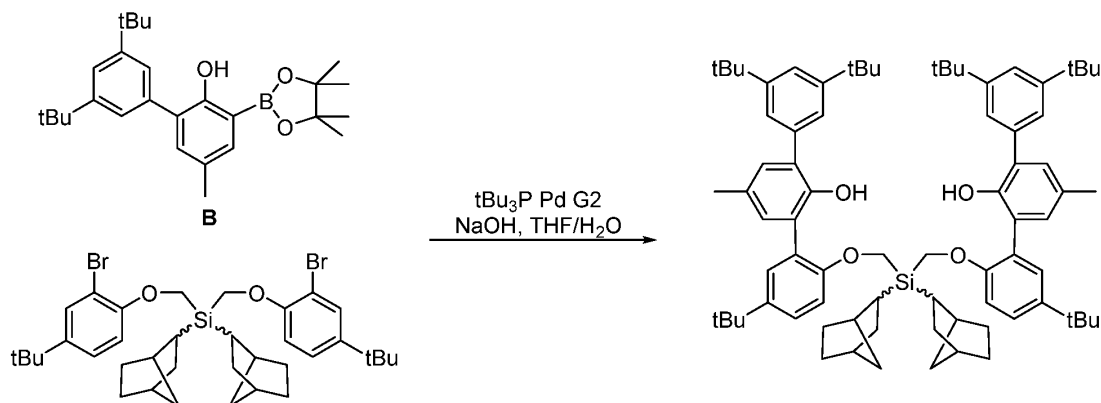
[0167] In a glove box, a 40 mL vial was charged with AlCl_3 (0.67 g, 5.0 mmol, 2.5 equiv), dinorbornylphenylsilane (0.59 g, 2.0 mmol, 1.0 equiv), and hexane (5 mL). A solution of AcCl (0.39 g, 5.0 mmol, 2.5 equiv) in hexane was added dropwise at room temperature. The mixture was stirred for 3 hours. The top layer was decanted, and the volatiles were removed under vacuum. The crude product was used for the next step without further purification.

[0168] In a glove box, a 100 mL RBF was charged with dichlorodinorbornylsilane (2.90 g, 10.0 mmol, 1.0 equiv) and THF (20 mL). The flask was sealed and taken out of glove box. Bromochloromethane (2.6 mL, 40.0 mmol, 4.0 equiv) was added and the reaction mixture was cooled to -78 °C in a dry ice-acetone bath. Then a solution of $n\text{-BuLi}$ in hexane (2.5 M, 9.2 mL, 23.0 mmol, 2.3 equiv) was added to the cooled wall of the flask over a period of 2 hours using a syringe pump. The mixture was allowed to warm up to room temperature overnight. Then saturated aqueous NH_4Cl (30 mL) was added. The two layers were separated. The aqueous layer was extracted with ether (2 x 60 mL). The combined organic layer was dried over MgSO_4 , filtered through a short pad of silica gel, concentrated under reduced pressure, and then dried under vacuum. The crude product was used for the next step without further purification.

Example 30: Preparation of bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dinorbornylsilane

[0169] In a glove box, a 40 mL vial was charged with bis(chloromethyl)dinorbornylsilane (1.59 g, 5.0 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)phenol (2.87 g, 12.0 mmol, 3.0 equiv), K_2CO_3 (2.77 g, 20.0 mmol, 4.0 equiv), and DMSO (6 mL). The reaction mixture was stirred at 80 °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. A yield of 2.7 g of a colorless oil was collected, providing a 77% yield.

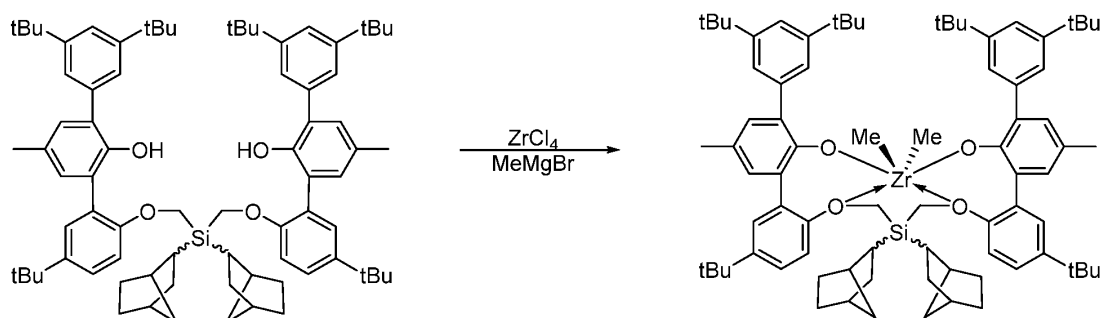
[0170] 1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.29 – 7.22 (m, 2H), 7.00 – 6.92 (m, 2H), 3.97 – 3.82 (m, 4H), 2.52 – 2.42 (m, 2H), 2.36 – 2.02 (m, 6H), 1.52 – 0.99 (m, 32H).

Example 31: Preparation of Ligand 8

[0171] In a glove box, a 40 mL vial equipped with stir bar was charged with compound **B** (2.08 g, 4.8 mmol, 2.8 equiv), bis((2-bromo-4-(tert-butyl)phenoxy)methyl)dinorbornylsilane (1.2 g, 1.7 mmol, 1.0 equiv), tBu_3P Pd G2 (0.026 g, 0.05 mmol, 0.03 equiv), THF (4 mL), and aqueous NaOH solution (2.6 mL, 10.2 mmol, 6.0 equiv). The vial was heated under nitrogen at 60 °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 purified by reverse phase column chromatography using THF/MeCN (0/100 $\rightarrow$ 100/0) as the eluent. A yield of 1.27 g was collected, providing a 66% yield.

[0172] ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.29 (m, 8H), 7.24 – 7.16 (m, 2H), 7.14 – 7.08 (m, 2H), 7.02 – 6.92 (m, 2H), 6.79 – 6.62 (m, 2H), 5.50 – 5.40 (m, 2H), 3.66 – 3.47 (m, 4H), 2.37 – 2.30 (m, 6H), 2.04 – 1.93 (m, 2H), 1.91 – 1.80 (m, 2H), 1.40 – 1.23 (m, 62H), 1.21 – 1.08 (m, 4H), 1.05 – 0.92 (m, 4H), 0.91 – 0.70 (m, 8H), 0.52 (t, $J = 8.7$ Hz, 2H).

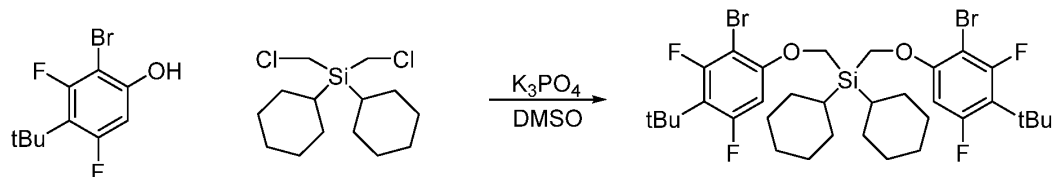
Example 32: Preparation of Procatalyst 8



[0173] In a glove box, an oven-dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL), and cooled to -30 °C in freezer. The vial was removed from the freezer and then MeMgBr in diethyl ether (3 M, 0.29 mL, 0.86 mmol, 4.3 equiv) was added with stirring. After stirring for 2 mins (the solution darkened), Ligand 8 (0.227 g, 0.2 mmol, 1.0 equiv) was added. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to ~ 2 -3 mL and kept at -30 °C for one day. The top solution was decanted and the remaining solid was dried under vacuum affording a white solid. A yield of 0.17 g of the white solid was collected, providing a 68% yield.

[0174] ^1H NMR (400 MHz, C_6D_6) δ 8.11 (br s, 2H), 7.83 – 7.75 (m, 2H), 7.64 (br s, 2H), 7.63 – 7.54 (m, 2H), 7.33 – 7.16 (m, 6H), 5.83 – 5.66 (m, 2H), 4.72 – 4.50 (m, 2H), 3.58 – 3.36 (m, 2H), 2.29 (s, 6H), 2.19 – 1.86 (m, 4H), 1.74 – 0.80 (m, 80H), 0.06 – 0.07 (m, 6H).

Example 33: Preparation of bis((2-bromo-4-(tert-butyl)-3,5-difluorophenoxy)methyl)dicyclohexylsilane

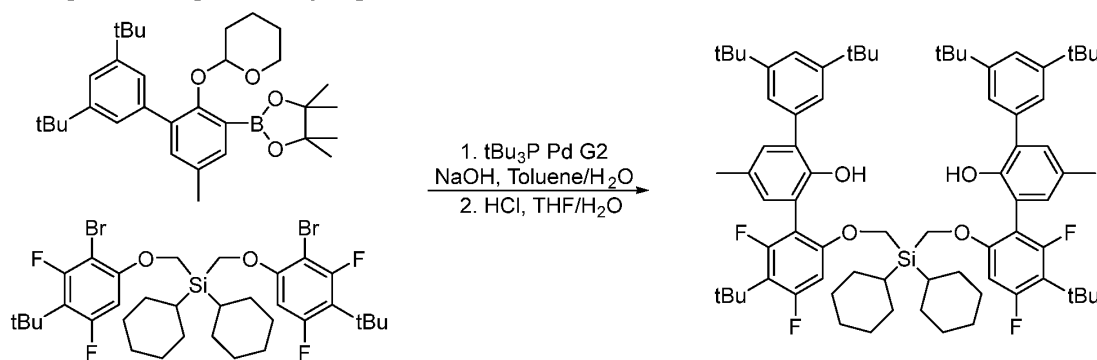


[0175] In a glove box, a 40 mL vial was charged with bis(chloromethyl)dicyclohexylsilane (1.77 g, 6.0 mmol, 1.0 equiv), 2-bromo-4-(tert-butyl)-3,5-difluorophenol (4.0 g, 15.0 mmol, 2.5 equiv), K_3PO_4 (4.48 g, 21.1 mmol, 3.5 equiv), and DMSO (10 mL). The reaction mixture was stirred at 80 °C for 2 hours. After cooling down to room temperature, the reaction mixture was purified by column chromatography using ether/hexane (0/100 → 30/70) as the eluent. A yield of 2.75 g of a colorless oil was collected, providing a 61% yield.

[0176] 1H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, J = 14.7, 2.1 Hz, 2H), 3.85 (s, 4H), 1.85 – 1.79 (m, 2H), 1.78 – 1.68 (m, 10H), 1.45 – 1.41 (m, 18H), 1.28 – 1.18 (m, 10H).

[0177] ^{19}F {1H} NMR (376 MHz, $CDCl_3$) δ -98.07 (d, J = 7.5 Hz, 2F), -105.68 (d, J = 7.5 Hz, 2F).

Example 34: Preparation of Ligand 9

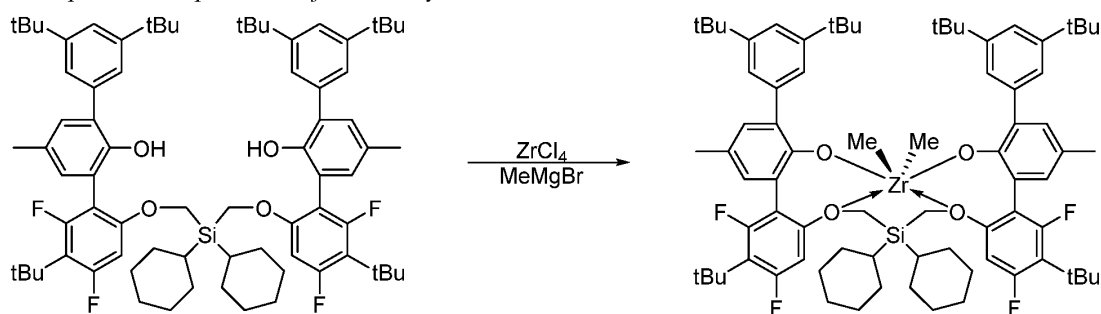


[0178] In a glove box, a 40 mL vial equipped with stir bar was charged with bis((2-bromo-4-(tert-butyl)-3,5-difluorophenoxy)methyl)dicyclohexylsilane (0.78 g, 1.0 mmol, 1.0 equiv), top group (1.47 g, 2.9 mmol, 2.8 equiv), aliquat 336 (10 mg), tBu_3P Pd G2 (0.016 g, 0.03 mmol, 0.03 equiv), toluene (3 mL), and NaOH 4N solution (1.56 mL, 6.2 mmol, 6.0 equiv). The vial was heated under nitrogen at 80 °C overnight. 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 (0.3 mL) was then added. The resulting mixture was heated at 70 °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. A yield of 0.75 g of product was collected, providing a 61% yield.

[0179] ^1H NMR (400 MHz, CDCl_3) δ 7.41 (t, J = 1.8 Hz, 2H), 7.29 (d, J = 1.8 Hz, 4H), 7.14 – 7.08 (m, 2H), 6.91 (dd, J = 6.0, 2.2 Hz, 2H), 6.31 (td, J = 16.1, 15.4, 2.4 Hz, 2H), 5.15 (s, 1H), 5.11 (s, 1H), 3.53 – 3.35 (m, 4H), 2.34 (d, J = 5.9 Hz, 6H), 1.45 (t, J = 2.0 Hz, 18H), 1.41 – 1.23 (m, 10H), 1.32 (s, 36H), 0.96 – 0.70 (m, 12H).

[0180] ^{19}F {1H} NMR (376 MHz, CDCl_3) δ -104.78 (d, J = 7.6 Hz, 1F), -104.94 (d, J = 7.6 Hz, 1F), -105.79 (dd, J = 13.8, 7.7 Hz, 2F).

Example 35: Preparation of Procatalyst 9



[0181] In a glove box, an oven dried 40 mL vial was charged with ZrCl_4 (0.047 g, 0.2 mmol, 1.0 equiv) and anhydrous toluene (6 mL). Cooled to $-30\text{ }^\circ\text{C}$ in freezer. Removed from freezer then added MeMgBr 3 M in ether (0.29 mL, 0.88 mmol, 4.4 equiv) with stirring. After 2 minutes, solution darkened. Added ligand (0.237 g, 0.2 mmol, 1.0 equiv), allowed to warm to room temperature with stirring overnight. Removed solvent under vacuum to yield a dark brown solid which was extracted with hexanes (12 mL) then filtered. The hexane extract was concentrated to ~ 2-3 mL and kept at $-30\text{ }^\circ\text{C}$ for one day. The top solution was decanted and the remaining solid was dried under vacuum affording a white solid. A yield of 0.2 g of product was collected, providing a 77% yield.

[0182] ^1H NMR (400 MHz, C_6D_6) δ 8.08 (br s, 2H), 7.84 (q, J = 1.7 Hz, 2H), 7.51 (br s, 2H), 7.27 (t, J = 3.0 Hz, 2H), 7.20 (d, J = 2.3 Hz, 2H), 5.32 (dd, J = 13.0, 1.8 Hz, 2H), 4.50 (d, J = 13.3 Hz, 2H), 3.45 (d, J = 13.4 Hz, 2H), 2.23 (s, 6H), 1.68 – 1.33 (m, 60H), 1.22 (d, J = 13.0 Hz, 2H), 1.10 – 0.92 (m, 8H), 0.75 – 0.63 (m, 2H), 0.60 – 0.47 (m, 2H), 0.22 – 0.13 (m, 2H), 0.10 (s, 6H).

[0183] ^{19}F {1H} NMR (376 MHz, C_6D_6) δ -101.95 (d, J = 7.1 Hz, 2F), -104.66 (d, J = 7.1 Hz, 2F).

[0184] Procedure for Batch Reactor Polymerization

[0185] 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) were purified with molecular sieves before introduction into the reaction environment. A one gallon (3.79 L) stirred autoclave reactor was charged with ISOPAR[®]E, and 1-octene. The reactor was then heated to the desired temperature and charged with ethylene to bring the total pressure to 410 psig. The catalyst composition was prepared in a drybox under inert atmosphere by mixing the desired metal–ligand complex and a co-catalyst ($[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$) along with modified methylaluminoxane (MMAO), with additional solvent to give a total volume of about 15-20 mL. The activated catalyst mixture was then quick-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.

[0186] Procedure for Continuous Polymerization

[0187] 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. MMAO, commercially available from AkzoNobel, was used as an impurity scavenger. The individual catalyst components (procatalyst or cocatalyst) were manually batch diluted to specified component concentrations with purified solvent (ISOPAR[®]E) and pressured to above reaction pressure. The cocatalyst is $[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and was used at a 1.2 molar ratio relative to the metal–ligand complex of formula (I). All reaction feed flows were measured with mass flow meters and independently controlled with computer automated valve control systems.

[0188] High purity hydrogen is supplied by shared pipeline and dried with molecular sieve. The reactor monomer feed stream is pressurized via a mechanical compressor to above reaction pressure. The solvent feed is pressurized via a pump to above reaction pressure. The comonomer feed is pressurized via a pump to above reaction pressure. The individual catalyst components 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 metering pumps.

[0189] The comonomer feed is mechanically pressurized and can be injected into the process at several potential locations depending on reactor configuration which include: only the feed stream for the first reactor, only the feed stream for the second reactor, or both the first and second reactor feed streams independently.

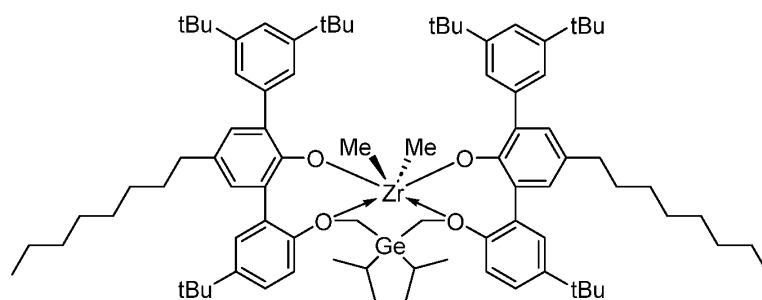
[0190] The continuous solution polymerization reactor consists of a liquid full, adiabatic, and continuously stirred tank reactor (CSTR). Independent control of all solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total feed stream to the reactor (solvent, monomer, comonomer, and hydrogen) is temperature controlled by passing the feed stream through a heat exchanger. The total feed to the polymerization reactor is injected into the reactor in one location. The catalyst components are injected into the polymerization reactor separate from the other feeds. An agitator in the reactor is responsible for continuously mixing of the reactants. An oil bath provides for some fine tuning of the reactor temperature control.

[0191] The final reactor effluent enters a zone where it is deactivated with the addition of and reaction with a suitable reagent (typically water). At this same reactor exit location other additives may also be added for polymer stabilization (Octadecyl 3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate, Tetrakis(Methylene(3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate))Methane, and Tris(2,4-Di-Tert-Butyl-Phenyl) Phosphite).

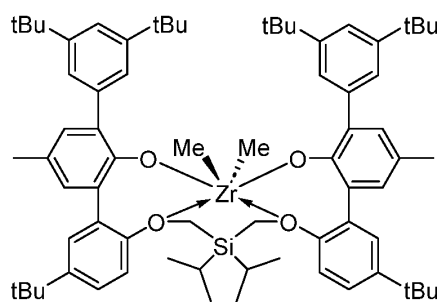
[0192] Following catalyst deactivation and any additive addition, the reactor effluent enters a devolatilization system where the polymer is removed from the non-polymer stream. The non-polymer stream is removed from the system. The isolated polymer melt is pelletized and collected. Catalyst efficiency and resulting polymer characteristics were assessed for Inventive Procatalysts 1–8 and Comparative Procatalysts C1 and C2. Each of Procatalysts 1–8 (shown above) had a structure according to formula (I), where each of Procatalysts 1–5 had a germanium bridge and each of Procatalysts 6–8 had a silicon bridge. For each of Procatalysts 1–8, the R^{17} and R^{18} substituents on the germanium or silicon bridges were independently (C_5 – C_{40})hydrocarbyl.

[0193] Each of comparative Procatalysts C1, C2, and C3 (shown below) had a structure deviating from formula (I) in that the R^{17} and R^{18} substituents on the germanium (C1) or

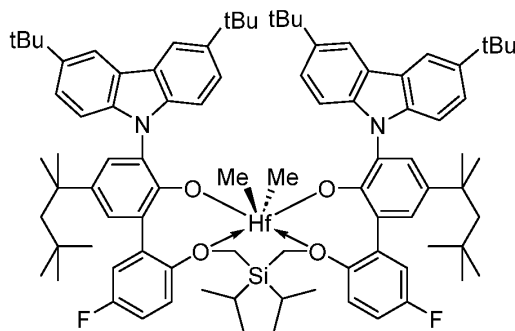
silicon (C2) bridges were isopropyl rather than independently (C₅–C₄₀)hydrocarbyl. Comparative Procatalyst C3 also deviates from formula (I) in terms of the R¹ and R¹⁶ groups are not radicals having formula (II).



Comparative Procatalyst C1



Comparative Procatalyst C2



Comparative Procatalyst C3

[0194] To investigate the effect of R¹⁷ and R¹⁸ of germanium-bridged metal–ligand complexes according to formula (I) being independently (C₅–C₄₀)hydrocarbyl, rather than isopropyl, polymerization reactions were carried out according to the conditions for a single-reactor system as previously described, in each of which reactions one of Procatalysts 1–5 or Comparative Procatalyst C1 was added as the metal–ligand complex of the catalyst

system. Properties for the resulting polymers produced using one of Procatalysts 1–5 or Comparative Procatalyst C1, each having a germanium bridge, are reported in Tables 1–3.

Table 1: Batch Reactor Polymerization Data

Procatalyst	Eff* (g/g)	T _m ** (°C)	MWD [†]	Mw (g/mol)
Procatalyst C1 (comparative)	860,000	104.0	2.03	740,604
Procatalyst 2	1,300,000	103.6	1.79	826,380

Polymerization conditions: 1.47 kg Isopar[®]E; 65 g octene; 100 g ethylene; temperature was 190 °C; total pressure was 410 psig; procatalyst:activator ratio was 1:1.2; activator was [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄]; MMAO was used as an impurity scavenger at a 50:1 molar ratio (Al:procatalyst); reaction time was 10 min.

* Efficiency (Eff) in units of grams of polymer per gram of active metal (Zr) in the catalyst.

** T_m is the melting temperature of the polymer.

[†] MWD is defined as M_w/M_n with M_w being the weight-average molecular weight and M_n being the number-average molecular weight

Table 2: Batch Reactor Polymerization Data

Procatalyst	Eff (g/g)	T _m (°C)	MWD	Mw (g/mol)
Procatalyst C1 (comparative)	580,000	105.2	1.98	582,617
Procatalyst 1	770,000	106.2	3.08	662,507
Procatalyst 3	780,000	104.5	2.39	534,256
Procatalyst 4	1,230,000	106.1	2.85	622,681

Polymerization conditions: same as described above for Table 1.

Table 3: Batch Reactor Polymerization Data

Procatalyst	Eff (g/g)	T _m (°C)	MWD	Mw (g/mol)
Procatalyst C1	390,000	103.8	2.01	564,106

(comparative)				
Procatalyst 4	960,000	104.3	2.22	608,481
Procatalyst 5	520,000	103.8	2.57	610,460

Polymerization conditions: same as described above for Table 1.

[0195] As can be seen from Tables 1–3, polymerization processes using Procatalysts 1–5, each having a metal–ligand complex according to formula (I) with a germanium bridge and with R¹⁷ and R¹⁸ being independently (C₅–C₄₀)hydrocarbyl, demonstrated improved catalyst efficiency relative to the same polymerization process using Comparative Procatalyst C1 (when comparing batch reactor polymerization data within the same campaign), which had the same metal–ligand complex as Procatalysts 1–5 except with respect to the R³ and R¹⁴ groups and the R¹⁷ and R¹⁸ groups. R¹⁷ and R¹⁸ of Comparative Procatalyst C1 were conventional isopropyl groups rather than (C₅–C₄₀)hydrocarbyl groups, and this difference is believed to have resulted in the lower catalyst efficiency of Comparative Procatalyst C1 relative to Procatalysts 1–5. Without wishing to be bound by theory, the R³ and R¹⁴ groups being n-octyl for Comparative Procatalyst C1 is believed to have minimal impact on catalyst efficiency (long alkyl group used mainly for better solubility). It can also be seen from Tables 1–3 that larger R¹⁷ and R¹⁸ groups tends to produce polymers having higher molecular weights.

[0196] To further demonstrate the advantage of R¹⁷ and R¹⁸ being independently (C₅–C₄₀)hydrocarbyl for metal–ligand complexes having a structure according to formula (I) with germanium bridges, the continuous polymerization data for Procatalyst 4 and Comparative Procatalyst C1 are presented in Table 4. The data were obtained at the same C2 conversion (10 g/L C₂ exit). The feed of H₂ was adjusted to reach the desired polymer melt index and the density was allowed to vary in accordance with the catalyst’s 1-octene sensitivity.

Table 4: Continuous Polymerization Data

Procatalyst	Temp (°C)	Eff (g/g)	I ₂ (g/10 min)	I ₁₀ /I ₂	Density (g/mL)
Procatalyst C1 (comparative)	175	0.95	0.37	6.1	0.9004
Procatalyst 4	175	2.80	0.36	6.0	0.8978

[0197] The continuous polymerization data for Procatalyst 4 and Comparative Procatalyst C1 reinforces the findings presented above for batch reactor polymerizations. In particular, the data shows that Procatalyst 4, having a metal–ligand complex according to formula (I) wherein R¹⁷ and R¹⁸ were independently (C₅–C₄₀) hydrocarbyl, rather than isopropyl, allows for improved catalyst efficiency relative to Comparative Procatalyst C1. Moreover, the lower density for Procatalyst 4 relative to Comparative Procatalyst C1, considered in view of the similar I₂ and I₁₀/I₂, indicates that Procatalyst 4 has better comonomer incorporation while having similar long chain branching.

[0198] To investigate the effect of R¹⁷ and R¹⁸ of silicon-bridged metal–ligand complexes according to formula (I) being independently (C₅–C₄₀) hydrocarbyl, rather than isopropyl, polymerization reactions were carried out according to the conditions for a single-reactor system as previously described, in each of which reactions one of Procatalysts 6–8 or Comparative Procatalyst C2 was added as the metal–ligand complex of the catalyst system. Properties for the resulting polymers produced using one of Procatalysts 6–8 or Comparative Procatalyst C2, each having a silicon bridge, are reported in Tables 5 and 6 along with the batch reactor polymerization results for Procatalyst 9 (Table 6).

Table 5: Batch Reactor Polymerization Data

Procatalyst	Eff (g/g)	T _m (°C)	MWD	Mw (g/mol)
Procatalyst C2 (comparative)	230,000	102.5	2.14	530,176
Procatalyst 6	430,000	103.0	2.14	657,973

Polymerization conditions: same as described above for Table 1.

Table 6: Batch Reactor Polymerization Data

Procatalyst	Eff (g/g)	T _m (°C)	MWD	Mw (g/mol)
Procatalyst 7	570,000	102.5	2.27	431,853
Procatalyst 8	330,000	103.3	2.19	425,084
Procatalyst 9	240,000	92.9	2.49	605,082

Polymerization conditions: same as described above for Table 1.

[0199] As can be seen from Tables 5 and 6, polymerization processes using Procatalysts 6–8, each having a metal–ligand complex according to formula (I) with a silicon bridge and with R¹⁷ and R¹⁸ being independently (C₅–C₄₀)hydrocarbyl, demonstrated improved catalyst efficiency relative to the same polymerization process using Comparative Procatalyst C2, which had the same metal–ligand complex as Procatalysts 6–8 except with respect to the R¹⁷ and R¹⁸ groups. R¹⁷ and R¹⁸ of Comparative Procatalyst C2 were conventional isopropyl groups rather than (C₅–C₄₀)hydrocarbyl groups, and this difference explains the lower catalyst efficiency of Comparative Procatalyst C2 relative to Procatalysts 6–8. As with Ge-bridged Procatalysts 1–5, it can also be seen from Tables 5 and 6 that larger R¹⁷ and R¹⁸ groups tends to produce polymers having higher molecular weights.

[0200] To further demonstrate the advantage of R¹⁷ and R¹⁸ being independently (C₅–C₄₀)hydrocarbyl for metal–ligand complexes having a structure according to formula (I) with silicon bridges, the continuous polymerization data for Procatalyst 6 and Comparative Procatalyst C2 are presented in Table 7. The data were obtained at the same C2 conversion (10 g/L C₂ exit). The feed of H₂ was adjusted to reach the desired polymer melt index and the density was allowed to vary in accordance with the catalyst's 1-octene sensitivity.

Table 7: Continuous Polymerization Data

Procatalyst	Temp (°C)	Eff (g/g)	I₂ (g/10 min)	I₁₀/I₂	Density (g/mL)
Procatalyst C2 (comparative)	175	0.95	0.37	6.1	0.9004
Procatalyst 6	175	1.80	0.27	6.3	0.8961

[0201] The continuous polymerization data for Procatalyst 6 and Comparative Procatalyst C2 reinforces the findings presented above for batch reactor polymerizations. In particular, the data shows that Procatalyst 6, having a metal–ligand complex according to formula (I) wherein R¹⁷ and R¹⁸ were independently (C₅–C₄₀)hydrocarbyl, rather than isopropyl, allows for improved catalyst efficiency relative to Comparative Procatalyst C2. Moreover, the lower density for Procatalyst 6 relative to Comparative Procatalyst C2 indicates that Procatalyst 6 has better comonomer incorporation.

[0202] To investigate the ethylene/1-butene copolymerization capabilities of the catalyst systems described herein, a study was conducted wherein Procatalyst 9, having a metal–ligand complex according to formula (I) wherein R¹⁷ and R¹⁸ are independently (C₅–C₄₀)hydrocarbyl, and Comparative Procatalyst C3, having conventional R¹⁷ and R¹⁸ groups rather than (C₅–C₄₀)hydrocarbyl groups, were used to produce a series ethylene/butene copolymer designs having specific density and melt index specifications. The process conditions used for the ethylene/1-butene copolymerization study are reported in Table 8, and various properties for the copolymers produced from this study are reported in Tables 9 and 10 and graphically presented in FIGS. 1A–4.

Table 8: Process Conditions Ethylene/1-Butene Copolymerization Study

Ex. No.	Copoly. Design	Procatalyst	Cocatalyst(s)	Feed Solvent/ Feed C2 Mass Flow Ratio	Feed C4/Feed C2 Mass Flow Ratio	Feed H2/Feed C 2 Mass Flow Ratio	Temp. (°C)	Pressure (barg)	C2 Conv. (%)	Al Content in Reactor from MMAO Cocatalyst (ppm-wt)	Cocat-C/ Procatalyst Molar Ratio	Res. Time (min)
EB-C1	A	Procatalyst C3 (comparative)	Cocat-B and Cocat-C	5.3	0.79	3.60E-04	160	45	89.7	0.27	1.2	39
EB-IE1	A	Procatalyst 9	Cocat-A	5.32	0.71	6.80E-05	160	45	90	3	-	39
EB-C2	C	Procatalyst C3 (comparative)	Cocat-B and Cocat-C	3.69	0.73	1.10E-03	160	45	87	0.13	1.2	13
EB-IE2	C	Procatalyst 9	Cocat-A	3.71	0.67	2.40E-04	160	45	85.2	2	-	13
EB-IE3	B	Procatalyst 9	Cocat-A	3.36	0.73	1.10E-04	165	45	88	4	-	16
EB-IE4	B	Procatalyst 9	Cocat-A	3.57	0.66	1.20E-04	165	45	87.4	4	-	16
EB-C3	B	Procatalyst C3 (comparative)	Cocat-B and Cocat-C	3.53	0.77	3.90E-04	165	45	90.8	0.22	1.2	17
EB-C4	B	Procatalyst C3 (comparative)	Cocat-B and Cocat-C	3.58	0.73	3.70E-04	165	45	90.8	0.38	1.2	15
EB-C5	B	Procatalyst C3 (comparative)	Cocat-B and Cocat-C	3.35	0.77	4.70E-04	165	45	87.8	0.33	1.2	20
EB-IE5	B	Procatalyst 9	Cocat-A	3.53	0.66	1.20E-04	165	45	87.4	2.6	-	16
EB-IE6	B	Procatalyst 9	Cocat-A	3.57	0.66	1.20E-04	165	45	87.4	4	-	16
EB-IE7	B	Procatalyst 9	Cocat-A	3.76	0.66	1.20E-04	155	45	87	3.5	-	16
EB-IE8	B	Procatalyst 9	Cocat-A	3.55	0.68	1.20E-04	165	45	87.3	3.5	-	17

Cocat-A = Modified methylalumoxane (MMAO), specifically, the compound is modified with n-octyl substituents such that the methyl:n-octyl ratio is approximately 6:1 and containing 10-20% trialkyl aluminum species. Each of the copolymerization runs were conducted in a well-mixed reactor.

Cocat-B = Modified methylalumoxane (MMAO) Type 3A (no further purification performed) (Akzo Nobel)

Cocat-C = A mixture of methyl/di(C₄-C₁₈ alkyl)ammonium salts of tetrakis(pentafluorophenyl)borate, prepared by reaction of a long chain trialkylamine (Armeen™ M2HT, available from Akzo-Nobel, Inc.), HCl and Li[B(C₆F₅)₄], substantially as disclosed in USP 5,919,983, Ex. 2 (no further purification performed) (Boulder Scientific).

Table 9: Results of Ethylene/1-Butene Copolymerization Study

Example No.	Copoly. Design	Procatalyst	Density (g/cc)	I ₂ (g/10 min)	I ₁₀ /I ₂	Ethylene (wt%)	Butene (wt%)	HCC (wt%)	BBB Content (per 1000C)	Vinyl Content (per 1000C)	Total unsat. (per 1000C)
EB-C1	A	Procatalyst C3 (comparative)	0.861	0.26	9.3	65.4	34.6	NM	0.012	0.021	0.052
EB-IE1	A	Procatalyst 9	0.861	0.27	8.3	67.7	32.3	0.64	0.007	0.007	0.072
EB-C2	C	Procatalyst C3 (comparative)	0.867	5.0	6.5	69.2	30.8	2.8	0.009	0.01	0.024
EB-IE2	C	Procatalyst 9	0.866	5.4	5.9	70.7	29.3	0.58	0.005	0.007	0.03
EB-IE3	B	Procatalyst 9	0.86	1.2	6.9	67.3	32.7	1.12	0.007	0.008	0.05
EB-IE4	B	Procatalyst 9	0.865	1.1	7.1	70	30	0.59	0.006	0.008	0.041
EB-C3	B	Procatalyst C3 (comparative)	0.861	1.4	7.3	64.7	35.3	4.1	0.014	0.012	0.039
EB-C4	B	Procatalyst C3 (comparative)	0.863	1.2	7.5	66.5	33.5	2.5	0.011	0.013	0.038
EB-C5	B	Procatalyst C3 (comparative)	0.863	1.2	7.0	67.3	32.7	1.5	0.011	0.013	0.032
EB-IE5	B	Procatalyst 9	0.865	1.2	6.7	70.2	29.8	0.80	0.005	0.008	0.043
EB-IE6	B	Procatalyst 9	0.865	1.2	6.7	70	30	0.62	0.006	0.008	0.041
EB-IE7	B	Procatalyst 9	0.863	1.2	6.5	69.7	30.3	0.58	0.005	0.006	0.031
EB-IE8	B	Procatalyst 9	0.863	1.2	6.8	69	31	0.77	0.006	0.008	0.044

NM = not measured

Table 10: Molecular Weight Results of Ethylene/1-Butene Copolymerization Study

Example No.	Copoly Design	Procatalyst	Mn (kg/mol)	Mw (kg/mol)	MWD	Mz (kg/mol)
EB-C1	A	Procatalyst C3 (comparative)	58.1	143	2.46	255
EB-IE1	A	Procatalyst 9	64.2	146	2.27	256
EB-C2	C	Procatalyst C3 (comparative)	30.6	73	2.39	126
EB-IE2	C	Procatalyst 9	33.7	72.9	2.16	121
EB-IE3	B	Procatalyst 9	46.7	105	2.26	182
EB-IE4	B	Procatalyst 9	46.5	105	2.25	182
EB-C3	B	Procatalyst C3 (comparative)	41.5	101	2.44	180
EB-C4	B	Procatalyst C3 (comparative)	41.9	102	2.43	183
EB-C5	B	Procatalyst C3 (comparative)	44.4	104	2.35	181
EB-IE5	B	Procatalyst 9	45.6	103	2.27	177
EB-IE6	B	Procatalyst 9	46.6	104	2.24	179
EB-IE7	B	Procatalyst 9	47.9	106	2.22	180
EB-IE8	B	Procatalyst 9	38.2	88.9	2.33	152

[0203] As can be seen from Table 9 above, ethylene/butene copolymerization processes employing Procatalyst 9, having a metal–ligand complex according to formula (I), allow for the production of ethylene/butene copolymers with reduced HCC fractions, narrow SCBDs, low vinyl unsaturation, and low levels of BBB triads. Without wishing to be bound by theory, it is believed that Comparative Procatalyst C3’s deviations with respect to formula (I) in terms of the R¹⁷ and R¹⁸ groups on the silicon bridge not being independently (C₅–C₄₀)hydrocarbyl, and in terms of the R¹ and R¹⁶ groups are not radicals having formula (II), result in increased HCC fractions, broader SCBDs, higher vinyl unsaturation, and higher levels of BBB triads.

[0204] FIGS. 1A–1C show TGIC SCBD curves of samples of similar copolymer designs where it can be seen that Procatalyst 9, having a metal–ligand complex according to formula (I), provides for narrower SCBD curves than Comparative Procatalyst C3 for each of the tested density and melt index specifications.

[0205] FIG. 2 graphically depicts HCC value (wt%) versus density (g/cc) for the ethylene/1-butene copolymers produced in the ethylene/butene copolymerization study, where it can be seen that, across the tested density range, inventive Procatalyst 9 consistently produces HCC values lower than 1.4 wt%, while Comparative Procatalyst C3 consistently produces HCC values higher than 1.4 wt%. As described above, this lower HCC value results in better solid handling performance of the polymer.

[0206] FIG. 3 graphically depicts BBB Triads Content (BBB triads per 1000 carbon atoms) versus density (g/cc) for the ethylene/1-butene copolymers produced in the ethylene/butene copolymerization study, where it can be seen that, across the tested density range, inventive Procatalyst 9 consistently produces polymers having less than or equal to 0.0075 BBB triads per 1000 carbons, while Comparative Procatalyst C3 consistently produces polymers having greater than or equal to 0.0075 BBB triads per 1000 carbons. The reduced BBB triads content of the polymers produced by inventive Procatalyst 9 are expected to result in improved solids handling and curing performance.

[0207] FIG. 4 graphically depicts Vinyl Content (vinyls per 1000 carbon atoms) versus density (g/cc) for the ethylene/1-butene copolymers produced in the ethylene/butene copolymerization study, where it can be seen that, across the tested density range, inventive Procatalyst 9 consistently produces polymers having less than 0.01 vinyls per 1000 carbons, while Comparative Procatalyst C3 consistently produces polymers having greater than or equal to 0.01 vinyls per 1000 carbons. The reduced vinyl unsaturation of the polymers produced by inventive Procatalyst 9 are expected to improve the environmental aging performance of the polymers.

TEST METHODS

[0208] Density

[0209] Samples that were measured for density were prepared according to ASTM D-1928, which is incorporated herein by reference in its entirety. Measurements were made within one hour of sample pressing using ASTM D-792, Method B, which is incorporated herein by reference in its entirety.

[0210] Melt Index

[0211] Melt index (I_2) was measured in accordance with ASTM-D 1238, which is incorporated herein by reference in its entirety, Condition 190 °C/2.16 kg, and was reported

in grams eluted per 10 minutes. Melt flow rate (I_{10}) was measured in accordance with ASTM-D 1238, Condition 190 °C/10 kg, and was reported in grams eluted per 10 minutes.

[0212] Gel Permeation Chromatography (GPC)

[0213] 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 °C and the column and detector compartment were set at 150 °C. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0214] 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 pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160 °C for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

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

where M is the molecular weight, A has a value of 0.4163 and B is equal to 1.0.

[0215] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[0216] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

[0217] 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.

[0218] The calculations of $Mn_{(GPC)}$, $MW_{(GPC)}$, and $MZ_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

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

$$MW_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ\ 3)$$

$$MZ_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (EQ\ 4)$$

[0219] 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. After calibrating

the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPC One™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)}/\text{RV(FM Sample)}) \quad (\text{EQ5})$$

[0220] Differential Scanning Calorimetry (DSC)

[0221] Baseline calibration of the DSC Q1000 is performed by using the calibration wizard in the software. First, a baseline is obtained by heating the cell from -80 °C to 280 °C without any sample in the aluminum DSC pan. After that, sapphire standards are used according to the instructions in the wizard. Then about 1 to 2 mg of a fresh indium sample is analyzed by heating the sample to 180 °C, cooling the sample to 120 °C at a cooling rate of 10 °C/min followed by keeping the sample isothermally at 120 °C for 1 minute, followed by heating the sample from 120 °C to 180 °C at a heating rate of 10 °C/min. The heat of fusion and the onset of melting of the indium sample are determined and checked to be within 0.5 °C from 156.6 °C for the onset of melting and within 0.5 J/g from 28.71 J/g for the heat of fusion. Then de-ionized water is analyzed by cooling a small drop of fresh sample in the DSC pan from 25 °C to -30 °C at a cooling rate of 10 °C/min. The sample is kept isothermally at -30 °C for 2 minutes and heated to 30 °C at a heating rate of 10 °C/min. The onset of melting is determined and checked to be within 0.5 °C from 0 °C. Samples of polymer are then pressed into a thin film at a temperature of 350 °F. About 5 to 8 mg of sample is weighed out and placed in a DSC pan. A lid is crimped on the pan to ensure a closed atmosphere. The sample pan is placed in the DSC cell and then heated at a high rate of about 100 °C/min to a temperature of about 30 °C above the polymer melt temperature. The sample is kept at this temperature for 5 minutes. Then the sample is cooled at a rate of 10 °C/min to -40 °C, and kept isothermally at that temperature for 5 minutes. Consequently, the sample is heated at a rate of 10 °C/min until melting is complete. The resulting enthalpy curves are analyzed.

[0222] Measurement for Efficiency

[0223] The catalytic efficiency was measured in terms of amount of polymer produced relative to the amount of catalyst (active metal) used in solution polymerization process.

[0224] ¹H NMR and ¹³C NMR

[0225] Methods for determining comonomer content (Comonomer Content Measurement Method), total unsaturation (Total Unsaturation Measurement Method), vinyl/1000C (Vinyl Content Measurement Method), and BBB triads (BBB Triads Measurement Method) using ^1H and ^{13}C NMR spectroscopy are provided below.

[0226] The total unsaturation level and vinyl/1000C are determined by ^1H NMR analysis. Approximately 3.25 grams of a 50/50 mixture of tetrachloroethane- d_2 /perchloroethylene, containing 0.001M chromium acetylacetonate as a relaxation agent, is added to 0.130 grams of the sample in a 10 mm NMR tube with 100 ppm I-168. The samples are dissolved and homogenized by heating the tube and its contents to 110 °C. Data is collected using a Bruker 600 MHz spectrometer equipped with a multinuclear high-temperature CryoProbe. The unsaturation data is collected using 16 scans per data file, a 15.8-second pulse repetition delay, and a sample temperature of 120 °C. The spectral width is set to 12,019 Hz with a file size of 32K data points. Presaturation experiments are conducted using 100 scans per data file.

[0227] For the ^1H NMR calculations of total unsaturation and vinyls/1000C, two experiments are performed: a control spectrum to quantify the total polymer protons and a double presaturation experiment to suppress the intense polymer backbone peaks, enabling high sensitivity spectra for quantifying the unsaturation. The signal from residual ^1H in TCE- d_2 (at 6.0 ppm) is integrated and set to a value of 100, and the integral from 3 to -0.5 ppm is used as the signal from the whole polymer in the control experiment. In the presaturation experiment, the TCE signal is also set to 100, and the corresponding integrals for unsaturation (vinylene, trisubstituted unsaturation, vinyl, and vinylidene) are obtained. The integrals of regions for cis- and trans-vinylene (from about 5.40 to 5.60 ppm), trisubstituted (from about 5.16 to 5.35 ppm), vinyl (from about 4.95 to 5.15 ppm), and vinylidene (from about 4.70 to 4.90 ppm) are obtained. The BHT -OH signal, or any other additive signals, if present, was not included in the integral areas.

[0228] The integral of the whole polymer from the control experiment is divided by 2 to obtain a value representing X thousands of carbons. The unsaturated group integrals, divided by the corresponding number of protons contributing to that integral, represents the moles of each type of unsaturation per X thousand carbons. Dividing the moles of each type of unsaturation by X gave the moles of unsaturated groups per 1000 moles of carbons. The total

unsaturation level is the sum of cis- and trans-vinylene, trisubstituted, vinyl, and vinylidene, all in units of moles of unsaturated groups per 1000 moles of carbons.

[0229] ^{13}C NMR

[0230] Comonomer content and sequence distribution are determined by ^{13}C NMR analysis. Approximately 2.6 grams of a 75/25 mixture of tetrachloroethane/tetrachloroethane- d_2 , containing 0.025M chromium acetylacetonate as a relaxation agent, is added to 0.2 grams of the sample in a 10 mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150 °C. Data is collected using a Bruker 600 MHz spectrometer equipped with a multinuclear high-temperature CryoProbe. The data acquisition involves 256 scans per data file, a 7.8-second pulse repetition delay, and a sample temperature of 120 °C. The spectral width is set to 35,700 Hz with a file size of 131K data points.

[0231] For the analysis of comonomer content and BBB triads mole fraction, the ^{13}C NMR spectra are integrated and analyzed using a Matrix Method. This method involves solving the vector equation $\mathbf{s}=\mathbf{fM}$, where $\mathbf{M}$ is an assignment matrix, $\mathbf{s}$ is a row vector representation of the spectrum, and $\mathbf{f}$ is a mole fraction composition vector. The elements of $\mathbf{f}$ represent triads of C2 and C4 with all permutations of C2 and C4. The assignment matrix $\mathbf{M}$ is constructed with one row for each triad in $\mathbf{f}$ and a column for each of the integrated NMR signals. The elements of the matrix are integral values determined by reference to established assignments in “Multidimensional NMR Studies of Poly(ethylene-co-1-butene) Microstructures,” Sahoo, S. K. et al., *Macromolecules*, Volume 34, Issue 2001, Pages 4757–67 (2003), which is incorporated by reference herein in its entirety. The equation is solved by varying the elements of $\mathbf{f}$ to minimize the error function between $\mathbf{s}$ and the integrated ^{13}C data for each sample. This process is executed using the Solver function in Microsoft Excel.

[0232] Thermal Gradient Interaction Chromatography (HCC Measurement Method)

[0233] A commercial Crystallization Elution Fractionation instrument (CEF) (Polymer Char, Spain) is used to perform the high temperature thermal gradient interaction chromatography (HT-TGIC, or TGIC) measurement (Cong, et al., *Macromolecules*, 2011, 44 (8), 3062-3072.). The CEF instrument is equipped with an IR-5 detector. Graphite has been used as the stationary phase in an HT TGIC column (Freddy, A. Van Damme et al., US8, 476,076; Winniford et al., US 8,318,896.). A single graphite column (250 X 4.6 mm) is used for the separation. Graphite is packed into a column using a dry packing technique followed

by a slurry packing technique (Cong et al., EP 2714226B1 and the reference cited). The experimental parameters are: top oven/transfer line/needle temperature at 150 °C, dissolution temperature at 150 °C, dissolution stirring setting of 2, pump stabilization time of 15 seconds, a pump flow rate for cleaning the column at 0.500 mL/min, pump flow rate of column loading at 0.300 mL/min, stabilization temperature at 150 °C, stabilization time (pre-, prior to load to column) at 1.0 min, stabilization time (post-, after load to column) at 1.0 min, SF(Soluble Fraction) time at 5.0 min, cooling rate of 3.00 °C/min from 150 °C to 30 °C, flow rate during cooling process of 0.03 mL/min, heating rate of 2.00 °C/min from 30 °C to 160 °C, isothermal time at 160 °C for 10 min, elution flow rate of 0.500 mL/min, and an injection loop size of 200 microliters.

[0234] The flow rate during cooling process is adjusted according to the length of graphite column such that all polymer fractions must remain on the column at the end of the cooling cycle.

[0235] Samples are prepared by the PolymerChar autosampler at 150 °C, for 120 minutes, at a concentration of 4.0 mg/mL in ODCB (defined below). Silica gel 40 (particle size 0.2 ~0.5 mm, catalogue number 10181-3, EMD) is dried in a vacuum oven at 160 °C, for about two hours, prior to use. For the CEF instrument equipped with an autosampler with N₂ purging capability, Silica gel 40 (5.0 grams) is added to two liters of ortho-dichlorobenzene (ODCB, 99% anhydrous grade, Sigma-Aldrich) or Silica gel 40 was packed into three 300 x 7.5 mm GPC size stainless steel columns and the Silica gel 40 columns are installed at the inlet of the pump of the CEF instrument to dry ODCB. This “ODCB containing silica gel” or ODCB dried with silica gel 40 is now referred to as “ODCB.” The TGIC data is processed on a PolymerChar (Spain) “GPC One” software platform. The temperature calibration is performed with a mixture of about 4 to 6 mg Eicosane, 14.0 mg of isotactic homopolymer polypropylene iPP (polydispersity of 3.6 to 4.0, and molecular weight Mw reported as polyethylene equivalent of 150,000 to 190,000, and polydispersity (Mw/Mn) of 3.6 to 4.0, wherein the iPP DSC melting temperature is measured to be 158-159 °C (DSC method described herein below). 14.0 mg of homopolymer polyethylene HDPE (having non-measurable comonomer content, weight average molecular weight (Mw) reported as polyethylene equivalent as 115,000 to 125,000, and polydispersity of 2.5 to 2.8), in a 10 mL vial filled with 7.0 mL of ODCB. The dissolution time is 2 hours at 160 °C.

[0236] For the calibration process, a solution of eicosane and HDPE is used. For elution temperatures in the range of 30 °C to 150 °C, the process consists of the following steps:

[0237] 1. Extrapolate eluting temperature for each of the isothermal steps during elution according to heating rate (demonstrated in FIG. 5).

[0238] 2. Calculate the delay volume. Shift the temperature (x-axis) corresponding to the IR measurement channel chromatogram (y-axis), so that the Eicosane peak maximum (y-axis) is coincident with the elution temperature at 30.0 °C. The delay volume is calculated from the temperature difference (30 °C – the actual elution temperature of Eicosane peak maximum) divided by the heating rate of the method, and then multiplied by the elution flow rate.

[0239] 3. Adjust each recorded elution temperature with this same delay volume adjustment.

[0240] 4. Linearly scale the heating rate, such that the observed HDPE reference has an elution peak maximum temperature of 150.0 °C, while the Eicosane elution peak maximum temperature remains at 30.0 °C.

[0241] The comonomer content versus elution temperature of HT TGIC is constructed by using at least 20 reference materials (ethylene homopolymer and ethylene-octene random copolymer made with single site metallocene catalyst, having ethylene equivalent weight average molecular weight ranging from 35,000 to 236,000 g/mol and polydispersity of 2.0–2.5). Cong et al., *Macromolecule*, 2011, 44 (8), 3062-3072). All of these reference materials are prepared at 4 mg/mL and analyzed the same way as specified previously. The mathematical fit of the reported elution peak temperatures as a function of octene mol% using linear regression resulted in Equation 6 (EQ6) for which R^2 was greater than 0.99.

$$(\text{Elution Temperature in Degrees C}) = -4.0831 \times (\text{Octene Mol\%}) + 149.6 \quad (\text{EQ6})$$

[0242] Data processing for polymer samples of HT-TGIC is described below.

[0243] A solvent blank (pure solvent injection) is run at the same experimental conditions as the polymer samples. Data processing for polymer samples includes: subtraction of the solvent blank for each detector channel, temperature extrapolation as described in the calibration process, compensation of temperature with the delay volume determined from the calibration process, and adjustment in elution temperature axis to the 30 °C and 160 °C range as calculated from the heating rate of the calibration.

[0244] The chromatogram (measurement channel of the IR-5 detector) is integrated with PolymerChar “GPC One” software. A straight baseline is drawn from the visible difference, when the peak falls to a flat baseline (roughly a zero value in the blank subtracted chromatogram) at high elution temperature and the minimum or flat region of detector signal on the low temperature side of the soluble fraction (SF).

[0245] The upper temperature integration limit is established based on the visible difference when the peak falls to the flat baseline region (roughly a zero value in the blank subtracted chromatogram). The lower temperature integration limit is established based on the intersection point of baseline with the chromatogram including the soluble fraction.

[0246] The “High Comonomer Content (HCC)” is defined as the polymer fraction eluting between the lower temperature integration limit to 52.0 °C. The HCC value is determined from the area from ~27.0 °C to 52.0 °C, divided by the total area (~27.0 °C. to 160 °C.), and this quotient multiplied by 100.

[0247] Below if the DSC method used to measure melting temperature of homopolymer polypropylene specified in HT-TGIC.

[0248] Melting point of iPP is determined using a differential scanning calorimeter (DSC). The temperature at the maximum heat flow rate with respect to a linear baseline is used as the melting point. The linear baseline is constructed from the beginning of the melting (above the glass transition temperature) and to the end of the melting. The temperature is raised from room temperature to 200 °C at 10 °C/min, maintained at 200 °C for 5 min, decreased to 0 °C at 10 °C/min, maintained at 0 °C for 5 min and then the temperature was raised from 0 °C to 200 °C at 10 °C/min, and the data are taken from this second heating cycle.

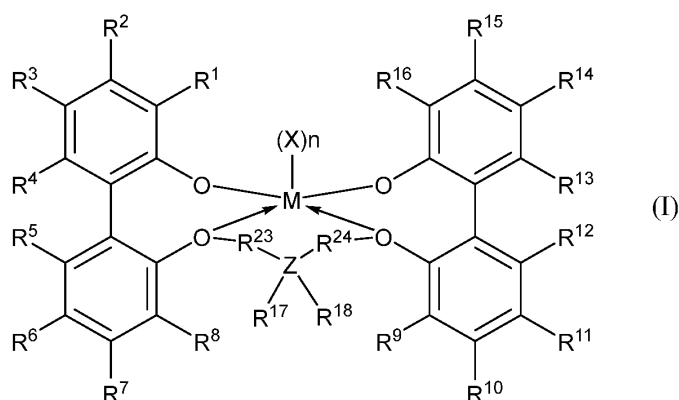
[0249] Reference throughout this specification to “one embodiment,” “certain embodiments,” “various embodiments,” “one or more embodiments” or “an embodiment” means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the disclosure. Thus, the appearances of the phrases such as “in embodiments,” “in one or more embodiments,” “in certain embodiments,” “in various embodiments,” “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment, or to only one embodiment. Furthermore, the particular features,

structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

[0250] It should be apparent to those skilled in the art that various modifications can be made to the described embodiments without departing from the spirit and scope of the claimed subject matter. Thus, it is intended that the specification cover modifications and variations of the described embodiments provided such modification and variations come within the scope of the appended claims and their equivalences.

CLAIMS

1. A catalyst system comprising a metal–ligand complex according to formula (I):



where:

M is a metal chosen from titanium, zirconium, or hafnium;

n is 1 or 2;

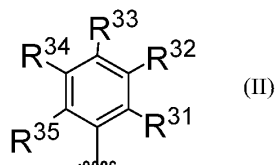
when n is 1, X is a monodentate ligand or a bidentate ligand;

when n is 2, each X is an independently chosen monodentate ligand;

the metal–ligand complex is overall charge-neutral;

each Z is independently chosen from silicon or germanium;

R¹ and R¹⁶ are independently radicals having formula (II):



where:

each of R^{31–35} is independently chosen from (C₁–C₄₀)hydrocarbyl,

(C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –OR^C, –SR^C, –CN, –CF₃, halogen,
and –H,

each of R^{2–4}, R^{5–8}, R^{9–12}, and R^{13–15} is independently selected from

(C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃,
–P(R^P)₂, –N(R^N)₂, –N=CHR^C, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–,

$R^C S(O)_2-$, $(R^C)_2 C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R^N)-$,
 $(R^C)_2 NC(O)-$, halogen, and $-H$;

R^{17} and R^{18} are independently (C_5-C_{40}) hydrocarbyl;

R^{23} and R^{24} are independently selected from $-(CR^C)_m-$, where m is 1 or 2; and

each R^C , R^P , and R^N in formula (I) is independently (C_1-C_{30}) hydrocarbyl,
 (C_1-C_{30}) heterohydrocarbyl, or $-H$.

2. The catalyst system according to claim 1, wherein R^{17} and R^{18} are independently (C_5-C_{20}) alkyl.
3. The catalyst system according to any one of the preceding claims, wherein R^{17} and R^{18} are connected to form a ring structure having at least 5 carbon atoms.
4. The catalyst system according to any one of the preceding claims, wherein R^6 and R^{11} are independently (C_2-C_{12}) alkyl.
5. The catalyst system according to any one of the preceding claims, wherein at least one of R^1 and R^{16} is a radical having formula (II), wherein R^{32} and R^{34} are *tert*-butyl.
6. The catalyst system according to any one of the preceding claims, wherein R^3 and R^{14} are independently (C_1-C_{12}) alkyl.
7. The catalyst system according to any of the preceding claims, wherein R^3 and R^{14} are independently *tert*-octyl, *n*-octyl, or methyl.
8. The catalyst system according to any one of the preceding claims, wherein R^6 and R^{11} are *tert*-butyl.
9. The catalyst system according to any one of the preceding claims, wherein R^8 and R^9 are $-H$.
10. The catalyst system according to any one of the preceding claims, wherein R^7 and R^{10} are halogen.
11. The catalyst system according to any one of the preceding claims, wherein R^5 and R^{12} are halogen.

12. The catalyst system according to any one of the preceding claims, wherein each X is a ligand independently chosen from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –CH₂Si(R^C)_{3-Q}(OR^C)_Q, –Si(R^C)_{3-Q}(OR^C)_Q, –OSi(R^C)_{3-Q}(OR^C)_Q, –CH₂Ge(R^C)_{3-Q}(OR^C)_Q, –Ge(R^C)_{3-Q}(OR^C)_Q, –P(R^C)_{2-W}(OR^C)_W, –P(O)(R^C)_{2-W}(OR^C)_W, –N(R^C)₂, –NH(R^C), –N(Si(R^C)₃)₂, –NR^CSi(R^C)₃, –NHSi(R^C)₃, –OR^C, –CN, –CF₃, and halogen, wherein each R^C is independently a substituted or unsubstituted (C₁–C₃₀)hydrocarbyl, or a substituted or unsubstituted (C₁–C₃₀)heterohydrocarbyl, each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2.
13. The catalyst system according to any one of the preceding claims, wherein R¹⁷ and R¹⁸ are independently (C₅–C₂₀)cycloalkyl.
14. A polymerization process for producing an ethylene-based polymer, the polymerization process comprising:
 polymerizing ethylene and optionally a (C₃–C₁₂)α-olefin in the presence of a catalyst system according to any one of claims 1–13, wherein the ethylene-based polymer has:
 a density from 0.850 g/cm³ to 0.970 g/cm³ measured according to ASTM D792;
 a melt flow ratio (I₁₀/I₂) from 5 to 15, where melt index I₂ is measured according to ASTM D1238 at 190 °C and 2.16 kg load, and melt index I₁₀ is measured according to ASTM D1238 at 190 °C and 10 kg load; and
 a molecular weight distribution (MWD) from 1 to 5, where MWD is a ratio of weight average molecular weight to number average molecular weight.
15. The polymerization process according to claim 14, wherein the catalyst system further comprises at least one cocatalyst.
16. The polymerization process according to claim 15, wherein the at least one cocatalyst comprises modified methylaluminoxane (MMAO).
17. The polymerization process according to claim 16, wherein the modified methylaluminoxane (MMAO) comprises 10–20% trialkyl aluminum species.

18. The polymerization process according to any one of claims 14 to 17, wherein the ethylene and the (C₃–C₁₂) α -olefin are polymerized via solution polymerization.
19. The polymerization process according to claim 18, wherein the ethylene and the (C₃–C₁₂) α -olefin are polymerized via solution polymerization in a loop reactor system.
20. The polymerization process according to any one of claims 14 to 19, wherein the (C₃–C₁₂) α -olefin is 1-butene.
21. The polymerization process according to claim 20, wherein the ethylene-based polymer comprises from 20 wt% to 40 wt% units derived from 1-butene, based on a total weight of the ethylene-based polymer.
22. The polymerization process according to any one of claims 14 to 21, wherein:
the density of the ethylene-based polymer is from 0.854 g/cm³ to 0.875 g/cm³; and
the melt index I₂ of the ethylene-based polymer is from 0.1 to 30 dg/min.
23. The polymerization process according to any one of claims 14 to 21, wherein:
the density of the ethylene-based polymer is from 0.854 g/cm³ to 0.875 g/cm³; and
the ethylene-based polymer has a weight average molecular weight from 50 kg/mol to 200 kg/mol.
24. The polymerization process according to any one of claims 14 to 23, wherein the ethylene-based polymer comprises less than 0.01 vinyls per 1000 carbons.
25. The polymerization process according to any one of claims 18 to 24, wherein the ethylene-based polymer has an HCC (high comonomer content) value of less than 3.0 wt%, wherein the HCC value is measured using thermal gradient interaction chromatography (TGIC) in accordance with HCC Measurement Method.
26. The polymerization process according to any one of claims 18 to 25, wherein the ethylene-based polymer has less than 0.0075 BBB triads per 1000 carbons, wherein the BBB triads content is measured in accordance with BBB Measurement Method.
27. An ethylene-based polymer comprising the polymerized reaction product of ethylene monomer and 1-butene comonomer, wherein the ethylene-based polymer has:

a density from 0.854 g/cm³ to 0.875 g/cm³ measured according to ASTM D792;
a melt index I₂ from 0.1 to 30 dg/min, where melt index I₂ is measured according to ASTM D1238 at 190 °C and 2.16 kg load;
a melt flow ratio (I₁₀/I₂) from 5 to 15, where melt index I₁₀ is measured according to ASTM D1238 at 190 °C and 10 kg load;
a molecular weight distribution (MWD) from 1.5 to 5, where MWD is a ratio of weight average molecular weight to number average molecular weight;
an HCC (high comonomer content) value of less than 1.4 wt%, wherein the HCC value is measured using thermal gradient interaction chromatography (TGIC) in accordance with HCC Measurement Method; and
a BBB triads content of less than 0.0075 BBB triads per 1000 carbons, wherein the BBB triads content is measured in accordance with BBB Measurement Method.

28. The ethylene-based polymer according to claim 27, wherein the ethylene-based polymer comprises from 20 wt% to 40 wt% units derived from 1-butene comonomer, based on a total weight of the ethylene-based polymer.

29. The ethylene-based polymer according to either one of claims 27 or 28, wherein the ethylene-based polymer comprises less than 0.01 vinyls per 1000 carbons.