

OLEFIN POLYMERIZATION ACTIVATORS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/516,600 filed July 31, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to olefin polymerization catalyst systems and processes and, more specifically to olefin polymerization catalyst systems including a group 4 metal–ligand complex and an activator or co-catalyst.

BACKGROUND

[0003] Olefin based polymers, such as ethylene-based polymers, are produced via various catalyst systems. Selection of such catalyst systems can be an important factor contributing to the characteristics and properties of olefin-based polymers. The catalyst systems for producing polyethylene-based polymers may include a chromium-based catalyst system, a Ziegler–Natta catalyst system, or a molecular (either metallocene or non-metallocene) catalyst system.

[0004] Often, the catalyst systems used for α -olefin polymerization reactions include a procatalyst that is activated to generate the catalytically active species for polymerization. The procatalyst can be activated by a number of means, such as by a co-catalyst or an activator. An activator may have characteristics that are beneficial for the production of the α -olefin polymer and for final polymer compositions including the α -olefin polymer. Activator characteristics that increase the production of α -olefin polymers include, but are not limited to: rapid procatalyst activation, high catalyst efficiency, high temperature capability, consistent polymer composition, and selective deactivation.

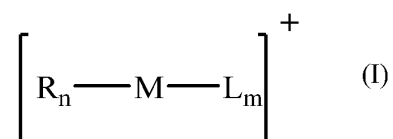
[0005] Presently, the number of available activators is very small compared to available procatalysts. Thus, there is a considerable need to expand the number of activators in order to identify the most commercially effective procatalyst/activator pair.

SUMMARY

[0006] One method of procatalyst activation employs a Brønsted acid activator. Brønsted acid salts containing weakly coordinating anions are commonly utilized to activate molecular polymerization procatalysts, particularly such procatalysts comprising Group IV metal complexes. Brønsted acid salts that are fully ionized are capable of transferring a proton to form a cationic derivative of such Group IV metal complexes. The cationic component of such activators may include cations capable of transferring a hydrogen ion, such as ammonium, sulfonium, or phosphonium; oxidizing cations, such as ferrocenium, silver, or lead; or highly Lewis acidic cations, such as carbonium or silylium.

[0007] Conventional olefin polymerization activators include weakly-coordinating or non-coordinating anions. For instance, such activators may include an R_2Al^+ cation (R =hydrocarbon, alkoxides, amines, phosphines) paired with the non-coordinating $^-B(C_6F_5)_4$ anion. However, R_2Al^+ cations have previously been reported to degrade $^-B(C_6F_5)_4$ in the absence of Lewis bases (Bochmann, M.; Sarsfield, M. J. *Organometallics* 1998, 17, 5908). Disclosed herein are activators comprising Lewis base additives to stabilize the cationic center and, hence, allow for shelf-stable, longer lived materials that still possess a high degree of Lewis acidity so as to be able to activate polyolefin procatalysts.

[0008] According to one or more embodiments disclosed herein, a process of polymerizing olefins includes polymerizing ethylene and optionally one or more α -olefin monomers in the presence of a catalyst system that includes a procatalyst metal-ligand complex and a metallic activator ionic complex. The metallic activator ionic complex includes a cation and a weakly coordinating counteranion, the cation having a structure according to formula (I):



[0009] The counteranion may be any weakly coordinating anion having a formal charge of -1. In formula (I), M is magnesium, boron, aluminum, gallium, zinc, germanium or silicon. When M is zinc or magnesium, n is 1; when M is boron, aluminum, or gallium, n is 2; and when M is silicon or germanium, n is 3. In formula (I), m is 1, 2, or 3. Each R is a ligand independently selected from the group consisting of (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-OR^C$, $-SiC^R$, $-CH_2Si(OR^C)_wR^C_Y$, $-CH_2Si(NR^N)_wR^C_Y$, $-NR^N$, and $-NR^N_2$; where R^C is

(C₁–C₃₀)hydrocarbyl, R^N is (C₁–C₃₀)hydrocarbyl or hydrogen, w is 1, 2, or 3, and y is 0, 1, or 2, provided that the sum of w plus y is 3. Each L is a neutral Lewis base. When n is 2 or 3, each R is optionally covalently connected to form a multidentate ligand. When m is 2 or 3, each L is optionally covalently connected to form a Lewis base having at least two coordinating atoms.

DETAILED DESCRIPTION

[0010] Specific embodiments of the process of polymerizing olefins will now be described. It should be understood that the process of polymerizing olefins 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.

[0011] The term “independently selected” is used herein to indicate that the R groups, such as, R¹, R², R³, R⁴, and R⁵, can be identical or different (e.g., R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc). A chemical name associated with an R group is intended to convey the chemical structure that is recognized in the art as corresponding to that of the chemical name. Thus, chemical names are intended to supplement and illustrate, not preclude, the structural definitions known to those of skill in the art.

[0012] 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.

[0013] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₅₀)alkyl is an alkyl group having from 1 to 50 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S. An R^S substituted chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–C₅₀)alkyl substituted with exactly one group R^S, where R^S is phenyl (–C₆H₅)” may contain from 7 to 56 carbon atoms. Thus, in general when a chemical group defined using the “(C_x–C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^S, the minimum and maximum total number of carbon atoms of the chemical group is determined

by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^S.

[0014] The term “substitution” means that at least one 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 “–H” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “–H” are interchangeable, and unless clearly specified have identical meanings.

[0015] The term “halogen-substituted” means that at least one hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a halogen. The term “halogen-substituted” and “halogenated” are interchangeable. The term “perhalogenated” means that every hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a halogen. The term “halogen-substituted” means that at least one hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a halogen atom.

[0016] In this disclosure, the term “halogen atom” or “halogen” means the radical of a fluorine atom (F) or chlorine atom (Cl). The term “halide” means anionic form of the halogen atom: fluoride (F[–]) or chloride (Cl[–]).

[0017] The term “(C₁–C₅₀)hydrocarbyl” means a hydrocarbon radical of from 1 to 50 carbon atoms and the term “(C₁–C₅₀)hydrocarbylene” means a hydrocarbon diradical of from 1 to 50 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (having three carbons or more, and including mono- and poly-cyclic, fused and non-fused polycyclic, and bicyclic) or acyclic, and substituted by one or more R^S or unsubstituted.

[0018] In this disclosure, a (C₁–C₅₀)hydrocarbyl may be an unsubstituted or substituted (C₁–C₅₀)alkyl, (C₃–C₅₀)cycloalkyl, (C₃–C₂₀)cycloalkyl-(C₁–C₂₀)alkylene, (C₆–C₄₀)aryl, or (C₆–C₂₀)aryl-(C₁–C₂₀)alkylene (such as benzyl (–CH₂–C₆H₅)).

[0019] The terms “(C₁–C₅₀)alkyl” and “(C₁–C₁₈)alkyl” mean a saturated straight or branched hydrocarbon radical of from 1 to 50 carbon atoms and a saturated straight or branched hydrocarbon radical of from 1 to 18 carbon atoms, respectively, that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted (C₁–C₅₀)alkyl are unsubstituted (C₁–C₂₀)alkyl; unsubstituted

(C₁–C₁₀)alkyl; unsubstituted (C₁–C₅)alkyl; methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2-butyl; 2-methylpropyl; 1,1-dimethylethyl; 1-pentyl; 1-hexyl; 1-heptyl; 1-nonyl; and 1-decyl. Examples of substituted (C₁–C₄₀)alkyl are substituted (C₁–C₂₀)alkyl, substituted (C₁–C₁₀)alkyl, trifluoromethyl, and [C₄₅]alkyl. The term “[C₄₅]alkyl” means there is a maximum of 45 carbon atoms in the radical, including substituents, and is, for example, a (C₂₇–C₄₀)alkyl substituted by one R^S, which is a (C₁–C₅)alkyl, respectively. Each (C₁–C₅)alkyl may be methyl, trifluoromethyl, ethyl, 1-propyl, 1-methylethyl, or 1,1-dimethylethyl.

[0020] The term “(C₆–C₅₀)aryl” means an unsubstituted or substituted (by one or more R^S) monocyclic, bicyclic, or tricyclic aromatic hydrocarbon radical of from 6 to 50 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms. A monocyclic aromatic hydrocarbon radical includes one aromatic ring; a bicyclic aromatic hydrocarbon radical has two rings; and a tricyclic aromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic aromatic hydrocarbon radical is present, at least one of the rings of the radical is aromatic. The other ring or rings of the aromatic radical may be independently fused or non-fused and aromatic or non-aromatic.

[0021] The term “(C₃–C₅₀)cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S. Other cycloalkyl groups (e.g., (C_x–C_y)cycloalkyl) are defined in an analogous manner as having from x to y carbon atoms and being either unsubstituted or substituted with one or more R^S.

[0022] Examples of (C₁–C₅₀)hydrocarbylene include unsubstituted or substituted (C₆–C₅₀)arylene, (C₃–C₅₀)cycloalkylene, and (C₁–C₅₀)alkylene (e.g., (C₁–C₂₀)alkylene). The diradicals may be 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., 1,3-diradicals, 1,4-diradicals, etc.). Some diradicals include 1,2-, 1,3-, 1,4-, or an α,ω -diradical, and others a 1,2-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. –CH₂CH(CH₃)CH₂–). Some examples of (C₆–C₅₀)arylene α,ω -diradicals include phenyl-1,4-diyl, naphthalen-2,6-diyl, or naphthalen-3,7-diyl.

[0023] The term “(C₁–C₅₀)alkylene” means a saturated straight chain or branched chain diradical (i.e., the radicals are not on ring atoms) of from 1 to 50 carbon atoms that is unsubstituted

or substituted by one or more R^S . Examples of unsubstituted (C_1-C_{50}) alkylene are unsubstituted (C_1-C_{20}) alkylene, including unsubstituted $-CH_2CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-(CH_2)_8-$, $-CH_2C^*HCH_3$, and $-(CH_2)_4C^*(H)(CH_3)$, 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 (C_1-C_{50}) alkylene are substituted (C_1-C_{20}) alkylene, $-CF_2-$, $-C(O)-$, and $-(CH_2)_{14}C(CH_3)_2(CH_2)_5-$ (i.e., a 6,6-dimethyl substituted normal-1,20-eicosylene).

[0024] The term “ (C_3-C_{50}) cycloalkylene” means a cyclic diradical (i.e., the radicals are on ring atoms) of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S .

[0025] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of groups containing one or more than one heteroatom include O, S, $S(O)$, $S(O)_2$, $Si(R^C)_2$, $P(R^P)$, $N(R^N)$, $-N=C(R^C)_2$, $-Ge(R^C)_2-$, or $-Si(R^C)-$, where each R^C and each R^P is unsubstituted (C_1-C_{18}) hydrocarbyl or $-H$, and where each R^N is unsubstituted (C_1-C_{18}) hydrocarbyl. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms of a hydrocarbon are replaced with a heteroatom. The term “ (C_1-C_{50}) heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 50 carbon atoms, and the term “ (C_1-C_{50}) heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 50 carbon atoms. The heterohydrocarbon of the (C_1-C_{50}) heterohydrocarbyl or the (C_1-C_{50}) heterohydrocarbylene has one or more heteroatoms. The radical of the heterohydrocarbyl may be on a carbon atom or a heteroatom. The two radicals of the heterohydrocarbylene may be on a single carbon atom or on a single heteroatom. Additionally, one of the two radicals of the diradical may be on a carbon atom and the other radical may be on a different carbon atom; one of the two radicals may be on a carbon atom and the other on a heteroatom; or one of the two radicals may be on a heteroatom and the other radical on a different heteroatom. Each (C_1-C_{50}) heterohydrocarbyl and (C_1-C_{50}) 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.

[0026] The term “ (C_4-C_{50}) heteroaryl” means an unsubstituted or substituted (by one or more R^S) monocyclic, bicyclic, or tricyclic heteroaromatic hydrocarbon radical of from 4 to 50 total carbon atoms and from 1 to 10 heteroatoms. A monocyclic heteroaromatic hydrocarbon radical includes one heteroaromatic ring; a bicyclic heteroaromatic hydrocarbon radical has two rings;

and a tricyclic heteroaromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic heteroaromatic hydrocarbon radical is present, at least one of the rings in the radical is heteroaromatic. The other ring or rings of the heteroaromatic radical may be independently fused or non-fused and aromatic or non-aromatic.

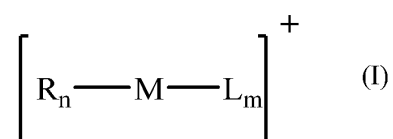
[0027] The 5-membered ring monocyclic heteroaromatic hydrocarbon radical has 5 minus h carbon atoms, where h is the number of heteroatoms and may be 1, 2, or 3; and each heteroatom may be O, S, N, or P. The 6-membered ring monocyclic heteroaromatic hydrocarbon radical has 6 minus h carbon atoms, where h is the number of heteroatoms and may be 1 or 2 and the heteroatoms may be N or P.

[0028] The term “(C₁–C₅₀)heteroalkyl” means a saturated straight or branched chain radical containing one to fifty carbon atoms, and one or more heteroatom. The term “(C₁–C₅₀)heteroalkylene” means a saturated straight or branched chain diradical containing from 1 to 50 carbon atoms and one or more than one heteroatoms. The heteroatoms of the heteroalkyls or the heteroalkylenes 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 are substituted by one or more R^S.

[0029] Embodiments of this disclosure include processes for polymerizing olefins, the processes include polymerizing ethylene and optionally one or more α-olefin monomers in the presence of a catalyst system. The catalyst system includes a metallic activator ionic complex and a procatalyst metal-ligand complex.

[0030] Metallic Activator Ionic Complex

[0031] The metallic activator ionic complex of this disclosure includes a cation and a weakly coordinating anion, the cation having a structure according to formula (I):



[0032] In formula (I), M is magnesium, boron, aluminum, gallium, zinc, silicon, or germanium. When M is zinc or magnesium, n is 1; when M is boron, aluminum, or gallium, n is 2; and when M is silicon or germanium, n is 3. In embodiments, m is 1, 2, or 3.

[0033] In embodiments, each R is a ligand independently selected from the group consisting of (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl –OR^C, –SiC^R, –CH₂Si(OR^C)_wR^{C_Y}, –CH₂Si(NR^N)_wR^{C_Y}, –N(R^N)–, and –NR^N₂. In such embodiments, R^C is (C₁–C₃₀)hydrocarbyl, R^N is (C₁–C₃₀)hydrocarbyl or hydrogen, w is 0, 1, 2, or 3, and y is 0, 1, 2, or 3, provided that the sum of w plus y is 3.

[0034] In some embodiments disclosed herein, R is (C₁–C₂₀)alkyl, –OR^C, or –NR^N₂. In various embodiments, R is (C₁–C₁₂)alkyl, –OR^C, wherein R^C is (C₁–C₁₀)alkyl, or –NR^N₂, where R^N is (C₆–C₁₅)aryl or (C₁–C₁₂)alkyl. In embodiments, each R is independently octyl, –CH₃, –OCH₃, or –NPh₂. In embodiments, n is 2 and each R is optionally covalently connected to form a multidentate ligand. In embodiments, n is 3 and each R is optionally covalently connected to form a multidentate ligand.

[0035] In some embodiments, each L is a neutral Lewis base. The term “Lewis base” refers to any species that has a filled orbital containing an electron pair which is not involved in bonding; that electron pair may form a dative bond with a Lewis acid. The Lewis base may be neutral or anionic. A neutral Lewis base has a formal charge of zero. In some embodiments, the Lewis base may be a heterohydrocarbon or a hydrocarbon. Examples of neutral heterohydrocarbon lewis bases includes, but are not limited to, amines, trialkylamines, ethers, cycloethers, or sulfides. An example of anionic hydrocarbon includes, but is not limited to, cyclopentadiene. An example of a neutral hydrocarbon includes, but is not limited to, 1,3-butadiene.

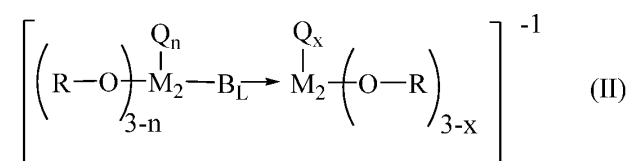
[0036] In various embodiments, the Lewis base is (C₁–C₂₀)heterohydrocarbon, wherein the hetero atom of the heterohydrocarbon is oxygen. In some embodiments, L is tetrahydrofuran, diethyl ether, or methyl *tert*-butyl ether (MTBE).

[0037] In various embodiments, L is tetrahydrofuran or trimethylamine. In some embodiments, m is 2 and each L is diethyl ether (OEt₂). In some embodiments, m is 2 and each L is optionally covalently connected to form a Lewis base having at least two coordinating atoms. In embodiments, m is 3 and each L is optionally covalently connected to form a Lewis base having at least two coordinating atoms.

[0038] In one or more embodiments, the anion of the metallic activator ionic complex has a formal charge of negative one (-1). In embodiments, the anion has the general formula [XQ₄]⁻. In such embodiments, X is boron, aluminum, or gallium. Also in such embodiments, each Q is independently selected from the group consisting of (C₆–C₄₀)aryl, (C₁–C₄₀)hydrocarbyl, –OR^C, –SiR^C, –CH₂Si(OR^C)_wR^{C_Y}, halogen substituted (C₆–C₄₀)aryl, halogen substituted

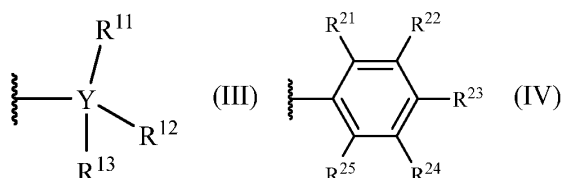
(C₁–C₄₀)hydrocarbyl, halogen substituted (–OR^C), halogen substituted –SiR^C, and halogen substituted –CH₂Si(OR^C)_wR^C_y, wherein R^C is (C₁–C₃₀)hydrocarbyl or halogen substituted (C₁–C₃₀)hydrocarbyl, w + y is 3 provided that at least three of the four group Q are fluorine atoms or fluorine substituted hydrocarbyl. In embodiments, the anion is [B(C₆F₅)₄][–].

[0039] In embodiments, the anion of the metallic activator ionic complex has the general formula (II):



[0040] In embodiments, each M₂ in formula (II) is independently aluminum, boron, or gallium. In embodiments, B_L is chosen from a species having at least two Lewis basic sites. In embodiments, each Q is independently a monodentate ligand. In embodiments, the subscript x is 0, 1, 2, or 3. In embodiments, when the subscript x is 0, Q of Q_x is not present. In embodiments, when the subscript x is 3, (O-R) is not present on the “x” portion connected to M₂. In embodiments, subscript n is 0, 1, 2, or 3. In embodiments, when subscript n is 0, Q of Q_n is not present. In embodiments, when the subscript n is 3, (O-R) is not present on the “n” portion connected to M₂.

[0041] In embodiments, each R in formula (II) is independently selected from the group consisting of radicals having formula (III) and radicals having formula (IV):

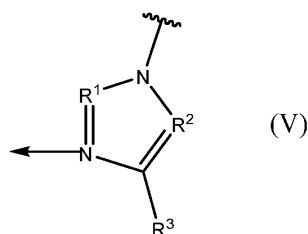


[0042] In formula (III), Y is independently carbon or silicon; R¹¹, R¹², R¹³ are independently chosen from (C₁–C₄₀)alkyl, (C₆–C₄₀)aryl, –H, –NR^N₂, –OR^C, –SR^C, or halogen. In one or more embodiments, when R is a radical having the formula (III), at least at least one of R¹¹, R¹², or R¹³ is perhalogenated (C₁–C₄)alkyl, perhalogenated (C₆–C₄₀)aryl, or –F. In some embodiments, when R is a radical having the formula (III), at least at least one of R¹¹, R¹², or R¹³ is a halogen-substituted (C₁–C₄₀)alkyl, a halogen-substituted (C₆–C₄₀)aryl, or –F; each R^N or R^C is independently (C₁–C₃₀)hydrocarbyl or –H.

[0043] In formula (IV), R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} are independently chosen from (C_1-C_{40}) alkyl, (C_6-C_{40}) aryl, $-H$, $-NR^N_2$, $-OR^C$, $-SR^C$, or halogen. In one or more embodiments, when R is a radical having the formula (IV), at least one of R^{21} , R^{22} , R^{23} , R^{24} , or R^{25} is perhalogenated (C_1-C_{40}) alkyl, perhalogenated (C_6-C_{40}) aryl, or $-F$. In some embodiments, when R is a radical having the formula (IV), at least one of R^{21} , R^{22} , R^{23} , R^{24} , or R^{25} is a halogen-substituted (C_1-C_{40}) alkyl, a halogen-substituted (C_6-C_{40}) aryl, or $-F$; each R^N or R^C is independently (C_1-C_{30}) hydrocarbyl or $-H$.

[0044] In one or more embodiments, in formula (II), B_L is a species containing two or more than two Lewis basic sites. In some embodiments, B_L is an anionic species containing at least two Lewis basic sites. The anionic species may be polyatomic or monoatomic (such as chloride or fluoride). Each Lewis basic site may be on a different atom of the anionic species or each Lewis basic site may be on the same atom of the anionic species. In some embodiments, B_L is chosen from (C_1-C_{20}) heterohydrocarbon anion, (C_2-C_{10}) heteroaromatic anion, $^-OC(O)R^L$, $^-S(O)_3R^L$, $^-P(O)_3R^L$, $^-P(O)_2(OR^L)_3$, $^-NR^L_2$, $^-OR^L$, $^-SR^L$, or halide, wherein R^L is $-H$, (C_1-C_{30}) hydrocarbyl, or halogen-substituted (C_1-C_{30}) hydrocarbyl. In some embodiments, B_L is $^-OC(O)R^L$, R^L is chosen from $-C_6F_5$, $-CH_3$ (methyl), ethyl, propyl, 2-propyl, n-butyl, tert-butyl, 2,2-dimethylethyl, n-octyl, or tert-octyl (also called 1,1,3,3-tetramethylbutyl). In some embodiments, R^L may be substituted with one or more than one halogen. In other embodiments, B_L is $-OS(O)_2CF_3$. In some embodiments, B_L anionic species containing two or more than two Lewis basic sites and is not a halogen or halide; specifically, L is anionic species containing two or more than two Lewis basic sites and is not fluoride ($-F$).

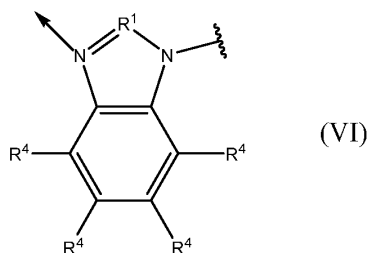
[0045] In some embodiments, B_L is an anionic compound having the formula (V):



[0046] In formula (V), R^1 and R^2 are independently selected from $-C(R^L)-$ or $-N-$, wherein R^L is $-H$, (C_1-C_{30}) hydrocarbyl, halogen-substituted (C_1-C_{30}) hydrocarbyl, and R^3 is chosen from $-H$, (C_1-C_{30}) hydrocarbyl, halogen-substituted (C_1-C_{30}) hydrocarbyl. In some embodiments, R^3 is (C_2-C_3) heterohydrocarbylene connected to R^2 .

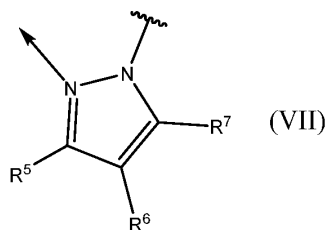
[0047] In some one or more embodiments, when B_L is according to formula (V), R^1 is $—C(C_{11}H_{23})—$ and R^2 is $—C(H)—$. In some embodiments, R is $—C(H)—$, R^2 is $—N—$, and R_3 is $—H$. In other embodiments, R^1 is $—N—$, R^2 is $—C(H)—$, and R^3 is $—H$.

[0048] In one or more embodiments, when R^2 and R^3 are linked together to form a ring, B_L is selected from a radical having the formula (VI):



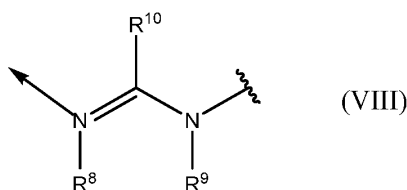
[0049] In formula (VI), each R^4 is independently a (C_1-C_{30}) hydrocarbyl or $—H$; and R^1 is as previously defined in formula (V).

[0050] In other embodiments, B_L is selected from radicals having a formula (VII):



[0051] In formula (VII), R^5 , R^6 , and R^7 are independently (C_1-C_{30}) hydrocarbyl or $—H$.

[0052] In one or more embodiments, B_L is selected from radicals having a formula (VIII):

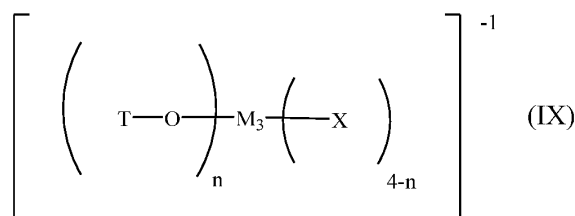


[0053] In formula (VIII), R^{10} is chosen from the group $—H$, $—NR^N_2$, $—SiR^C_3$, $—PR^P_3$, (C_1-C_{30}) hydrocarbyl; and each of R^8 and R^9 is chosen from $—H$ or (C_1-C_{30}) alkyl.

[0054] In some embodiments, each R of formula (II) is a radical having the formula (III), wherein Y is carbon, R^{11} , R^{12} , and R^{13} are fluorine.

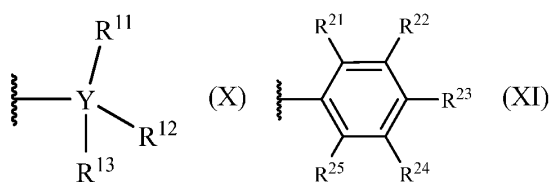
[0055] In some embodiments, each Q of formula (II) is independently a monodentate is chosen from unsaturated (C₂-C₅₀)hydrocarbon, unsaturated (C₂-C₅₀)heterohydrocarbon, (C₁-C₅₀)hydrocarbyl, (C₆-C₅₀)aryl, (C₆-C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C₄-C₁₂)diene, halogen, —N(R^N)₂, and —NCOR^C, in which each R^N and each R^C are independently (C₁-C₂₀)alkyl. In various embodiments, X is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments, each Q is identical. In one or more embodiments, subscript x of Q_x is 0. In various embodiments, subscript n of Q_n is 0.

[0056] In embodiments, the anion of the metallic activator ionic complex has the general formula (IX):



[0057] In formula (IX), each X is a monodentate ligand independently chosen from halogen, halogen-substituted (C₁-C₂₀)alkyl, (C₁-C₂₀)alkyl, halogen-substituted (C₆-C₄₀)aryl, (C₆-C₄₀)aryl, or —S(O)₃R^C.

[0058] In formula (IX), each M₃ is independently aluminum, boron, or gallium; subscript n is 0, 1, 2, 3, or 4. Each T is independently selected from the group consisting of radicals having formula (X) and radicals having formula (XI):



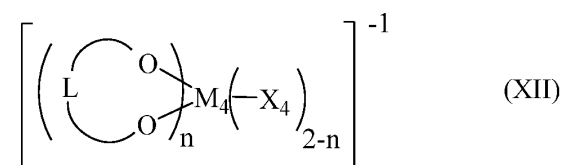
[0059] In formula (XI), each Y is independently carbon or silicon; each R¹¹, R¹², R¹³, is independently chosen from (C₁-C₄₀)alkyl, (C₆-C₄₀)aryl, —H, —NR^N₂, —OR^C, —SR^C, or halogen. In some embodiments of formula (IX), when each R is a radical according to formula (X) and Y is carbon, at least one of R¹¹⁻¹³ is a halogen-substituted (C₁-C₄₀)alkyl, a halogen-substituted (C₆-C₄₀)aryl, or —F. In other embodiments of formula (IX), when M is aluminum, n is 4, each R

is a radical according to formula (X), and each Y is carbon (1) each R^{11} , R^{12} , and R^{13} of each R is a halogen-substituted (C_1 – C_{40})alkyl, a halogen-substituted (C_6 – C_{40})aryl, or $-F$; or (2) a total number of fluorine atoms in R^{11} , R^{12} , and R^{13} of each R is at least six (specifically, the number of fluorine atoms on R^{11} , R^{12} , and R^{13} is greater than or equal to six (total number of $F_{atom} = R^{11} + R^{12} + R^{13} \geq 6$)).

[0060] In formula (XI), each R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from (C_1 – C_{40})alkyl, (C_6 – C_{40})aryl, $-H$, $-NR^N_2$, $-OR^C$, $-SR^C$, or halogen. When T is a radical according to formula (XI), at least one of R^{21-25} is a halogen-substituted (C_1 – C_{40})alkyl, a halogen-substituted (C_6 – C_{40})aryl, or $-F$.

[0061] In one or more embodiments of anion of formula (IX), subscript n is 4 and each T group is independently $-C(H)(CF_3)_2$, $-C_6F_5$, or $-C(CF_3)_3$. In other embodiments, subscript n is 4, and three of the four T groups are $-C(CF_3)_3$ and one of the four T groups is $-C_6F_5$. In some embodiments, n is 3 and X is chosen from $-OH$, triflate ($-OTf$), methyl, or halogen.

[0062] In one or more embodiments of the anion of formula (IX), two T groups are covalently connected and the anion has a structure according to formula (XII):

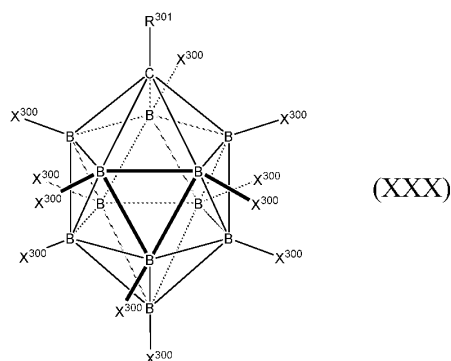


[0063] In formula (XII), M_4 and X_4 are as defined in formula (IX); subscript n is 1 or 2. L represents the two groups R that are covalently connected; and each L is independently chosen from (C_2 – C_{40})alkylene, or (C_2 – C_{40})heteroalkylene.

[0064] In formula (XII), when n is 1, X_4 is a monodentate ligand independently chosen from halogenated-(C_1 – C_{20})alkyl.

[0065] In one or more embodiments of the anion of formula (XII), L is a halogenated biphenyl diradical ion or halogenated naphthalene-diyl. The halogenated biphenyl diradical ion may have a single radical on each of the phenyl rings. The diradicals on the halogenated naphthalene-diyl may be separated by four or more carbon atoms in the naphthalene.

[0066] In some embodiments, the anion has a structure according to formula (XXX):



[0067] In formula (XXX), R^{301} and each X^{300} are each independently selected from the following: a halogen, a substituted or unsubstituted (C_1-C_{40}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{40}) heterohydrocarbyl, $Si(R^C)_3$, $Si(N(R^C)_2)_3$, $Si(O(R^C)_2)_3$, $Ge(R^C)_3$, $Ge(N(R^C)_2)_3$, $Ge(O(R^C)_2)_3$, $P(R^C)_2$, $P(N(R^C)_2)_2$, $P(OR^C)_2$, $N(R^C)_2$, $NH(R^C)$, NH_2 , OH , SH , OR^C , SR^C , NO_2 , CN , $-CF_3$, $-CF_2R^C$, $-CF(R^C)_2$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^C)-$, $(R^C)_2NC(O)-$, or hydrogen. In formula (XXX), at least one of X^{300} or R^{301} is a halogen atom.

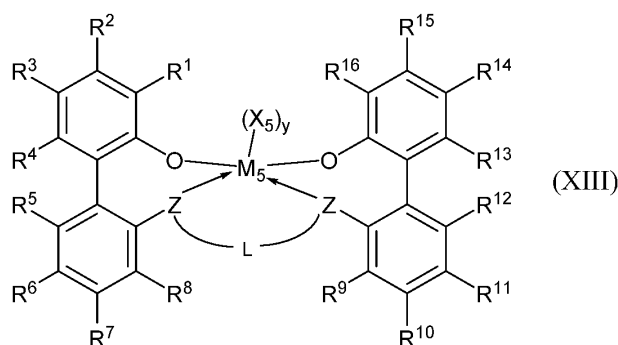
[0068] In formula (XXX), each R^C is independently a substituted or unsubstituted (C_1-C_{35}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{35}) heterohydrocarbyl. In some embodiments, two or more of X^{300} may optionally form one or more ring structures. In various embodiments, two or more of X^{300} and R^{301} may optionally form one or more ring structures. One or more hydrogen atoms may optionally be substituted with deuterium.

[0069] In embodiments, halogen atom includes the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). In some embodiments, X^{300} is fluorine. In some embodiments, each X^{300} is chlorine. In other embodiments, each X^{300} is bromine.

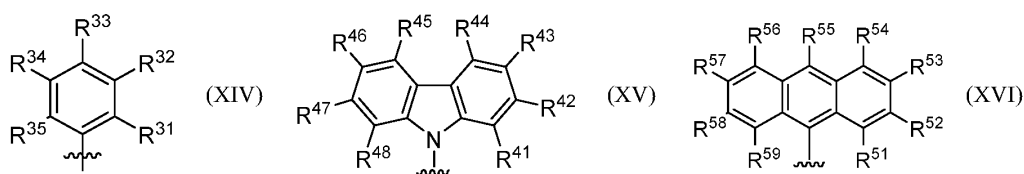
[0070] A person of ordinary skill in the art would recognize that the structure of formula (XXX) is a carborane anion. When each X^{300} is chlorine, the structure of formula (XXX) has an empirical formula of $^-B_{11}CR^{301}Cl_{11}$, in which B are boron atoms, C is a carbon atom, Cl are chlorine atoms, and R^{301} is previously defined. Each chlorine atom of formula (XXX) is bonded to the boron atom.

[0071] **Procatalyst Metal-Ligand Complex**

[0072] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XIII):



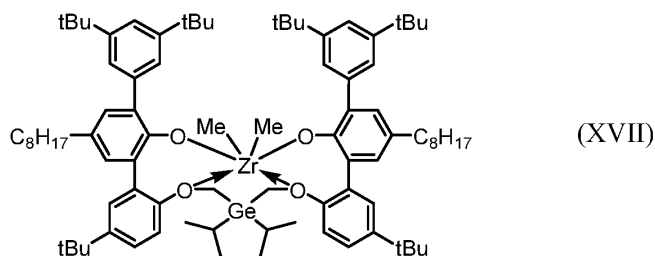
[0073] In formula (XIII), M_5 is a metal chosen from titanium, zirconium, or hafnium, the metal being in a formal oxidation state of +2, +3, or +4. Subscript n of $(X)_n$ is 0, 1, or 2. When subscript n is 1, X_5 is a monodentate ligand or a bidentate ligand, and when subscript n is 2, each X_5 is a monodentate ligand. Each Z is independently chosen from $-O-$, $-S-$, $-N(R^N)-$, or $-P(R^P)-$; R^{2-4} , R^{5-8} , R^{9-12} and R^{13-15} are independently selected from the group consisting of $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N=C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen. In formula (XIII), R^1 and R^{16} are selected from radicals having formula (XIV), radicals having formula (XV), and radicals having formula (XVI):



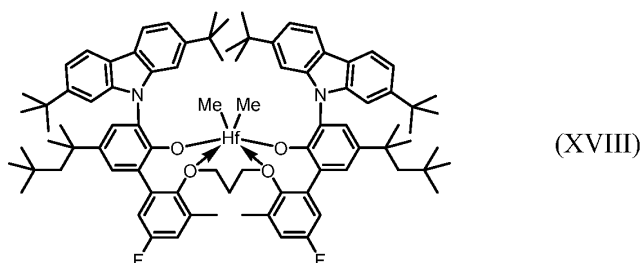
[0074] In formulas (XIV), (XV), and (XVI), each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, or halogen.

[0075] In one or more embodiments, each X_5 of formula (XIII) can be a monodentate ligand that, independently from any other ligands X_5 , is a halogen, unsubstituted (C_1-C_{20}) hydrocarbyl, unsubstituted (C_1-C_{20}) hydrocarbyl $C(O)O-$, or $R^K R^L N-$, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{20}) hydrocarbyl.

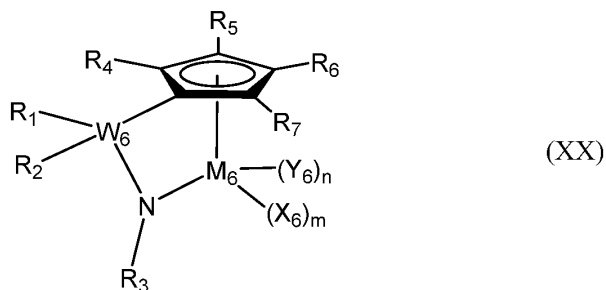
[0076] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XVII):



[0077] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XVIII):



[0078] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XX):



[0079] In formula (XX), M_6 is hafnium, titanium or zirconium; n is 0, 1, or 2, m is 0, 1, or 2, provided that when m is 2, n is 0, and when n is 2, m is 0; and each X_6 is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbon, (C_1-C_{50}) heterohydrocarbon, (C_1-C_{50}) hydrocarbyl, (C_6-C_{50}) aryl, (C_6-C_{50}) heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4-C_{12}) diene, halogen, hydrogen, $-N(R^N)_2$, and $-NCOR^C$. The metal-ligand complex is overall charge-neutral.

[0080] In formula (XX), N is nitrogen; W₆ is carbon or silicon and is covalently bonded to cyclopentadiene; and R₁ and R₂ are independently selected from -H, (C₁-C₄₀)hydrocarbyl, and (C₁-C₄₀)heterohydrocarbyl; R₃ are independently selected from (C₁-C₄₀)hydrocarbyl, and (C₁-C₄₀)heterohydrocarbyl.

[0081] In formula (XX), Y₆ is independent Lewis base. In some embodiments, Y₆ is chosen from (C₁-C₂₀)heterohydrocarbon, wherein the hetero atom of the heterohydrocarbon is oxygen. In some embodiments, Y₆ is tetrahydrofuran, diethyl ether, or methyl *tert*-butyl ether (MTBE).

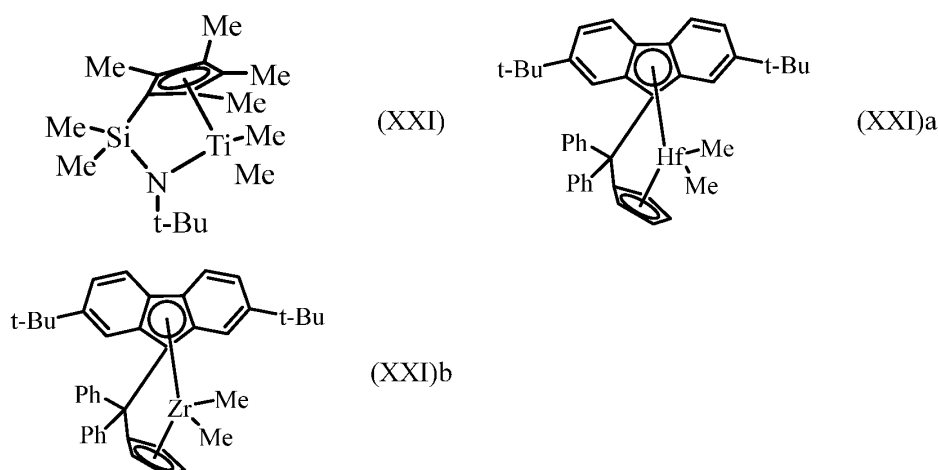
[0082] In formula (XX), R₄, R₅, R₆, and R₇ are independently (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl wherein any of the R₄, R₅, R₆, and R₇ optionally are connected to form a ring structure.

[0083] In some embodiments, when n is 1, m is 1. In embodiments, m + n is 2.

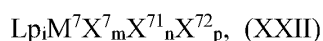
[0084] In various embodiments, in formula (XX), R₄, R₅, R₆, and R₇ are (C₁-C₁₂)alkyl; or R₄ and R₇ are (C₁-C₁₂)alkyl, or R₅ and R₆ are (C₁-C₁₂)alkyl or R₆ and R₇ are (C₁-C₁₂)alkyl.

[0085] In one or more embodiments, in formula (XX), R₁ and R₂ are methyl, ethyl, propyl, or phenyl. In some embodiments, R₃ is independently (C₁-C₁₂)alkyl. In various embodiments, R₃ is independently *tert*-butyl, *tert*-octyl, or *n*-octyl.

[0086] In some embodiments, the process includes a procatalyst of formula (XX). An illustrative, non-limiting list of the procatalyst of formula (XX) has the structure according to formula (XXI), (XXI)a, and (XXI)b:



[0087] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XXII):

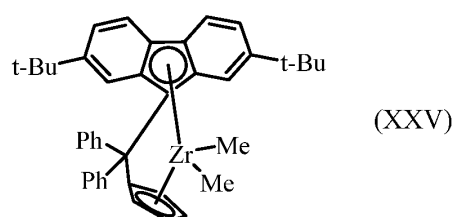
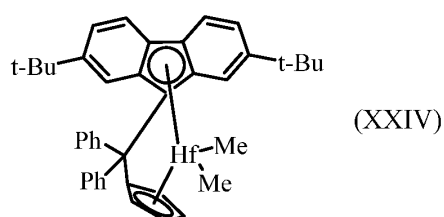


or a dimer thereof (XXIII).

[0088] In formula (XXII), Lp is an anionic, delocalized, π -bonded group that is bound to M^7 , containing up to 50 non-hydrogen atoms. In some embodiments of formula (XXIII), two Lp groups may be joined together forming a bridged structure, and further optionally one Lp may be bound to X.

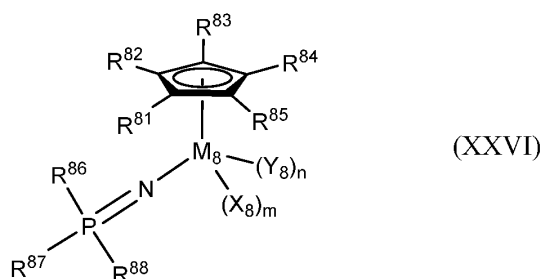
[0089] In formulas (XXII) and (XXIII), M^7 is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state. X^7 is an optional, divalent substituent of up to 50 non-hydrogen atoms that together with Lp forms a metallocycle with M. X^{71} is a neutral or monoanionic ligand independently selected from $(\text{C}_1\text{--}\text{C}_{20})$ hydrocarbyl or $(\text{C}_1\text{--}\text{C}_{20})$ heterohydrocarbyl; each X^{72} is independently a monovalent, anionic moiety independently selected from $(\text{C}_1\text{--}\text{C}_{40})$ hydrocarbyl or $(\text{C}_1\text{--}\text{C}_{40})$ heterohydrocarbyl. Optionally, two X^{72} groups may be covalently bound together forming a divalent dianionic moiety having both valences bound to M^7 , or, optionally two X^{72} groups may be covalently bound together to form a neutral, conjugated or nonconjugated diene that is π -bonded to M^7 , in which M is in the +2 oxidation state. In other embodiments, one or more X^{72} and one or more X^{71} groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality. Subscript i of Lp_i is 0, 1, or 2; subscript n of X^{71}_n is 0, 1, 2, or 3; subscript m of X^7_m is 0 or 1; and subscript p of X^{72}_p is 0, 1, 2, or 3. The sum of i + m + p is equal to the formula oxidation state of M^7 .

[0090] In some embodiments, the process includes a procatalyst of formula (XXII). An illustrative, non-limiting list of the procatalyst of formula (XXII) has the structure according to formulas (XXIV) and (XXV):



[0091] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XXVI):

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[0092] In formula (XXVI), each X is a monodentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)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, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, a halogen, wherein each R^C is independently a (C₁–C₃₀)hydrocarbyl, or (C₁–C₃₀)heterohydrocarbyl, and each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^Y is –H, (C₁–C₃₀)hydrocarbyl, or halogen atom, wherein two X ligands can be connected to form a ring, wherein one member of the ring is M₈.

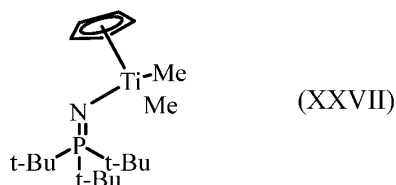
[0093] In formula (XXVI), each Y₈ is independently Lewis Base; optionally, X and Y can be linked to form a ring. Each subscript m is 1 and 2; and each subscript n is 0, 1 and 2. The metal–ligand complex is overall charge-neutral.

[0094] In formula (XXVI), M₈ is titanium, zirconium, or hafnium; R⁸¹, R⁸², R⁸³, R⁸⁴, and R⁸⁵ are independently (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl wherein any of the R⁸², R⁸³, R⁸⁴, and R⁸⁵ optionally are connected to form a ring structure; R⁸⁶, R⁸⁷, and R⁸⁸ are independently (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, (C₆–C₃₀)aryl, (C₅–C₃₀)heteroaryl wherein two of R⁸⁶, R⁸⁷, and R⁸⁸ are optionally connected to form a ring; and

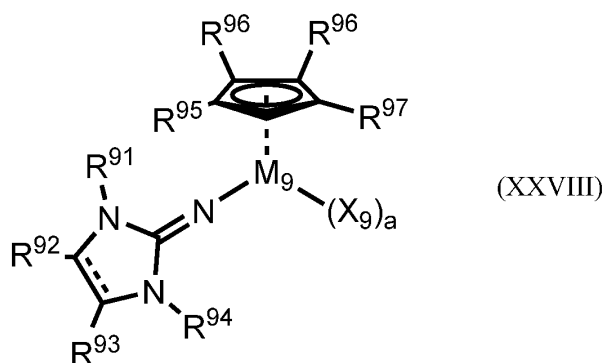
[0095] In some embodiments, R⁸¹, R⁸², R⁸³, R⁸⁴, and R⁸⁵ are independently (C₁–C₅₀)hydrocarbyl, wherein R⁸¹ and R⁸² are optionally connected to form a ring, or R⁸² and R⁸³ are optionally connected to form a ring, R⁸³ and R⁸⁴ are optionally connected to form a ring, R⁸⁴ and R⁸⁵ optionally are connected to form a ring. In various embodiments, R⁸⁶, R⁸⁷, and R⁸⁸ are independently (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, (C₆–C₃₀)aryl, (C₅–C₃₀)heteroaryl wherein two of R⁸⁶, R⁸⁷, and R⁸⁸ are optionally connected to form a ring.

[0096] In formula (XXVI), each R^C, R^P, and R^N is independently a (C₁–C₃₀)hydrocarbyl, (C₁–C₃₀)heterohydrocarbyl, or –H.

[0097] In some embodiments, the process includes a procatalyst of formula (XXVI). An illustrative, non-limiting list of the procatalyst of formula (XXVI) has the structure according to formula (XXVII):



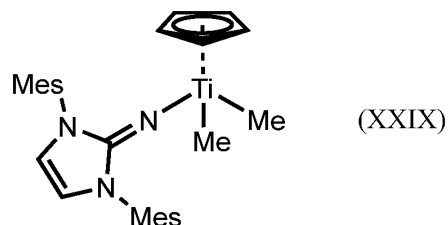
[0098] In embodiments of the process disclosed herein, the procatalyst of the catalyst system has the structure according to formula (XXVIII):



[0099] In formula (XXIX), each X is a monodentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl or (C₁–C₅₀)heterohydrocarbyl, or a halogen. Subscript a is 1 or 2. In formula (XXIX), R⁹¹, R⁹², R⁹³, R⁹⁴, R⁹⁵, R⁹⁶, and R⁹⁷ are independently (C₁–C₅₀)hydrocarbyl or (C₁–C₅₀)heterohydrocarbyl.

[00100] In one or more embodiments, R⁹² and R⁹³ are optionally connected to form a ring structure.

[00101] In some embodiments, the process includes a procatalyst of formula (XXVIII). An illustrative, non-limiting list of the procatalyst of formula (XXVIII) has the structure according to formula (XXIX):



[00102] **Polymerization**

[00103] Embodiments of the process described herein may be utilized in the polymerization of ethylene and optionally one or more α -olefin monomers in the presence of the catalyst system described in the previous paragraphs. In some embodiments, there is only a single olefin, ethylene, in the polymerization scheme, creating a polyethylene 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, 4-methyl-1-pentene, 5-ethylidene-2-norbornene, and 5-vinyl-2-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.

[00104] Ethylene-based polymers, for example homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins, may comprise from at least 50 mole percent (mol%) monomer units derived from ethylene. All individual values and subranges encompassed by “from at least 50 mol%” 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 mol% monomer units derived from ethylene; at least 70 mol% monomer units derived from ethylene; at least 80 mol% monomer units derived from ethylene; or from 50 to 100 mol% monomer units derived from ethylene; or from 80 to 100 mol% units derived from ethylene.

[00105] In some embodiments, the ethylene-based polymers may comprise at least 90 mole percent units derived from ethylene. All individual values and subranges from at least 90 mole percent are included herein and disclosed herein as separate embodiments. For example, the ethylene-based polymers may comprise at least 93 mole percent units derived from ethylene; at least 96 mole percent units; at least 97 mole percent units derived from ethylene; or in the alternative, from 90 to 100 mole percent units derived from ethylene; from 90 to 99.5 mole percent units derived from ethylene; or from 97 to 99.5 mole percent units derived from ethylene.

[00106] In some embodiments of the ethylene-based polymer, the ethylene-based polymers may comprise an amount of $(C_3-C_{20})\alpha$ -olefin. The amount of $(C_3-C_{20})\alpha$ -olefin is less than 50 mol%. In some embodiments, the ethylene-based polymer may include at least 0.5 mol% to

25 mol% of (C₃–C₂₀) α -olefin; and in further embodiments, the ethylene-based polymer may include at least 5 mol% to 10 mol%. In some embodiments, the additional α -olefin is 1-octene.

[00107] Any conventional polymerization process, in combination with a catalyst system according to embodiments of this disclosure may be used 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, batch reactors in parallel, series, or any combinations thereof, for example.

[00108] In embodiments of the process disclosed herein, an ethylene-based polymer may be produced in reactor at a reaction temperature. In embodiments, the reaction temperature may be from 100 °C to 200 °C, such as from 100 °C to 125 °C, from 125 °C to 150 °C, from 150 °C to 175 °C, or from 175 °C to 200 °C. In some embodiments, the reactor may be a solution reactor. In such embodiments, the solution reactor may comprise one or more solvents. In embodiments, the one or more solvents may be a hydrocarbon, an aliphatic hydrocarbon, a non-halogenated hydrocarbon, a non-aromatic hydrocarbon, or combinations thereof.

[00109] In one embodiment, an 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.

[00110] 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.

[00111] The polymer process may further include incorporating 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.

[00112] In some embodiments, a polymerization process for producing an ethylene-based polymer may include polymerizing ethylene and at least one additional α -olefin in the presence of a catalyst system, wherein the catalyst system incorporates at least one procatalyst metal–ligand complex and a metallic activator ionic complex. The polymer resulting from such a catalyst system that incorporates the procatalyst metal–ligand complex and the metallic activator ionic complex may have a density according to ASTM D792 (incorporated herein by reference in its entirety) from 0.850 g/cm^3 to 0.967 g/cm^3 , from 0.870 g/cm^3 to 0.920 g/cm^3 , from 0.870 g/cm^3 to 0.910 g/cm^3 , or from 0.870 g/cm^3 to 0.900 g/cm^3 , for example.

[00113] In another embodiment, the polymer resulting from the catalyst system that includes the procatalyst metal–ligand complex and a metallic activator ionic complex has a melt flow ratio (I_{10}/I_2) from 5 to 15, in which melt index I_2 is measured according to ASTM D1238 (incorporated herein by reference in its entirety) at 190°C and 2.16 kg load, and melt index I_{10} is measured according to ASTM D1238 at 190°C and 10 kg load. In other embodiments the melt flow ratio (I_{10}/I_2) is from 5 to 10, and in others, the melt flow ratio is from 5 to 9.

[00114] In some embodiments, the polymer resulting from the catalyst system that includes the procatalyst metal–ligand complex and the metallic activator ionic complex has a molecular-weight distribution (MWD) from 1 to 25, where MWD is defined as M_w/M_n with M_w being a weight-average molecular weight and M_n being a number-average molecular weight. In other

embodiments, the polymers resulting from the catalyst system have a MWD from 1 to 6. Another embodiment includes a MWD from 1 to 3; and other embodiments include MWD from 1.5 to 2.5.

[00115] Compositional Conventional Gel Permeation Chromatography

[00116] The chromatographic system consisted of a Polymer Char GPC-IR (Valencia, Spain) high temperature GPC chromatograph, equipped with an internal IR5 infrared detector (IR5). The autosampler oven compartment was set at 160° Celsius, and the column compartment was set at 150° Celsius. The columns were one Agilent PLgel MIXED 7.5 x 50 mm, 20 µm linear mixed-bed guard column and four Agilent PLgel MIXED-A 7.5 x 300 mm, 20 µm linear mixed-bed columns. The chromatographic solvent was 1,2,4-trichlorobenzene, which contained 300 ppm of butylated hydroxytoluene (BHT) and was nitrogen sparged. The injection volume used was 200 microliters, and the flow rate was 1.0 milliliters/minute.

[00117] Calibration of the GPC column set was performed using Agilent EasiCal Polystyrene standards (EasiCal PS-1 and EasiCal PS-2). Each EasiCal system consisted of two different spatulas supporting a mixture of 5 polymer standards (approximately 5 mg) to obtain 20 molecular weights points ranging from approximately 580 to 6,570,000 g/mole. Individual spatulas were added to septa-capped vials, sealed, and loaded into the Polymer Char autosampler. Polymer Char Instrument Control Software was utilized to add 8 mL of solvent to each vial and the standards were dissolved for 15 minutes at 160° Celsius under high-speed shaking prior to injection to the chromatography system. 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 0.41 and B is equal to 1.0.

[00118] A third order polynomial was used to fit the nominal polystyrene standard peak molecular weights to obtain molecular weight equivalent calibration points at each chromatographic slice.

[00119] The total plate count of the GPC column set was performed with decane [3% v/v in 1,2,4-trichlorobenzene (TCB) introduced via micropump]. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30 cm 20-micron linear mixed-bed columns.

[00120] Samples were prepared in a semi-automatic manner with the Polymer Char Instrument Control Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent was

added to a septa-capped sealed vial *via* the Polymer Char high temperature autosampler. The samples were dissolved for two hours at 160° Celsius under high-speed shaking.

[00121] The calculations of $M_n(\text{GPC})$, $M_w(\text{GPC})$, and $M_z(\text{GPC})$ were based on GPC results using the internal IR5 detector (measurement channel) of the Polymer Char GPC-IR chromatograph according to Equations 2-4. Using Polymer Char GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i) was converted to the polystyrene equivalent molecular weight, obtained from the narrow standard calibration curve, for the equivalent chromatographic data point (i). Equations 2-4 are as follows:

$$\text{[00122]} \quad M_n(\text{GPC}) = \frac{\sum^i IR_i}{\sum^i \left(IR_i / M_{\text{polystyrene}_i} \right)} \quad (\text{EQ 2})$$

$$\text{[00123]} \quad M_w(\text{GPC}) = \frac{\sum^i (IR_i * M_{\text{polystyrene}_i})}{\sum^i IR_i} \quad (\text{EQ 3})$$

$$\text{[00124]} \quad M_z(\text{GPC}) = \frac{\sum^i (IR_i * M_{\text{polystyrene}_i}^2)}{\sum^i (IR_i * M_{\text{polystyrene}_i})} \quad (\text{EQ 4})$$

[00125] In order to monitor the deviations over time, a flowrate marker (3% v/v decane in solvent) was introduced into each sample *via* a micropump controlled with the Polymer Char 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 were 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 Polymer Char GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.7% of the nominal flowrate.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (\text{EQ 5})$$

[00126] Octene Composition Calibration

[00127] A calibration for the IR5 detector was performed using at least ten (co)polymer standards. Homopolyethylene and ethylene/octene copolymers of a narrow short-chain branching (SCB) distribution and known comonomer content (as measured by ¹³C NMR Method, Qiu et al.,

Anal. Chem. 2009, 81, 8585–8589) were prepared using a single-site metallocene catalyst in a single reactor in solution process. SCB ranged from 0 SCB/1000 total C (homopolyethylene) to approximately 40 SCB/1000 total C, where total C = carbons in backbone + carbons in branches. Each standard had a weight-average molecular weight from 36,000 g/mole to 126,000 g/mole, as measured by GPC. Each standard had a molecular weight distribution (M_w/M_n) from 2.0 to 2.5. Polymer properties for the SCB standards are shown in Table A.

[00128] Table A: “Copolymer” Standards

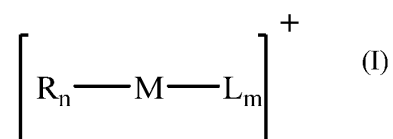
wt % Comonomer	IR5 Area ratio	SCB / 1000 Total C	M_w	M_w/M_n
23.1	0.2411	28.9	37,300	2.22
14.0	0.2152	17.5	36,000	2.19
0.0	0.1809	0.0	38,400	2.20
35.9	0.2708	44.9	42,200	2.18
5.4	0.1959	6.8	37,400	2.16
8.6	0.2043	10.8	36,800	2.20
39.2	0.2770	49.0	125,600	2.22
1.1	0.1810	1.4	107,000	2.09
14.3	0.2161	17.9	103,600	2.20
9.4	0.2031	11.8	103,200	2.26

[00129] The “IR5 Area Ratio (or “IR5 Methyl Channel Area / IR5 Measurement Channel Area”)” of “the baseline-subtracted area response of the IR5 methyl channel sensor” to “the baseline-subtracted area response of IR5 measurement channel sensor” (standard filters and filter wheel as supplied by Polymer Char: Part Number IR5_FWM01 included as part of the GPC-IR instrument) was calculated for each of the “Copolymer” standards. A linear fit of the wt % comonomer frequency versus the “IR5 Area Ratio” was constructed in the form of the following Equation 6:

$$\text{wt \% Comonomer} = A_0 + [A_1 \times (\text{IR5 Methyl Channel Area} / \text{IR5 Measurement Channel Area})] \quad (\text{EQ 6})$$

[00130] where A_0 is the “wt % Comonomer” intercept at an “IR5 Area Ratio” of zero, and A_1 is the slope of the “wt % Comonomer” versus “IR5 Area Ratio” and represents the increase in the wt % Comonomer as a function of “IR5 Area Ratio.” The IR5 area ratio is equal to the IR5 height ratio for narrow PDI and narrow SCBD standard materials.

[00131] A first aspect of the present disclosure is directed to a process of polymerizing olefins, the process comprising polymerizing ethylene and optionally one or more α -olefin monomers in the presence of a catalyst system, the catalyst system comprising a procatalyst and a metallic activator ionic complex, wherein the metallic activator ionic complex comprises a cation and a weakly coordinating anion, the cation having a structure according to formula (I):



where:

M is magnesium, boron, aluminum, gallium, zinc, silicon or germanium;

when M is zinc or magnesium, n is 1;

when M is boron, aluminum, or gallium, n is 2;

when M is silicon or germanium, n is 3;

m is 1, 2, or 3;

each R is a ligand independently selected from the group consisting of

(C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –OR^C, –SiC^R, –

CH₂Si(OR^C)_wR^{C_Y}, –CH₂Si(NR^N)_wR^{C_Y}, –NR^N, and –NR^N₂; where R^C is

(C₁–C₃₀)hydrocarbyl, R^N is (C₁–C₃₀)hydrocarbyl or hydrogen, w is 1, 2, or 3, and

y is 0, 1, or 2, provided that the sum of w plus y is 3; and

each L is a neutral Lewis base; and

provided that:

when n is 2 or 3, each R is optionally covalently connected to form a multidentate ligand;

and

when m is 2 or 3, each L is optionally covalently connected to form a Lewis base having at least two coordinating atoms.

[00132] A second aspect may include the first aspect, wherein n is 2 or 3 and at least two groups R in formula (I) are covalently connected.

[00133] A third aspect may include either one of the first aspect or the second aspect, wherein m is 2 or 3 and at least two groups L in formula (I) are covalently connected.

[00134] A fourth aspect may include any one of the first through third aspects, wherein R is (C₁–C₁₀)alkyl, –OR^C, wherein R^C is (C₁–C₁₀)alkyl, or –NR^N₂, where R^N is (C₆–C₁₅)aryl.

[00135] A fifth aspect may include any one of the first through fourth aspects, wherein L is tetrahydrofuran or trimethylamine or wherein m is 2 and each L is OEt₂.

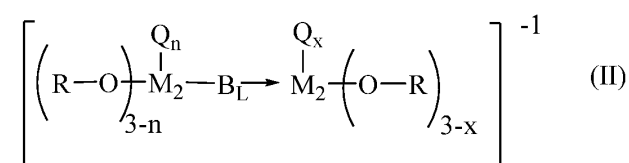
[00136] A sixth aspect may include any one of the first through fifth aspects, wherein L is tetrahydrofuran or trimethylamine or wherein m is 2 and each L is OEt₂.

[00137] A seventh aspect may include any one of the first through sixth aspects, wherein the anion has a formal charge of negative one (-1).

[00138] An eighth aspect may include any one of the first through seventh aspects, wherein the anion has the general formula $[XQ_4]^-$, wherein X is boron, aluminum, or gallium and each Q is independently selected from the group consisting of (C_6-C_{40}) aryl, (C_1-C_{40}) hydrocarbyl, $-OR^C$, $-SiC^R$, $-CH_2Si(OR^C)_wR^C_y$, halogen substituted (C_6-C_{40}) aryl, halogen substituted (C_1-C_{40}) hydrocarbyl, halogen substituted $(-OR^C)$, halogen substituted $-SiC^R$, and halogen substituted $-CH_2Si(OR^C)_wR^C_y$, wherein R^C is (C_1-C_{30}) hydrocarbyl, $w + y$ is 3 provided that at least three of the four group Q are fluorine atom or substituted with one or more fluorine atoms.

[00139] A ninth aspect may include any one of the first through eighth aspects, wherein the anion is $[B(C_6F_5)_4]^-$.

[00140] A tenth aspect may include any one of the first through seventh aspects, wherein the anion has a structure according to formula (II):



where:

each M_2 is independently aluminum, boron, or gallium;

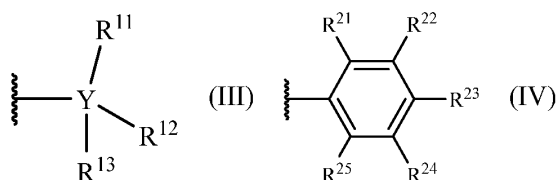
B_L is chosen from a species having at least two Lewis basic sites;

each Q is independently a monodentate ligand;

n is 0, 1, 2, or 3, wherein when n is 0, Q of Q_n is not present;

x is 0, 1, 2, or 3, wherein when x is 0, Q of Q_x is not present;

each R is independently selected from the group consisting of radicals having formula (III) and radicals having formula (IV):



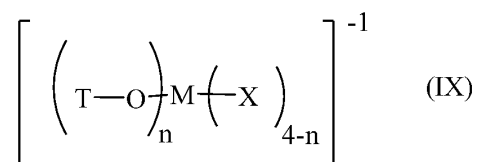
each Y is independently carbon or silicon;

each R^{11} , R^{12} , R^{13} , R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} , is independently chosen from (C_1-C_{40}) alkyl, (C_6-C_{40}) aryl, $-H$, $-NR^N_2$, $-OR^C$, $-SR^C$, or halogen, wherein when R is a radical according to formula (III), at least one of R^{11} , R^{12} , or R^{13} is perhalogenated (C_1-C_{40}) alkyl, perhalogenated (C_6-C_{40}) aryl, or $-F$; and when R is a radical according to formula (IV), at least one of R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is perhalogenated (C_1-C_{40}) alkyl, perhalogenated (C_6-C_{40}) aryl, or $-F$;

optionally, when n is 0 or 1, two R groups in formula (II) are covalently connected; and

each R^N or R^C is independently (C_1-C_{30}) hydrocarbyl or $-H$.

[00141] An eleventh aspect may include any one of the first through seventh aspects, wherein the anion has a structure according to formula (IX):

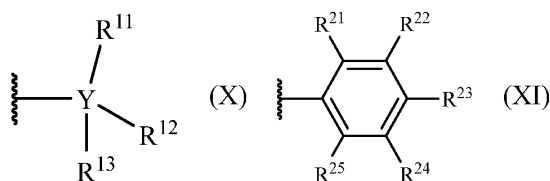


where:

M is aluminum, boron, or gallium;

n is 1, 2, 3, or 4;

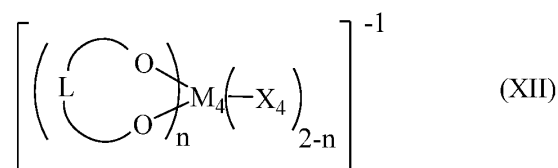
each T is independently selected from the group consisting of radicals having formula (X) and radicals having formula (XI):



where each Y , R^{11} , R^{12} , R^{13} , R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is defined in claim 10 and

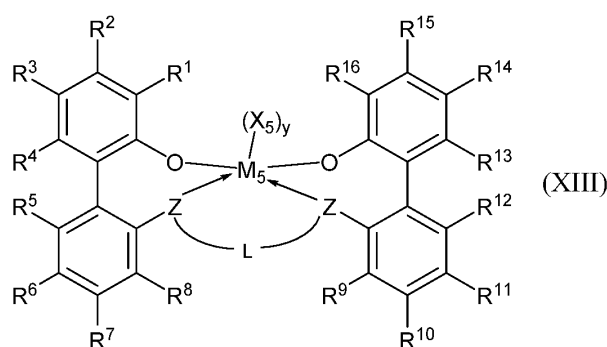
each X is a monodentate ligand independently chosen from halogen-substituted (C_1-C_{20}) alkyl, (C_1-C_{20}) alkyl, halogen-substituted (C_6-C_{40}) aryl, (C_6-C_{40}) aryl, triflate, or $-S(O)_3R^C$;

optionally, two groups T in formula (IX) are covalently connected and the anion has a structure according to formula (XII):



each R^C is independently (C₁–C₃₀)hydrocarbyl or –H.

[00142] A twelfth aspect may include any one of the first through eleventh aspects, wherein the procatalyst has the structure according to formula (XIII):



where:

M₅ is titanium, zirconium, or hafnium;

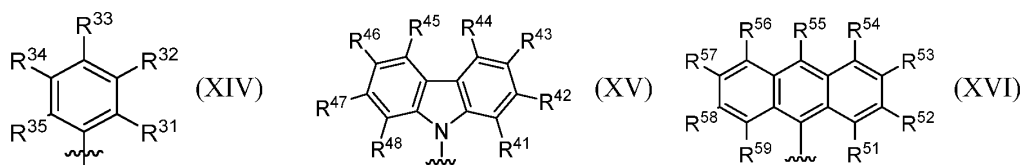
y is 1, 2, or 3;

each X₅ is a monodentate ligand independently chosen from unsaturated (C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, saturated (C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C₄–C₁₂)diene, halogen, –N(R^N)₂, and –N(R^N)COR^C;

the metal–ligand complex is overall charge-neutral;

each Z is independently chosen from –O–, –S–, –N(R^N)–, or –P(R^P)–;

R¹ and R¹⁶ are independently selected from the group consisting of –H, (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, –N=C(R^C)₂, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, radicals having formula (XIV), radicals having formula (XV), and radicals having formula (XVI):



where each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-H$,

(C_1-C_{40}) hydrocarbonyl, (C_1-C_{40}) heterohydrocarbonyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$,

$-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$,

$R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, or halogen;

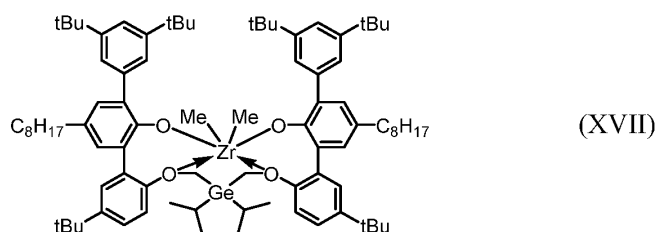
R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently selected from $-H$, (C_1-C_{40}) hydrocarbonyl, (C_1-C_{40}) heterohydrocarbonyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen;

L is (C_1-C_{40}) hydrocarbonylene or (C_2-C_{40}) heterohydrocarbonylene; and

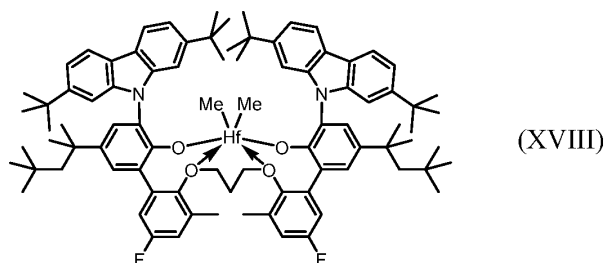
each R^C , R^P , and R^N in formula (I) is independently a (C_1-C_{30}) hydrocarbonyl,

(C_1-C_{30}) heterohydrocarbonyl, or $-H$.

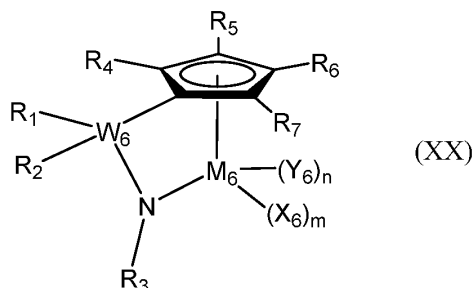
[00143] A thirteenth aspect may include any one of the first through twelfth aspects, wherein the procatalyst has the structure according to formula (XVII):



[00144] A fourteenth aspect may include any one of the first through thirteenth aspects, wherein the procatalyst has the structure according to formula (XVIII):



[00145] A fifteenth aspect may include any one of the first through fourteenth aspects, wherein the procatalyst has the structure according to formula (XX):



where

M_6 is hafnium, titanium or zirconium; n is 0, 1, or 2; m is 0, 1, or 2, provided that when m is 2, n is 0 and when n is 2, m is 0; and

each X_6 is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbon, (C_1-C_{50}) heterohydrocarbon, (C_1-C_{50}) hydrocarbyl, (C_6-C_{50}) aryl, (C_6-C_{50}) heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4-C_{12}) diene, halogen, hydrogen, $-N(R^N)_2$, and $-NCOR^C$. The metal-ligand complex is overall charge-neutral;

each Y_6 is independently a Lewis base;

N is nitrogen; W_6 is carbon or silicon and is covalently bonded to cyclopentadiene; and R_1 and R_2 are independently selected from $-H$, (C_1-C_{40}) hydrocarbyl, and (C_1-C_{40}) heterohydrocarbyl; R_3 are independently selected from (C_1-C_{40}) hydrocarbyl, and (C_1-C_{40}) heterohydrocarbyl; and

R_4 , R_5 , R_6 , and R_7 are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl wherein any of the R_4 , R_5 , R_6 , and R_7 optionally are connected to form a ring structure.

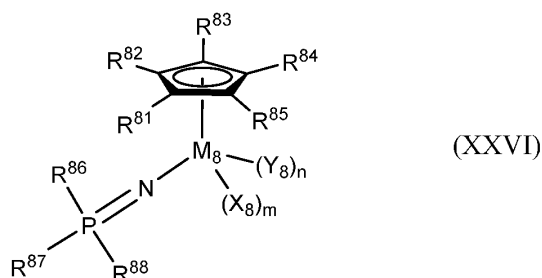
[00146] A sixteenth aspect may include any one of the first through fifteenth aspects, wherein the process further comprises a reactor at a reaction temperature.

[00147] A seventeenth aspect may include the sixteenth aspect, wherein the reactor is a solution reactor comprising one or more solvents.

[00148] An eighteenth aspect may include the seventeenth aspect, wherein the solvent is a hydrocarbon, an aliphatic hydrocarbon, a non-halogenated hydrocarbon, a non-aromatic hydrocarbon or combinations thereof.

[00149] A nineteenth aspect may include any one of the sixteenth through eighteenth aspects, wherein the reaction temperature is 120 °C-225 °C.

[00150] A twentieth aspect may include any one of the first through eleventh aspects, wherein the procatalyst has the structure according to formula (XXVI):



each X is a monodentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)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, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, a halogen, wherein each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; wherein two X ligands can be connected to form a ring, wherein one member of the ring is M₈;

each Y₈ is independently Lewis Base; optionally, X and Y can be linked to form a ring. Each subscript m is 1 and 2; and each subscript n is 0, 1 and 2. The metal–ligand complex is overall charge-neutral;

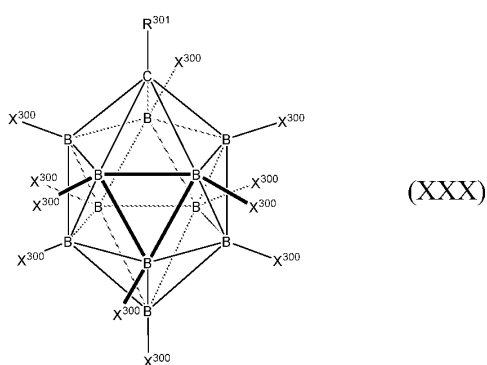
M₈ is titanium, zirconium, or hafnium; R⁸¹, R⁸², R⁸³, R⁸⁴, and R⁸⁵ are independently (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl wherein any of the R⁸², R⁸³, R⁸⁴, and R⁸⁵ optionally are connected to form a ring structure; R⁸⁶, R⁸⁷, and R⁸⁸ are independently (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, (C₆–C₃₀)aryl, (C₅–C₃₀)heteroaryl wherein two of R⁸⁶, R⁸⁷, and R⁸⁸ are optionally connected to form a ring; and

R⁸¹, R⁸², R⁸³, R⁸⁴, and R⁸⁵ are independently (C₁–C₅₀)hydrocarbyl, wherein R⁸¹ and R⁸² are optionally connected to form a ring, or R⁸² and R⁸³ are optionally connected to form a ring, R⁸³ and R⁸⁴ are optionally connected to form a ring, R⁸⁴ and R⁸⁵ optionally are connected to form a ring. In various embodiments, R⁸⁶, R⁸⁷, and R⁸⁸ are independently (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, (C₆–C₃₀)aryl,

(C₅–C₃₀)heteroaryl wherein two of R⁵⁶, R⁵⁷, and R⁵⁸ are optionally connected to form a ring; and

each R^C, R^P, and R^N in formula (XXVI) is independently a (C₁–C₃₀)hydrocarbonyl, (C₁–C₃₀)heterohydrocarbonyl, or –H.

[00151] A twenty-first aspect may include any one of the first through seventh aspects, wherein the anion has a structure according to formula the anion has a structure according to formula (XXX):



R³⁰¹ and each X³⁰⁰ are each independently selected from a halogen, a substituted or unsubstituted (C₁–C₄₀)hydrocarbonyl, or a substituted or unsubstituted (C₁–C₄₀)heterohydrocarbonyl, Si(R^C)₃, Si(N(R^C)₂)₃, Si(O(R^C)₂)₃, Ge(R^C)₃, Ge(N(R^C)₂)₃, Ge(O(R^C)₂)₃, P(R^C)₂, P(N(R^C)₂)₂, P(OR^C)₂, N(R^C)₂, NH(R^C), NH₂, OH, SH, OR^C, SR^C, NO₂, CN, –CF₃, –CF₂R^C, –CF(R^C)₂, R^CS(O)–, R^CS(O)₂–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R^C)–, (R^C)₂NC(O)–, or hydrogen, wherein each R^C is independently a substituted or unsubstituted (C₁–C₃₅)hydrocarbonyl, or a substituted or unsubstituted (C₁–C₃₅)heterohydrocarbonyl; wherein:

two or more of X³⁰⁰ may optionally form one or more ring structures;

two or more of X³⁰⁰ and R³⁰¹ may optionally form one or more ring structures;

and

one or more hydrogen atoms may optionally be substituted with deuterium; and

at least one of X³⁰⁰ or R³⁰¹ is a halogen atom.

EXAMPLES

[00152] The synthetic protocols for the illustrative embodiments of the activator are disclosed in Examples 1 to 4. In Example 5, the polymerization examples described herein were performed in a two-liter Parr reactor, which was heated via an electrical heating mantle and cooled via an internal serpentine cooling coil containing water. Both the reactor and the heating/cooling system were controlled and monitored by a Camile TG process computer.

[00153] **Example 1: Synthesis of alumocenium borate salt (A1):**

[00154] In a nitrogen-filled glovebox, a reaction vial was charged with trityl tetrakis(pentafluorophenyl)borate (500 mg, 0.5421 mmol, 1 equiv.) Trioctylaluminum (198.8 mg, 0.5421 mmol, 1 equiv.) in diethyl ether (15 mL) was added to the trityl vial. The vibrant orange trityl solution lost almost all color, but remained a pale yellow. After stirring at room temperature for 30 min, the solution had slightly darkened. The solution was concentrated *in vacuo* to yield a white solid with a light grey gel. The material was triturated with hexane (5 mL) and concentrated *in vacuo* (this process was repeated for a total of two times) to afford a white solid with a grey oil (726.9 g). After sitting a room temperature, the grey oil turned light yellow/brown. To remove triphenylmethane, the resulting residue was triturated with hexane (20 mL), resulting in a small amount of light brown oil below the bulk, slightly turbid hexane layer. Stirring was ceased, and the biphasic mixture was allowed to settle. The majority of the hexane layer was carefully pipetted off of the brown oil bottom layer. This process was then repeated a second time with hexanes (20 mL). The resulting brown oil was then concentrated *in vacuo* to afford the product (579 mg, 98% yield).

[00155] ^1H NMR (500 MHz, chlorobenzene-*d*₅) δ 3.72 (q, J = 7.3 Hz, 8H), 1.33 – 1.14 (m, 24H), 1.00 (t, J = 7.1 Hz, 12H), 0.91 – 0.78 (m, 6H), -0.04 (t, J = 7.2 Hz, 4H). ^{11}B NMR (160 MHz, chlorobenzene-*d*₅) δ -16.15. ^{13}C NMR (126 MHz, chlorobenzene-*d*₅) δ 150.11 – 149.06 (m), 147.99 – 147.19 (m), 139.75 – 139.11 (m), 138.04 – 136.86 (m), 135.92 – 135.22 (m), 69.50, 35.45, 31.94, 29.29 (d, J = 13.5 Hz), 23.98, 22.73, 13.95, 12.77, 6.90. ^{19}F NMR (376 MHz, chlorobenzene-*d*₅) δ -132.31 – -132.65 (m), -162.63 – -163.02 (m), -166.54 – -167.05 (m). HRMS (ESI) Calculated for $\text{C}_{24}\text{H}_{54}\text{AlO}_2$ [M^+] 401.3934; found 401.3923. Calculated for $\text{C}_{24}\text{B}_4\text{F}_{20}$ [M^-] 678.9779; found 678.9780.

[00156] **Example 2: Synthesis zinc borate salt (A2) – $(\text{C}_2\text{H}_5)_3\text{Zn}(\text{OEt})_3 \text{B}(\text{C}_6\text{F}_5)_4$**

[00157] In a nitrogen-filled glovebox, a reaction vial was charged with trityl tetrakis(pentafluorophenyl)borate (500 mg, 0.5421 mmol, 1 equiv.) and subsequently dissolved in

toluene (3 mL). A 1 M solution of diethylzinc in hexane (0.5421 mL, 66.95 mg diethylzinc, 0.5421 mmol, 1 equiv.) was added to diethyl ether (15 mL). The trityl solution was added dropwise to the stirring diethylzinc solution. Residual trityl borate was further extracted by washing the trityl vial with additional toluene and added to the diethylzinc solution. The vibrant orange trityl solution changed to a pale yellow when added to the reaction. The solution was concentrated *in vacuo* to yield a light beige solid. The material was triturated with hexane (6 mL) and concentrated *in vacuo* (this process was repeated for a total of two times) to afford a white solid. To remove triphenylmethane, the resulting residue was triturated with hexane (20 mL). Stirring was ceased, and the biphasic mixture was allowed to settle. Most of the hexane layer was carefully pipetted off of the bottom layer. This process was then repeated a second time with hexanes (20 mL). The resulting material was then concentrated *in vacuo* for 24 h to afford the product as a white powder (406.0 mg, 75% yield).

[00158] ^1H NMR (500 MHz, bromobenzene- d_5) δ 3.60 (q, $J = 7.1$ Hz, 12H), 1.21 (t, $J = 8.1$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 18H), 0.54 (q, $J = 8.1$ Hz, 2H). ^{13}C NMR (126 MHz, bromobenzene- d_5) δ 148.77 (d, $J = 241.4$ Hz), 140.42 – 134.77 (m), 68.49, 14.14, 11.36, 2.21. ^{19}F NMR (471 MHz, bromobenzene- d_5) δ -131.60 (q, $J = 10.0$ Hz), -161.83 (t, $J = 21.0$ Hz), -165.84 (t, $J = 19.7$ Hz). ^{11}B NMR (160 MHz, bromobenzene- d_5) δ -15.98.

[00159] Example 3: Synthesis of bis(dodecyl)magnesium

[00160] In a nitrogen-filled glovebox, a solution of 1.0 M solution of dodecylMgBr (70 mL, 70 mmol, 1 equiv.) was cooled in a -30°C freezer for 1 h. A small amount of solid precipitated from solution. The vessel was removed from the freezer and dioxane (6.0 mL) was added dropwise to the vigorously stirring solution, resulting in the precipitation of copious amounts of a white solid. The reaction was allowed to stir at room temperature for 30 min. A thick paste was obtained. Additional diethyl ether (approximately 40 mL) was added to thin out the mixture. The majority of the slurry was transferred to a set of four centrifuge tubes, sealed, and removed from the glovebox. Centrifugation at 14,000 rpm for 10 min allowed for clean separation of the solid magnesium salts from the supernatant solution. The tubes were transferred back into the glovebox and the supernate was decanted into a jar to afford an amber solution. The resulting material was titrated in triplicate against solutions of iodine in 0.5 M LiCl in THF and found to be 0.36 M. ^1H NMR (400 MHz, THF- d_8) δ 1.52 (p, $J = 7.7$ Hz, 4H), 1.38 – 1.17 (m, 36H), 0.88 (t, $J = 6.9$ Hz, 6H), -0.67 (t, $J = 8.0$ Hz, 4H). ^{13}C NMR (101 MHz, THF- d_8) δ 40.05, 33.02, 31.48, 31.25, 31.10, 31.01, 30.93, 30.82, 30.48, 23.69, 14.59, 8.64.

[00161] Example 4: Synthesis of magnesium borate salt (**A3**) – $(C_{12}H_{25})Mg(OEt)_3 B(C_6F_5)_4$

[00162] In a nitrogen-filled glovebox, a reaction vial was charged with trityl tetrakis(pentafluorophenyl)borate (500 mg, 0.5421 mmol, 1 equiv.) Bis(dodecyl)magnesium in diethyl ether (0.36 M, 1.51 mL, 0.5421 mmol, 1 equiv.) was further diluted with diethyl ether (15 mL) and added to the trityl vial. Immediately, the bright yellow color of the trityl disappeared and yielded a pale tan solution with some brown/yellow solids. The solution was stirred at room temperature for 1 h. A small amount of solid remained in the light tan solution. Stirring was ceased for 1 h. The solution was filtered through a 0.45 μ m PTFE syringe filter in line with a 0.2 μ m PTFE syringe filter. The filters were washed with diethyl ether (3 mL), and the combined filtrates were concentrated *in vacuo* to afford an off-white solid in an oil. The material was triturated with hexane (5 mL) and all volatiles were removed *in vacuo* (this process was repeated for a total of two times) to afford an off-white solid in an oil. The resulting residue was triturated with hexane (20 mL), resulting in a small amount of oil below the bulk, slightly turbid hexane layer. Stirring was ceased, and the biphasic mixture was allowed to settle. The majority of the hexane layer was carefully pipetted off of the pale yellow oil bottom layer. This process was then repeated a second time with hexanes (20 mL). The resulting solution was then concentrated *in vacuo* to afford a thick pale yellow oil with a small amount of residual solids at the top of the vial (545.9 mg). The material was triturated with toluene (5 mL). A second liquid phase was present at the bottom. The material was passed through a 0.2 μ m PTFE syringe filter. The vial and filters were washed with toluene (3x2 mL), and the combined filtrates were concentrated *in vacuo* to afford a thick pale yellow oil. The material was triturated with hexane (3 mL) and all volatiles were removed *in vacuo* (this process was repeated for a total of two times) to afford the product as a pale yellow oil (504.6 mg, 85% yield). 1H NMR (500 MHz, chlorobenzene- d_5) δ 3.48 (s, 12H), 1.53 – 1.13 (m, 20H), 0.98 (t, J = 7.2 Hz, 18H), 0.90 – 0.79 (m, 3H), -0.49 (d, J = 4.7 Hz, 2H). ^{11}B NMR (160 MHz, chlorobenzene- d_5) δ -16.15. ^{19}F NMR (471 MHz, chlorobenzene- d_5) δ -132.00 (q, J = 10.1 Hz, 8F), -162.41 (t, J = 20.7 Hz, 4F), -166.45 (t, J = 19.4 Hz, 8F). ^{13}C NMR (126 MHz, chlorobenzene- d_5) δ 151.53 – 146.28 (m), 139.91 – 135.19 (m), 66.17, 38.88, 32.00, 30.14, 30.06, 29.94, 29.84, 29.66, 29.50, 29.08, 22.77, 14.02, 13.16, 6.20.

[00163] Example 5 - Polymerization

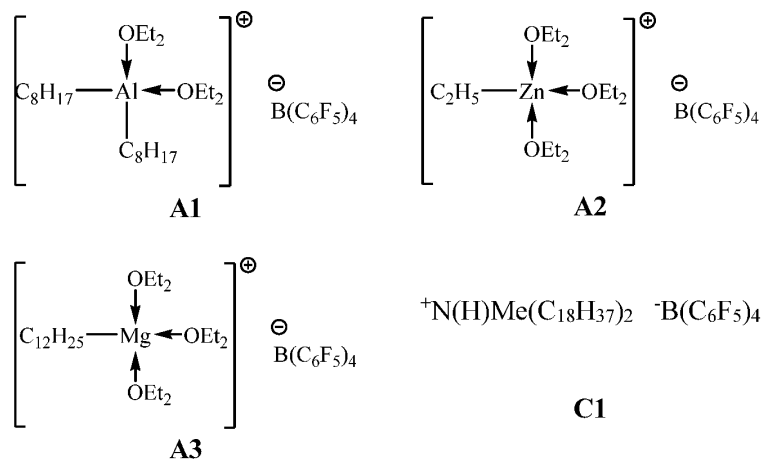
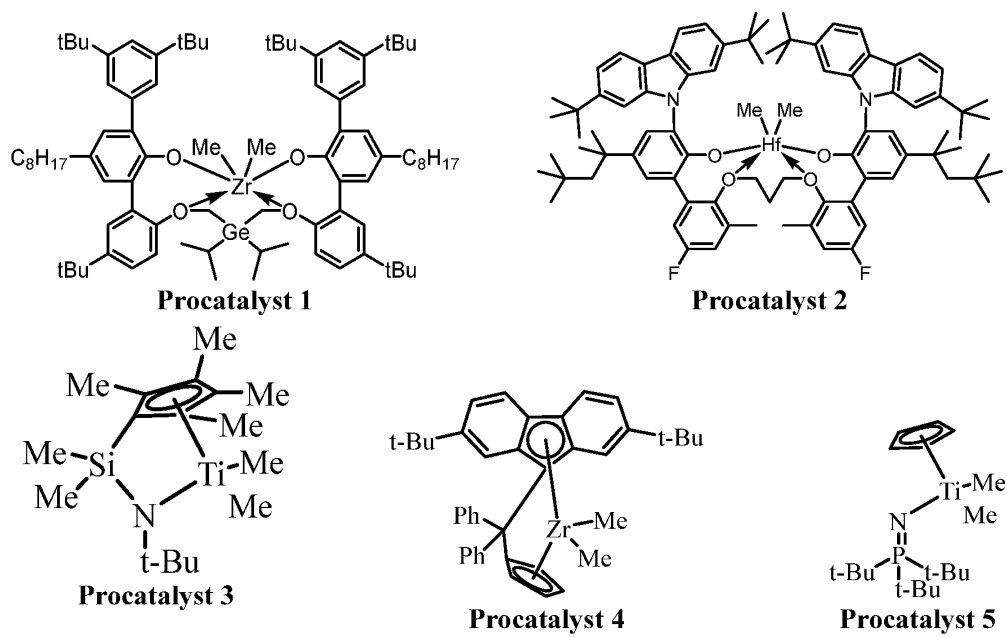
[00164] All chemicals used for polymerization or for the catalyst were purified before introduction into the reaction environment. Specifically, 1-octene, toluene, and ISOPAR E (a mixed alkanes solvent available from ExxonMobil, Inc.) were passed through an A2 alumina

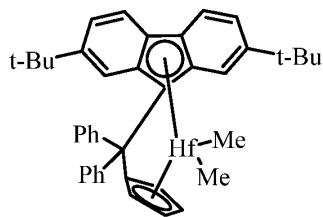
column then through a column containing Q5 reactant (available from Engelhard Chemicals Inc.). Ethylene gas was passed through a first column containing A204 alumina and activated 4Å molecular sieves and a second column containing Q5 reactant. Hydrogen gas was passed through Q5 reactant and A2 alumina. Nitrogen gas was passed through a single column containing A204 alumina, activated 4Å molecular sieves, and Q5 reactant. Procatalyst and activator solutions were handled in a nitrogen-filled glovebox.

[00165] The load column was filled with ISOPAR E and 1-octene to the load set points by use of an Ashcroft differential pressure cell, and the material was transferred into the reactor. Once complete, the reactor immediately began heating toward the reaction temperature set point. Hydrogen was loaded into the reactor, via a shot tank with an internal volume of approximately 75 milliliters (“mL”), immediately following the solvent/comonomer addition. A solution containing a modified methylaluminoxane (“MMAO”) scavenger was optionally added to the reactor via the shot tank once the reactor temperature reached 25 degrees Celsius (°C) under the reaction temperature set point. At 10°C under the reaction temperature set point, ethylene was added to the specified pressure as monitored via a micro-motion flow meter. Finally, at this same time, dilute toluene solutions (or chlorobenzene for A2) of the activator (Table 1) and the procatalyst (Table 2) were mixed, transferred to the shot tank, and added to the reactor to begin the polymerization reaction.

[00166] The polymerization conditions were typically maintained for 10 minutes with supplemental ethylene added on demand to maintain the specified pressure. Exothermic heat was continuously removed from the reaction vessel via the internal cooling coil. The resulting solution was removed from the reactor and stabilized by addition of 5 mL of a toluene solution containing approximately 33.5 milligrams (“mg”) of a hindered phenol antioxidant (Irganox 1010 from Ciba Geigy Corp.) and 66.5 mg of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corp.). Polymer resins were recovered by evaporating in a hood overnight and then drying for about 12 h in a temperature-ramped vacuum oven with a final set point of 140 °C. Between polymerization runs, at least one wash cycle was conducted in which ISOPAR E (850 g) was added and the reactor was heated to a setpoint between 160 °C and 190 °C. The reactor was then emptied of the heated solvent immediately before beginning a new polymerization run.

[00167] For Examples 1-6, Inventive Activators A1-A3 and Comparative Activator C1, shown in Table 1, were used to synthesize ethylene-based polymers according to the procedure described above. The procatalysts used for the polymerization reactions are shown in Table 2.

Table 1 - Activators**Table 2 – Procatalysts**



Procatalyst 6

[00168] Most polymerizations were performed at 140 °C with 288 psi of ethylene and 300 g of 1-octene. The polymerizations were performed in 605 g ISOPAR E. The ratio of procatalyst to activator ratio was 1:1.2; or the polymerizations were performed at temperature of 190 °C with 400 psi ethylene, 300 g 1-octene, and 520 g Isopar-E. The ratio of procatalyst to activator ratio was 1:1.2.

[00169] Each polymerization reaction using an Inventive Activator A1-A3 was compared to the same polymerization under the same reaction conditions using Comparative Activator C1. The polymerizations using C1 were each performed three times and the data for each run is reported. The efficiency with respect to C1 was calculated according to Equation 7:

$$\frac{\text{Efficiency of Individual Run}}{\text{Average Efficiency of 3 C1 Runs}} \times 100 \tag{EQ. 7}$$

Table 3 – Batch Reactor Polymerization Results with Procatalyst 1

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp C1 (%)	M _w (g/mol)	PDI	T _m (°C)	Octene (mol %)
Comp. C1	12.1	29.7	217,048	89.3	435,624	2.4	46.9	14.9
Comp. C1	14.5	34.1	249,203	102.5	425,795	2.4	45.2	15.2
Act. A1	18.6	41.0	299,629	123.2	448,546	2.5	46.4	14.8
Act. A1	18.4	43.6	318,630	131.1	439,161	2.5	47.4	14.8
Comp. C1	15.7	36.0	263,089	108.2	437,668	2.5	45.9	15.1

[00170] Batch reactor conditions for Table 3 includes temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 10 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2, with the catalyst loading of 1.8 μmol.

Table 4 – Batch Reactor Polymerization Results with Procatalyst 2

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w (g/mol)	PDI	T _m (°C)	Octene (mol %)
C1	11.6	10.3	1,923,544	115.3	214,367	2.2	119.4	0.7

C1	10.9	8.4	1,568,715	94.0	227,630	2.2	122	0.7
A1	5.3	4.2	784,358	47.0	219,951	2.1	121.7	0.7
A1	5.8	4.9	915,084	54.9	224,226	2.1	121.4	0.6
C1	10.9	8.1	1,512,690	90.7	223,717	2.1	119.6	0.7

[00171] Batch reactor conditions in Table 4 is: Temperature was 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, Procatalyst:Activator ratio = 1:1.2; catalyst loading was 0.03 μmol.

Table 5 – Batch Reactor Polymerization Results with Procatalyst 2

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/ g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	5.3	4.0	373,504	115.4	219,600	2.3	120.6	1.7
C1	5.5	3.4	317,478	98.1	215,826	2.1	118.8	1.3
A2	3.8	2.3	214,765	66.3	220,685	2.2	120.1	1.9
A2	3.6	2.3	214,765	66.3	224,661	2.1	119.2	1.8
C1	5.2	3.0	280,128	86.5	220,319	2.1	119.4	1.2

[00172] Batch reactor conditions in Table 5 is: Temperature was 140 °C, 288 psi C₂H₄, 605 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, Procatalyst:Activator ratio = 1:1.2; catalyst loading was 0.6 μmol.

Table 6 – Batch Reactor Polymerization Results with Procatalyst 3

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/ g metal)	Efficiency wrt Comp. C1 (%)	M _w (g/mol)	PDI	Octene (mol %)
C1	53.2	106.4	3,703,704	93.7	29,327	2.7	21.3
C1	55.5	116.3	4,048,315	102.5	29,695	2.8	20.7
A1	44.9	120.3	4,187,552	106.0	20,530	2.9	25.0
A1	48.0	123.2	4,288,499	108.5	20,933	2.8	24.7
C1	49.7	117.8	4,100,529	103.8	27,591	2.7	22.2

[00173] Batch reactor conditions in Table 6 is: Temperature was 140 °C, 288 psi C₂H₄, 605 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, Procatalyst:Activator ratio = 1:1.2; catalyst loading was 0.6 μmol.

Table 7 – Batch Reactor Polymerization Results with Procatalyst 4

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/ g metal)	Efficiency wrt Comp. C1 (%)	M _w (g/mol)	PDI	T _m (°C)	Octene (mol %)
C1	8.2	9.9	542,620	80.1	54,180	2.0	89.2	6.2
C1	10.2	12.1	663,203	97.8	53,565	2.0	88.9	6.3
A1	24.6	30.5	1,671,709	246.6	49,393	2.1	88.4	6.4

A1	26.6	32.4	1,775,848	262.0	48,639	2.0	88.5	6.5
C1	12.4	15.1	827,633	122.1	51,749	2.0	88.7	6.5

[00174] Batch reactor conditions in Table 7 is: Temperature was 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, Procatalyst:Activator ratio = 1:1.2. The procatalyst loading was 0.2 μmol.

Table 8 – Batch Reactor Polymerization Results with Procatalyst 1

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	10.9	14.5	105,966	112.4	323,194	2.3	44.7	14.7
C1	10.4	12.7	92,812	98.4	324,814	2.2	42.7	14.9
A2	10.4	13.7	100,120	106.2	304,981	2.2	40.8	15.3
A2	10.9	12.7	92,812	98.4	323,043	2.1	42.2	15.0
C1	8.5	11.5	84,042	89.1	318,776	2.1	41.9	15.1

[00175] Batch reactor conditions for Table 8 includes a temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, Procatalyst:Activator ratio = 1:1.2 with the procatalyst loading of 1.5 μmol.

Table 9 – Batch Reactor Polymerization Results with Procatalyst 3

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	Octene (mol %)
C1	6.5	8.2	570,872	71.5	32,483	2.8	26.5
C1	6.9	10.0	696,185	87.2	31,201	2.7	26.7
A2	11.6	21.2	1,475,912	184.9	24,278	2.7	28.5
A2	13.2	24.4	1,698,691	212.8	23,005	2.8	28.9
C1	10.1	16.2	1,127,820	141.3	28,835	2.7	27.2

[00176] The batch reactor conditions for Table 9 includes a temperature of 140 °C, 288 psi C₂H₄, 605 g Isopar-E, 300 g 1-octene, and 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.3 μmol.

Table 10 – Batch Reactor Polymerization Results with Procatalyst 4

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	10.5	12.0	657,722	97.0	48,070	2.4	88.5	6.4
C1	10.5	11.0	602,912	88.9	49,998	2.1	89.1	6.5
A2	11.9	14.4	789,266	116.4	48,859	2.1	88.5	6.4

A2	11.8	14.3	783,785	115.6	48,638	2.1	88.5	6.5
C1	12.3	14.1	772,823	114.0	49,593	2.0	89.1	6.3

[00177] The batch reactor conditions for Table 10 includes a temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.2 μmol.

Table 11 – Batch Reactor Polymerization Results with Procatalyst 1

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	8.7	11.4	83,311	99.7	329,334	2.1	48.7	13.3
C1	8.5	11.0	80,388	96.2	334,093	2.1	48.2	13.4
A3	17.7	24.5	179,046	214.3	325,778	2.2	48	13.3
A3	18.6	24.1	176,123	210.8	335,028	2.2	48.8	13.3
C1	10.2	11.9	86,965	104.1	327,647	2.1	49	13.5

[00178] The batch reactor conditions for Table 11 includes a temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 1.5 μmol.

Table 12 – Batch Reactor Polymerization Results with Procatalyst 2

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	8.1	7.3	681,644	110.1	227,591	2.2	120.2	0.9
C1	5.8	5.4	504,230	81.4	233,335	2.1	122.3	0.8
A3	0.8	0.8	74,701	12.1	223,210	2.1	120.7	0.9
A3	1.0	0.6	56,026	9.0	229,186	2.1	121.9	0.9
C1	8.9	7.2	672,307	108.5	231,722	2.2	119.4	0.8

[00179] The batch reactor conditions for Table 12 includes a temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.06 μmol.

Table 13 – Batch Reactor Polymerization Results with Procatalyst 3

Activator	C ₂ H ₄ Uptake	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	Octene (mol %)
C1	8.6	16.8	1,169,591	99.2	32,993	2.7	23.2
C1	11.3	16.7	1,162,629	98.6	33,326	2.6	22.2

A3	4.4	1.1	76,580	6.5	43,071	2.4	21.3
A3	4.7	1.6	111,390	9.4	43,865	2.4	21.1
C1	12.7	17.3	1,204,400	102.2	33,384	2.6	22.3

[00180] The batch reactor conditions for Table 13 includes a temperature of 140 °C, 288 psi C₂H₄, 605 g Isopar-E, 300 g 1-octene, and 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.3 μmol.

Table 14 – Batch Reactor Polymerization Results with Procatalyst 4

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	5.3	5.4	295,975	61.1	54,017	2.0	89.2	6.4
C1	8.6	9.5	520,696	107.5	52,227	2.0	89.1	6.4
A3	8.8	9.0	493,291	101.9	52,714	2.1	89.6	6.3
A3	9.1	9.2	504,253	104.2	52,914	2.1	89.5	6.3
C1	10.7	11.6	635,798	131.3	50,933	2.2	89	5.7

[00181] The batch reactor conditions for Table 14 includes a temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.2 μmol.

Table 15 – Batch Reactor Polymerization Results with Procatalyst 5

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	T _m (°C)	Octene (mol %)
C1	6.6	1.3	271,512	49.4	460,332	2.2	101.5	3.0
C1	6.8	3.3	689,223	125.3	519,054	2.1	101.9	2.8
A1	19.3	17.7	3,696,742	672.2	334,864	2.2	103.4	3.1
A2	6.2	2.9	605,681	110.1	443,891	2.1	101.9	3.0
A3	7.1	3.7	772,765	140.5	451,383	2.1	102.9	3.0
C1	7.0	3.3	689,223	125.3	456,043	2.1	101.8	3.1

[00182] The batch reactor conditions for Table 15 includes a temperature of 140 °C, 288 psi C₂H₄, 605 g Isopar-E, 300 g 1-octene, and 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.1 μmol.

Table 16 – Batch Reactor Polymerization Results with Procatalyst 6

Activator	C ₂ H ₄ Uptake (g)	Polymer Yield (g)	Efficiency (g polymer/g metal)	Efficiency wrt Comp. C1 (%)	M _w	PDI	Octene (mol %)
C1	8.3	13.5	151,269	76.4	35,595	2.2	20.0

C1	12.9	15.1	169,197	85.5	34,041	2.3	19.8
A1	8.0	1.4	15,687	7.9	37,211	2.3	18.8
A2	13.7	26.1	292,453	147.7	34,748	2.3	19.2
A3	3.1	2.2	24,651	12.5	39,840	2.2	19.8
C1	13.5	24.4	273,405	138.1	34,197	2.3	19.4

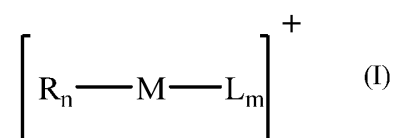
[00183] The batch reactor conditions for Table 16 includes a temperature of 190 °C, 400 psi C₂H₄, 520 g Isopar-E, 300 g 1-octene, and 0 μmol MMAO-3A, The Procatalyst:Activator ratio is 1:1.2 with a procatalyst loading of 0.5 μmol.

[00184] In each of the Examples in Tables 1-16, there is a steady ethylene uptake, which indicates that the activators in combination with the procatalysts provide a high catalyst efficiency as supported by the data in the Tables.

[00185] In several Examples the polymerization efficiencies of Inventive Activators A1, A2, and A3 were comparable or superior to that of Comparative Activator C1. The data in Tables 3 and 9 indicates that A1 and A2 out-performed C1 when used in conjunction with Procatalyst 1 and Procatalyst 3. The performance of the Inventive Activator A3 was also notably superior to C1 when used in conjunction with Procatalyst 1, as shown by Table 11. In Table 7, the Activator A1 was more than double the efficiency of the Comparative Activator C1 when coupled with Procatalyst 4.

CLAIMS

1. A process of polymerizing olefins, the process comprising polymerizing ethylene and optionally one or more α -olefin monomers in the presence of a catalyst system, the catalyst system comprising a procatalyst and a metallic activator ionic complex, wherein the metallic activator ionic complex comprises a cation and a weakly coordinating anion, the cation having a structure according to formula (I):



where:

M is magnesium, boron, aluminum, gallium, zinc, silicon or germanium;

when M is zinc or magnesium, n is 1;

when M is boron, aluminum, or gallium, n is 2;

when M is silicon or germanium, n is 3;

m is 1, 2, or 3;

each R is a ligand independently selected from the group consisting of

(C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –OR^C, –SiC^R, –

CH₂Si(OR^C)_wR^C_Y, –CH₂Si(NR^N)_wR^C_Y, –NR^N, and –NR^N₂; where R^C is

(C₁–C₃₀)hydrocarbyl, R^N is (C₁–C₃₀)hydrocarbyl or hydrogen, w is 1, 2, or 3, and

y is 0, 1, or 2, provided that the sum of w plus y is 3; and

each L is a neutral Lewis base; and

provided that:

when n is 2 or 3, each R is optionally covalently connected to form a multidentate ligand;

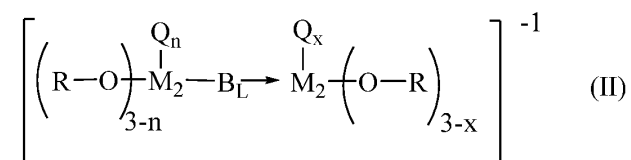
and

when m is 2 or 3, each L is optionally covalently connected to form a Lewis base having at least two coordinating atoms.

2. The process of claim 1, wherein n is 2 or 3 and at least two groups R in formula (I) are covalently connected.

3. The process of claim 1 or claim 2, wherein m is 2 or 3 and at least two groups L in formula (I) are covalently connected.

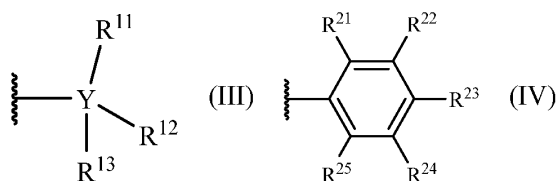
4. The process of any previous claim, wherein R is (C₁–C₁₀)alkyl, –OR^C, wherein R^C is (C₁–C₁₀)alkyl, or –NR^N₂, where R^N is (C₆–C₁₅)aryl.
5. The process of any previous claim, wherein L is tetrahydrofuran or trimethylamine or wherein m is 2 and each L is OEt₂.
6. The process of any previous claim, wherein each R is octyl, –CH₃, –OCH₃, or –NPh₂.
7. The process of any previous claim, wherein the anion has a formal charge of negative one (-1).
8. The process of any previous claim, wherein the anion has the general formula [XQ₄]⁻, wherein X is boron, aluminum, or gallium and each Q is independently selected from the group consisting of (C₆–C₄₀)aryl, (C₁–C₄₀)hydrocarbyl, –OR^C, –SiC^R, –CH₂Si(OR^C)_wR^C_y, halogen substituted (C₆–C₄₀)aryl, halogen substituted (C₁–C₄₀)hydrocarbyl, halogen substituted (–OR^C), halogen substituted –SiC^R, and halogen substituted –CH₂Si(OR^C)_wR^C_y, wherein R^C is (C₁–C₃₀)hydrocarbyl, w + y is 3 provided that at least three of the four group Q are fluorine atom or substituted with one or more fluorine atoms.
9. The process of any previous claim, wherein the anion is [B(C₆F₅)₄]⁻.
10. The catalyst system of any one of claims 1 to 7, wherein the anion has a structure according to formula (II):



where:

- each M₂ is independently aluminum, boron, or gallium;
- B_L is chosen from a species having at least two Lewis basic sites;
- each Q is independently a monodentate ligand;
- n is 0, 1, 2, or 3, wherein when n is 0, Q of Q_n is not present;
- x is 0, 1, 2, or 3, wherein when x is 0, Q of Q_x is not present;
- each R is independently selected from the group consisting of radicals having formula (III) and radicals having formula (IV):

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each Y is independently carbon or silicon;

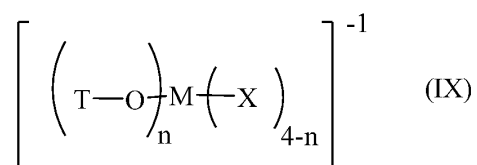
each R^{11} , R^{12} , R^{13} , R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} , is independently chosen from

(C_1-C_{40}) alkyl, (C_6-C_{40}) aryl, $-H$, $-NR^N_2$, $-OR^C$, $-SR^C$, or halogen, wherein when R is a radical according to formula (III), at least one of R^{11} , R^{12} , or R^{13} is perhalogenated (C_1-C_{40}) alkyl, perhalogenated (C_6-C_{40}) aryl, or $-F$; and when R is a radical according to formula (IV), at least one of R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is perhalogenated (C_1-C_{40}) alkyl, perhalogenated (C_6-C_{40}) aryl, or $-F$;

optionally, when n is 0 or 1, two R groups in formula (II) are covalently connected; and

each R^N or R^C is independently (C_1-C_{30}) hydrocarbyl or $-H$.

11. The process of any one of claims 1 to 7, wherein the anion has a structure according to formula (IX):



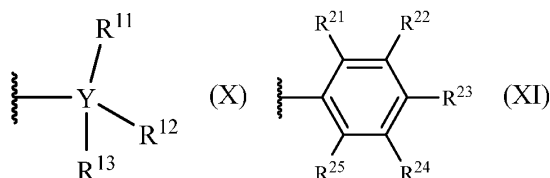
where:

M is aluminum, boron, or gallium;

n is 1, 2, 3, or 4;

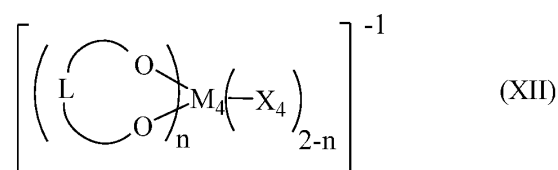
each T is independently selected from the group consisting of radicals having formula

(X) and radicals having formula (XI):



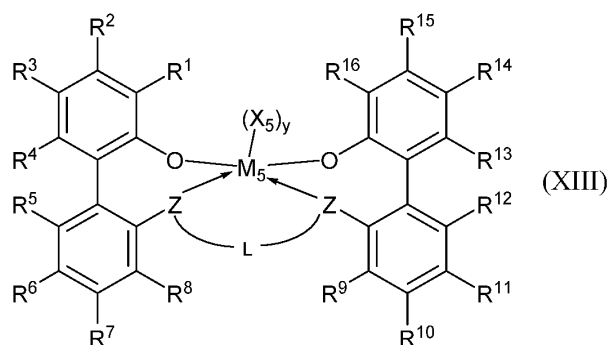
where each Y, R^{11} , R^{12} , R^{13} , R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is defined in claim 10 and

each X is a monodentate ligand independently chosen from halogen-substituted (C₁–C₂₀)alkyl, (C₁–C₂₀)alkyl, halogen-substituted (C₆–C₄₀)aryl, (C₆–C₄₀)aryl, triflate, or –S(O)₃R^C;
optionally, two groups T in formula (IX) are covalently connected and the anion has a structure according to formula (XII):



each R^C is independently (C₁–C₃₀)hydrocarbyl or –H.

12. The process of any one previous claims, wherein the procatalyst has the structure according to formula (XIII):



where:

M₅ is titanium, zirconium, or hafnium;

y is 1, 2, or 3;

each X₅ is a monodentate ligand independently chosen from unsaturated

(C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, saturated

(C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl,

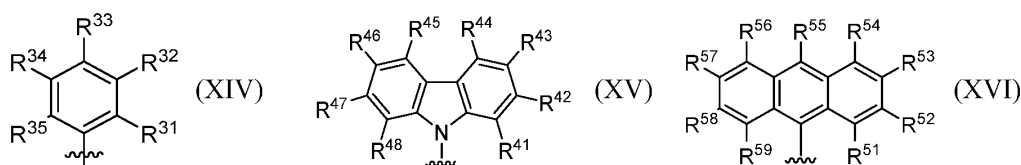
(C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl,

(C₄–C₁₂)diene, halogen, –N(R^N)₂, and –N(R^N)COR^C;

the metal–ligand complex is overall charge-neutral;

each Z is independently chosen from –O–, –S–, –N(R^N)–, or –P(R^P)–;

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



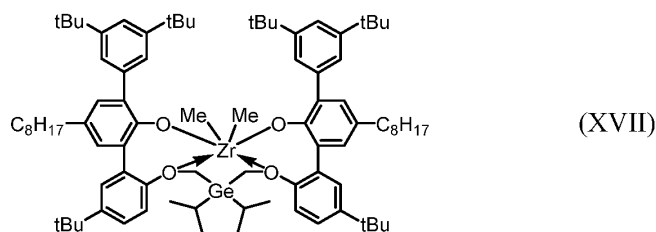
where each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^C\text{S}(\text{O})-$, $R^C\text{S}(\text{O})_2-$, $(R^C)_2\text{C}=\text{N}-$, $R^C\text{C}(\text{O})\text{O}-$, $R^C\text{OC}(\text{O})-$, $R^C\text{C}(\text{O})\text{N}(R^N)-$, $(R^C)_2\text{NC}(\text{O})-$, or halogen;

R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently selected from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^C\text{S}(\text{O})-$, $R^C\text{S}(\text{O})_2-$, $(R^C)_2\text{C}=\text{N}-$, $R^C\text{C}(\text{O})\text{O}-$, $R^C\text{OC}(\text{O})-$, $R^C\text{C}(\text{O})\text{N}(R)-$, $(R^C)_2\text{NC}(\text{O})-$, and halogen;

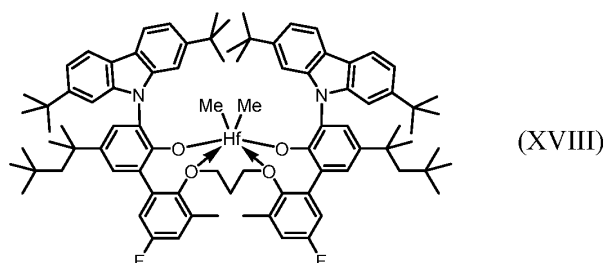
L is (C_1-C_{40}) hydrocarbylene or (C_2-C_{40}) heterohydrocarbylene; and

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

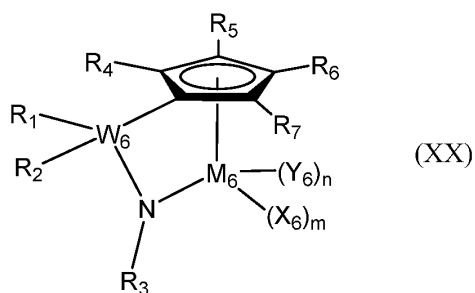
13. The process of any previous claim, wherein the procatalyst has the structure according to formula (XVII):



14. The process of any previous claim, wherein the procatalyst has the structure according to formula (XVIII):



15. The process of any one of claims 1 to 11, wherein the procatalyst has the structure according to formula (XX):



where

M_6 is hafnium, titanium or zirconium; n is 0, 1, or 2; m is 0, 1, or 2, provided that when m is 2, n is 0 and when n is 2, m is 0; and

each X_6 is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbon, (C_1-C_{50}) heterohydrocarbon, (C_1-C_{50}) hydrocarbyl, (C_6-C_{50}) aryl, (C_6-C_{50}) heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4-C_{12}) diene, halogen, hydrogen, $-N(R^N)_2$, and $-NCOR^C$. The metal-ligand complex is overall charge-neutral;

each Y_6 is independently a Lewis base;

N is nitrogen; W_6 is carbon or silicon and is covalently bonded to cyclopentadiene; and R_1 and R_2 are independently selected from $-H$, (C_1-C_{40}) hydrocarbyl, and (C_1-C_{40}) heterohydrocarbyl; R_3 are independently selected from (C_1-C_{40}) hydrocarbyl, and (C_1-C_{40}) heterohydrocarbyl; and

R₄, R₅, R₆, and R₇ are independently (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl wherein any of the R₄, R₅, R₆, and R₇ optionally are connected to form a ring structure.

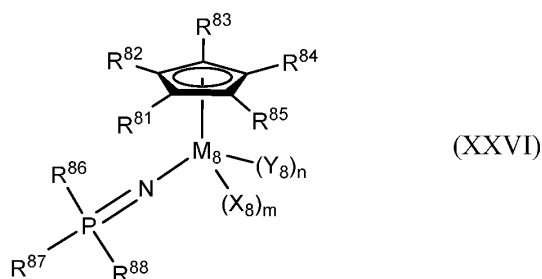
16. The process according to any previous claim, wherein the process further comprises a reactor at a reaction temperature.

17. The process of claim 16, wherein the reactor is a solution reactor comprising one or more solvents.

18. The process of claim 17, wherein the solvent is a hydrocarbon, an aliphatic hydrocarbon, a non-halogenated hydrocarbon, a non-aromatic hydrocarbon or combinations thereof.

19. The process according to any one of claims 16-18, wherein the reaction temperature is 120 °C-225 °C.

20. The process of any one of claims 1 to 11, wherein the procatalyst has the structure according to formula (XXVI):



each X is a monodentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)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, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, a halogen, wherein each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; wherein two X ligands can be connected to form a ring, wherein one member of the ring is M₈;

each Y_8 is independently Lewis Base; optionally, X and Y can be linked to form a ring.

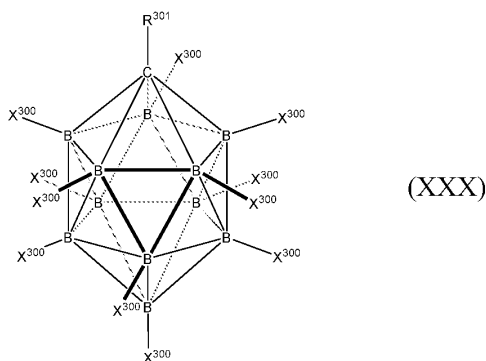
Each subscript m is 1 and 2; and each subscript n is 0, 1 and 2. The metal–ligand complex is overall charge-neutral;

M_8 is titanium, zirconium, or hafnium; R^{81} , R^{82} , R^{83} , R^{84} , and R^{85} are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl wherein any of the R^{82} , R^{83} , R^{84} , and R^{85} optionally are connected to form a ring structure; R^{86} , R^{87} , and R^{88} are independently (C_1-C_{20}) hydrocarbyl, (C_1-C_{20}) heterohydrocarbyl, (C_6-C_{30}) aryl, (C_5-C_{30}) heteroaryl wherein two of R^{86} , R^{87} , and R^{88} are optionally connected to form a ring; and

R^{81} , R^{82} , R^{83} , R^{84} , and R^{85} are independently (C_1-C_{50}) hydrocarbyl, wherein R^{81} and R^{82} are optionally connected to form a ring, or R^{82} and R^{83} are optionally connected to form a ring, R^{83} and R^{84} are optionally connected to form a ring, R^{84} and R^{85} optionally are connected to form a ring. In various embodiments, R^{86} , R^{87} , and R^{88} are independently (C_1-C_{20}) hydrocarbyl, (C_1-C_{20}) heterohydrocarbyl, (C_6-C_{30}) aryl, (C_5-C_{30}) heteroaryl wherein two of R^{86} , R^{87} , and R^{88} are optionally connected to form a ring; and

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

21. The process of any one of claims 1 to 7, wherein the anion has a structure according to formula the anion has a structure according to formula (XXX):



R^{301} and each X^{300} are each independently selected from a halogen, a substituted or unsubstituted (C_1-C_{40}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{40}) heterohydrocarbyl, $Si(R^C)_3$, $Si(N(R^C)_2)_3$, $Si(O(R^C)_2)_3$, $Ge(R^C)_3$, $Ge(N(R^C)_2)_3$, $Ge(O(R^C)_2)_3$, $P(R^C)_2$, $P(N(R^C)_2)_2$, $P(OR^C)_2$, $N(R^C)_2$, $NH(R^C)$, NH_2 , OH , SH , OR^C , SR^C , NO_2 , CN , $-CF_3$, $-CF_2R^C$, $-CF(R^C)_2$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^C)-$, $(R^C)_2NC(O)-$, or hydrogen, wherein each R^C is independently a substituted or unsubstituted (C_1-C_{35}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{35}) heterohydrocarbyl; wherein:

- two or more of X^{300} may optionally form one or more ring structures;
- two or more of X^{300} and R^{301} may optionally form one or more ring structures;
- and
- one or more hydrogen atoms may optionally be substituted with deuterium; and
- at least one of X^{300} or R^{301} is a halogen atom.