

**Title: NON-COORDINATING ANION TYPE ACTIVATORS CONTAINING
CATION HAVING LARGE ALKYL GROUPS**

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PRIORITY

[0001] This application claims priority to and the benefit of USSN 62/662,972, filed April 26, 2018 and USSN 62/769,208, filed November 19, 2018.

10 **CROSS REFERENCE TO RELATED APPLICATIONS**

[0002] This invention also relates to:

1) USSN _____, filed concurrently herewith, entitled "*Alkyl Ammonium (Fluoroaryl)Borate Activators*", attorney docket number (2018EM113/2-US) which claims priority to and the benefit of USSN 62/662,981, filed April 26, 2018; and

15 2) USSN _____, filed concurrently herewith, entitled "Non- Coordinating Anion Type Activators Containing Cation Having Branched Alkyl Groups", attorney docket number (2019EM137/2-US), which claims priority to and the benefit of USSN 62/662,972, filed April 26, 2018 and USSN 62/769,208, filed November 19, 2018.

FIELD

20 [0003] The present disclosure provides group 13 metallate (such as borate or aluminate) activators, catalyst systems comprising, and methods for polymerizing olefins using such activators.

BACKGROUND

25 [0004] Polyolefins are widely used commercially because of their robust physical properties. Polyolefins are typically prepared with a catalyst that polymerizes olefin monomers. Therefore, there is interest in finding new catalysts and catalyst systems that provide polymers having improved properties.

[0005] Catalysts for olefin polymerization are often based on metallocenes as catalyst precursors, which are activated either with an alumoxane or an activator containing a non-
30 coordinating anion. A non-coordinating anion, such as tetrakis(pentafluorophenyl)borate, is capable of stabilizing the resulting metal cation of the catalyst. Because such activators are fully ionized and the corresponding anion is highly non-coordinating, such activators can be effective as olefin polymerization catalyst activators. However, because they are ionic salts,

such activators are insoluble in aliphatic hydrocarbons and only sparingly soluble in aromatic hydrocarbons. It is desirable to conduct most polymerizations of α -olefins in aliphatic hydrocarbon solvents due to the compatibility of such solvents with the olefin monomer and in order to reduce the aromatic hydrocarbon content of the resulting polymer product. Typically, 5 ionic salt activators are added to such polymerizations in the form of a solution in an aromatic solvent such as toluene. The use of even a small quantity of such an aromatic solvent for this purpose is undesirable since it must be removed in a post-polymerization devolatilization step and separated from other volatile components, which is a process that adds significant cost and complexity to any commercial process. In addition, the activators often exist in the form of an 10 oily, intractable material which is not readily handled and metered or precisely incorporated into the reaction mixture.

[0006] In addition, polymer products, such as isotactic polypropylene, formed using such activators can have lower molecular weights (e.g., Mw less than about 100,000) and a high melt temperature (Tm) (e.g., Tm greater than about 110°C).

15 [0007] US 5,919,983 discloses polymerization of ethylene and octene using a catalyst system comprising $[(C_{18})_2MeN]^+[B(PhF_5)_4]^-$ activator having four fluoro-phenyl groups bound to the boron atom and two linear C_{18} groups bound to the nitrogen, as well as describing other linear groups at column 3, line 51 et seq.

[0008] US 8,642,497 discloses the preparation of N,N-dimethylanilinium 20 tetrakis(heptafluoronaphth-2-yl)borate anion.

[0009] US 2003/0013913 (granted as US 7,101,940) discloses various activators such as N,N-dimethylcyclohexylammoniumtetrakis(pentafluorophenyl)borate [0070], and N,N-diethylbenzylammoniumtetrakis(pentafluorophenyl)borate [0124].

[0010] US 2002/0062011 discloses phenyl dioctadecylammonium(hydroxyphenyl) 25 tris(pentafluorophenyl) borate at paragraph [0200] and (pentafluorophenyl) dioctadecylammonium tetrakis(pentafluorophenyl) borate at paragraph [0209].

[0011] US 7,799,879, US 7,985,816, US 8,580,902, US 8,835,587, and WO2010/014344 describe ammonium borate activators that include some that use a tetrakis(heptafluoronaphth-2-yl)borate anion.

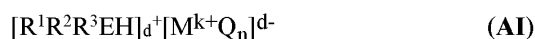
30 [0012] There is a need for activators that are soluble in aliphatic hydrocarbons and capable of producing polyolefins having a high molecular weight and high melt temperature. Likewise, there is a need for activators that are soluble in aliphatic hydrocarbons and capable of producing

polyolefins at high activity levels where the polymers preferably have high molecular weight and/or high melt temperature.

[0013] References of interest include: WO 2002/002577; US 7,087,602; US 8,642,497; US 6,121,185; US 8,642,497; US2015/0203602; and USSN 62/662,972 filed April 26, 2018, CAS number 909721-53-5, CAS number 943521-08-2.

SUMMARY

[0014] This invention relates to activator compounds represented by Formula (AI):



wherein:

- 10 E is nitrogen or phosphorous;
 d is 1, 2 or 3; k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6; n - k = d (preferably d is 1, 2 or 3; k is 3; n is 4, 5, or 6);
 R¹ is a C₁-C₂₀ linear alkyl group; (preferably a C₁-C₁₀ linear alkyl group), wherein R¹ is optionally substituted,
 15 each of R² and R³ is independently an optionally substituted C₁-C₄₀ linear alkyl group or a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group, an optionally substituted alkoxy group, an optionally substituted silyl group, a halogen, or a halogen containing group, wherein R¹, R², and R³ together comprise 15 or more carbon atoms;
 20 M is an element selected from group 13 of the Periodic Table of the Elements; and
 each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical, provided that when Q is a fluorophenyl group, then R² is not a C₁-C₄₀ linear alkyl group (alternately R² is not an optionally substituted C₁-C₄₀ linear
 25 alkyl group).

[0015] This invention also relates to activator compounds represented by Formula (I):



wherein:

- E is nitrogen or phosphorous;
 30 each of R¹, R², and R³ is independently C₁-C₄₀ linear alkyl or C₅-C₂₂-aryl, wherein each of R¹, R², and R³ is independently unsubstituted or substituted with at least one of halide, C₁-C₁₀ alkyl, C₅-C₁₅ aryl, C₆-C₂₅ arylalkyl, or C₆-C₂₅ alkylaryl, wherein R¹, R², and R³ together comprise 15 or more carbon atoms; and

each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.

[0016] This invention also relates to activator compounds represented by Formula (I):



5 wherein:

E is nitrogen or phosphorous;

each of R¹, R², and R³ is independently C₁-C₄₀ linear alkyl or C₅-C₅₀-aryl, wherein each of R¹, R², and R³ is independently unsubstituted or substituted with at least one of halide, C₁-C₅₀ alkyl, C₅-C₅₀ aryl, C₆-C₃₅ arylalkyl, or C₆-C₃₅ alkylaryl, wherein R¹, R², and R³ together

10 comprise 15 or more carbon atoms; and

each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.

[0017] This invention further relates to activator compounds represented by Formula (I):



15 wherein:

E is nitrogen or phosphorous;

R¹ is a methyl group;

R² is C₆-C₅₀ aryl group; and

R³ is independently C₁-C₄₀ linear alkyl or C₅-C₅₀-aryl group,

20 wherein each of R² and R³ is independently unsubstituted or substituted with at least one of halide, C₁-C₃₅ alkyl, C₅-C₁₅ aryl, C₆-C₃₅ arylalkyl, C₆-C₃₅ alkylaryl, wherein R², and R³ together comprise 20 or more carbon atoms; and each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.

[0018] In yet another embodiment, the present disclosure provides a catalyst system
25 comprising an activator as described herein and a catalyst compound.

[0019] In yet another embodiment, the present disclosure provides a catalyst system comprising an activator as described herein, a catalyst support, and a catalyst compound.

[0020] In still another embodiment, the present disclosure provides a polymerization process comprising a) contacting one or more olefin monomers with a catalyst system
30 comprising: i) an activator as described herein, ii) a catalyst compound, and iii) optional support.

[0021] In still another embodiment, the present disclosure provides a polyolefin formed by a catalyst system and or method of the present disclosure.

BRIEF DESCRIPTION OF THE FIGURES

[0022] FIG. 1 is a graph illustrating polymer Mn data versus activator equivalent and μmol of TNOAL, according to one aspect of the present disclosure.

[0023] FIG. 2 is a graph illustrating catalyst activity data for examples in Table 5.

5 [0024] FIG. 3 is a graph illustrating Mn data for the examples in Table 5.

[0025] FIG. 4 is a graph comonomer content (mol%) data for the examples in Table 5.

[0026] FIG. 5 shows pathways to prepare various aniline materials.

[0027] FIG. 6 is a graph of activity for different activators in the propylene polymerizations reported in Table 7.

10 **DETAILED DESCRIPTION**

Definitions

[0028] Unless otherwise noted all melt temperatures (T_m) are DSC second melt and are determined using the following DSC procedure according to ASTM D3418-03. Differential scanning calorimetric (DSC) data are obtained using a TA Instruments model Q200 machine.

15 Samples weighing about 5 to about 10 mg are sealed in an aluminum hermetic sample pan. The DSC data are recorded by first gradually heating the sample to about 200°C at a rate of about 10°C/minute. The sample is kept at about 200°C for about 2 minutes, then cooled to about -90°C at a rate of about 10° /minute, followed by an isothermal for about 2 minutes and heating to about 200°C at about 10°C/minute. Both the first and second cycle thermal events are recorded. The melting points reported herein are obtained during the second heating/cooling cycle unless otherwise noted.

[0029] All molecular weights are weight average (M_w) unless otherwise noted. All molecular weights are reported in g/mol unless otherwise noted. Melt index (MI) also referred to as I2, reported in g/10 min, is determined according to ASTM D-1238, 190°C, 2.16 kg load.

25 High load melt index (HLMI) also referred to as I21, reported in g/10 min, is determined according to ASTM D-1238, 190°C, 21.6 kg load. Melt index ratio (MIR) is MI divided by HLMI as determined by ASTM D1238.

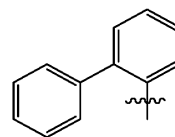
[0030] The specification describes catalysts that can be transition metal complexes. The term complex is used to describe molecules in which an ancillary ligand is coordinated to a central transition metal atom. The ligand is bulky and stably bonded to the transition metal so as to maintain its influence during use of the catalyst, such as polymerization. The ligand may be coordinated to the transition metal by covalent bond and/or electron donation coordination or intermediate bonds. The transition metal complexes are generally subjected to activation to

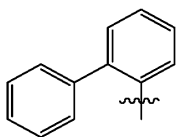
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perform their polymerization or oligomerization function using an activator which is believed to create a cation as a result of the removal of an anionic group, often referred to as a leaving group, from the transition metal.

[0031] For the purposes of the present disclosure, the numbering scheme for the Periodic Table Groups is the "New" notation as described in *Chemical and Engineering News*, 63(5), pg. 27 (1985). Therefore, a "Group 8 metal" is an element from Group 8 of the Periodic Table, e.g., Fe, and so on.

[0032] The following abbreviations are used through this specification: o-biphenyl is an



ortho-biphenyl moiety represented by the structure , dme is 1,2-dimethoxyethane, Me is methyl, Ph is phenyl, Et is ethyl, Pr is propyl, iPr is isopropyl, n-Pr is normal propyl, cPr is cyclopropyl, Bu is butyl, iBu is isobutyl, tBu is tertiary butyl, p-tBu is para-tertiary butyl, nBu is normal butyl, sBu is sec-butyl, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TNOAL is tri(n-octyl)aluminum, MAO is methylalumoxane, p-Me is para-methyl, Ph is phenyl, Bn is benzyl (i.e., CH₂Ph), THF (also referred to as thf) is tetrahydrofuran, RT is room temperature (and is 23°C unless otherwise indicated), tol is toluene, EtOAc is ethyl acetate, MeCy is methylcyclohexane, and Cy is cyclohexyl.

[0033] Unless otherwise indicated (e.g., the definition of "substituted hydrocarbyl", etc.), the term "substituted" means that at least one hydrogen atom has been replaced with at least a non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*, -SiR*₃, -GeR*, -GeR*₃, -SnR*, -SnR*₃, -PbR*₃, and the like, where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a ring structure.

[0034] The terms "hydrocarbyl radical," "hydrocarbyl," and "hydrocarbyl group," are used interchangeably throughout this disclosure. Likewise, the terms "group", "radical", and "substituent" are also used interchangeably in this disclosure. For purposes of this disclosure, "hydrocarbyl radical" is defined to be C₁-C₁₀₀ radicals of carbon and hydrogen, that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such

radicals can include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like.

[0035] Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom of the hydrocarbyl radical has been replaced with a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*, -SiR*₃, -GeR*, -GeR*₃, -SnR*, -SnR*₃, -PbR*₃, and the like, where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0036] Substituted cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl groups are cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl groups where at least one hydrogen atom has been replaced with at least a non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*, -SiR*₃, -GeR*, -GeR*₃, -SnR*, -SnR*₃, -PbR*₃, and the like, where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a ring structure.

[0037] Halocarbyl radicals (also referred to as halocarbyls, halocarbyl groups or halocarbyl substituents) are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one halogen (*e.g.*, F, Cl, Br, I) or halogen-containing group (*e.g.*, CF₃). Substituted halocarbyl radicals are radicals in which at least one halocarbyl hydrogen or halogen atom has been substituted with at least one functional group such as NR*₂, OR*, SeR*, TeR*, PR*₂, AsR*₂, SbR*₂, SR*, BR*₂, SiR*₃, GeR*₃, SnR*₃, PbR*₃, and the like or where at least one non-carbon atom or group has been inserted within the halocarbyl radical such as --O--, --S--, --Se--, --Te--, --N(R*)--, =N--, --P(R*)--, =P--, --As(R*)--, =As--, --Sb(R*)--, =Sb--, --B(R*)--, =B--, --Si(R*)₂--, --Ge(R*)₂--, --Sn(R*)₂--, --Pb(R*)₂-- and the like, where R* is independently a hydrocarbyl or halocarbyl radical provided that at least one halogen atom remains on the original halocarbyl radical.

Additionally, two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

- [0038]** Hydrocarbylsilyl groups, also referred to as silylcarbyl groups, are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one SiR*₃ containing group or where at least one -Si(R*)₂- has been inserted within the hydrocarbyl radical where R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Silylcarbyl radicals can be bonded via a silicon atom or a carbon atom.
- [0039]** Substituted silylcarbyl radicals are silylcarbyl radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR*₂, OR*, SeR*, TeR*, PR*₂, AsR*₂, SbR*₂, SR*, BR*₂, GeR*₃, SnR*₃, PbR₃ and the like or where at least one non-hydrocarbon atom or group has been inserted within the silylcarbyl radical, such as --O--, --S--, --Se--, --Te--, --N(R*)--, =N--, --P(R*)--, =P--, --As(R*)--, =As--, --Sb(R*)--, =Sb--, --B(R*)--, =B--, --Ge(R*)₂--, --Sn(R*)₂--, --Pb(R*)₂-- and the like, where R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

- [0040]** Germylcarbyl radicals (also referred to as germylcarbyls, germylcarbyl groups or germylcarbyl substituents) are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one GeR*₃ containing group or where at least one -Ge(R*)₂- has been inserted within the hydrocarbyl radical where R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Germylcarbyl radicals can be bonded via a germanium atom or a carbon atom.

- [0041]** Substituted germylcarbyl radicals are germylcarbyl radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR*₂, OR*, SeR*, TeR*, PR*₂, AsR*₂, SbR*₂, SR*, BR*₂, SiR*₃, SnR*₃, PbR₃ and the like or where at least one non-hydrocarbon atom or group has been inserted within the germylcarbyl radical, such as --O--, --S--, --Se--, --Te--, --N(R*)--, =N--, --P(R*)--, =P--, --As(R*)--, =As--, --Sb(R*)--, =Sb--, --B(R*)--, =B--, --Si(R*)₂--, --Sn(R*)₂--, --Pb(R*)₂-- and the like, where R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to

form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

[0042] The terms “alkyl radical,” and “alkyl” are used interchangeably throughout this disclosure. For purposes of this disclosure, “alkyl radicals” are defined to be C₁-C₁₀₀ alkyls that may be linear, branched, or cyclic. Examples of such radicals can include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like. Substituted alkyl radicals are radicals in which at least one hydrogen atom of the alkyl radical has been substituted with at least a non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR^{*}₂, -OR^{*}, -SeR^{*}, -TeR^{*}, -PR^{*}₂, -AsR^{*}₂, -SbR^{*}₂, -SR^{*}, -BR^{*}₂, -SiR^{*}, -SiR^{*}₃, -GeR^{*}, -GeR^{*}₃, -SnR^{*}, -SnR^{*}₃, -PbR^{*}₃, and the like, where each R^{*} is independently a hydrocarbyl or halocarbyl radical, and two or more R^{*} may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0043] The term “branched alkyl” means that the alkyl group contains a tertiary or quaternary carbon (a tertiary carbon is a carbon atom bound to three other carbon atoms. A quaternary carbon is a carbon atom bound to four other carbon atoms). For example, 3,5,5-trimethylhexylphenyl is an alkyl group (hexyl) having three methyl branches (hence, one tertiary and one quaternary carbon) and thus is a branched alkyl bound to a phenyl group.

[0044] The term “alkenyl” means a straight-chain, branched-chain, or cyclic hydrocarbon radical having one or more carbon-carbon double bonds. These alkenyl radicals may be substituted. Examples of suitable alkenyl radicals can include ethenyl, propenyl, allyl, 1,4-butadienyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl and the like.

[0045] The term “arylalkenyl” means an aryl group where a hydrogen has been replaced with an alkenyl or substituted alkenyl group. For example, styryl indenyl is an indene substituted with an arylalkenyl group (a styrene group).

[0046] The term “alkoxy”, “alkoxyl”, or “alkoxide” means an alkyl ether or aryl ether radical wherein the terms alkyl and aryl are as defined herein. Examples of suitable alkyl ether radicals can include methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, phenoxy, and the like.

[0047] The term "aryloxy" or "aryloxide" means an aryl ether radical wherein the term aryl is as defined herein.

[0048] The term "aryl" or "aryl group" means a carbon-containing aromatic ring such as phenyl. Likewise, heteroaryl means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, such as N, O, or S. As used herein, the term "aromatic" also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic.

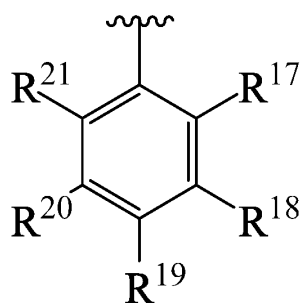
[0049] Heterocyclic means a cyclic group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, such as N, O, or S. A heterocyclic ring is a ring having a heteroatom in the ring structure as opposed to a heteroatom substituted ring where a hydrogen on a ring atom is replaced with a heteroatom. For example, tetrahydrofuran is a heterocyclic ring and 4-N,N-dimethylamino-phenyl is a heteroatom substituted ring.

[0050] Substituted heterocyclic means a heterocyclic group where at least one hydrogen atom of the heterocyclic radical has been substituted with at least a non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR^{*}₂, -OR^{*}, -SeR^{*}, -TeR^{*}, -PR^{*}₂, -AsR^{*}₂, -SbR^{*}₂, -SR^{*}, -BR^{*}₂, -SiR^{*}, -SiR^{*}₃, -GeR^{*}, -GeR^{*}₃, -SnR^{*}, -SnR^{*}₃, -PbR^{*}₃, and the like, where each R^{*} is independently a hydrocarbyl or halocarbyl radical.

[0051] A substituted aryl is an aryl group where at least one hydrogen atom of the aryl radical has been substituted with at least a non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR^{*}₂, -OR^{*}, -SeR^{*}, -TeR^{*}, -PR^{*}₂, -AsR^{*}₂, -SbR^{*}₂, -SR^{*}, -BR^{*}₂, -SiR^{*}, -SiR^{*}₃, -GeR^{*}, -GeR^{*}₃, -SnR^{*}, -SnR^{*}₃, -PbR^{*}₃, and the like, where each R^{*} is independently a hydrocarbyl or halocarbyl radical, and two or more R^{*} may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a hydrocarbyl ring, for example 3,5-dimethylphenyl is a substituted aryl group.

[0052] The term "substituted phenyl," or "substituted phenyl group" means a phenyl group having one or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR^{*}₂, -OR^{*}, -SeR^{*}, -TeR^{*}, -PR^{*}₂, -AsR^{*}₂, -SbR^{*}₂, -SR^{*}, -BR^{*}₂, -SiR^{*}, -SiR^{*}₃, -GeR^{*}, -GeR^{*}₃, -SnR^{*}, -SnR^{*}₃, -PbR^{*}₃, and the like, where each R^{*}

is independently a hydrocarbyl, halogen, or halocarbyl radical. Preferably the "substituted phenyl" group is represented by the formula:



, where each of R¹⁷, R¹⁸, R¹⁹, R²⁰, and R²¹ is independently selected from hydrogen, C₁-C₄₀ hydrocarbyl or C₁-C₄₀ substituted hydrocarbyl, a heteroatom, such as halogen, or a heteroatom-containing group (provided that at least one of R¹⁷, R¹⁸, R¹⁹, R²⁰, and R²¹ is not H), or a combination thereof.

[0053] A "fluorophenyl" or "fluorophenyl group" is a phenyl group substituted with one, two, three, four or five fluorine atoms.

[0054] The term "arylalkyl" means an aryl group where a hydrogen has been replaced with an alkyl or substituted alkyl group. For example, 3,5'-di-tert-butyl-phenyl indenyl is an indene substituted with an arylalkyl group. When an arylalkyl group is a substituent on another group, it is bound to that group via the aryl. For example in Formula AI, the aryl portion is bound to E.

[0055] The term "alkylaryl" means an alkyl group where a hydrogen has been replaced with an aryl or substituted aryl group. For example, phenethyl indenyl is an indene substituted with an ethyl group bound to a benzene group. When an alkylaryl group is a substituent on another group, it is bound to that group via the alkyl. For example in Formula AI, the alkyl portion is bound to E.

[0056] Reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (*e.g.*, butyl) expressly discloses all isomers (*e.g.*, n-butyl, iso-butyl, sec-butyl, and tert-butyl), unless otherwise indicated.

[0057] The term "ring atom" means an atom that is part of a cyclic ring structure. Accordingly, a benzyl group has six ring atoms and tetrahydrofuran has 5 ring atoms.

[0058] For purposes of the present disclosure, a "catalyst system" is a combination of at least one catalyst compound, an activator, and an optional support material. The catalyst systems may further comprise one or more additional catalyst compounds. For the purposes of the present disclosure, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form

of the component is the form that reacts with the monomers to produce polymers. Catalysts of the presented disclosure and activators represented by Formula (I) or (AI) are intended to embrace ionic forms in addition to the neutral forms of the compounds.

[0059] “Complex” as used herein, is also often referred to as catalyst precursor, precatalyst, catalyst, catalyst compound, transition metal compound, or transition metal complex. These words are used interchangeably.

[0060] A scavenger is a compound that is typically added to facilitate polymerization by scavenging impurities. Some scavengers may also act as activators and may be referred to as co-activators. A co-activator, that is not a scavenger, may also be used in conjunction with an activator in order to form an active catalyst. In some embodiments a co-activator can be pre-mixed with the transition metal compound to form an alkylated transition metal compound.

[0061] In the description herein, a catalyst may be described as a catalyst precursor, a precatalyst compound, a catalyst compound or a transition metal compound, and these terms are used interchangeably. A polymerization catalyst system is a catalyst system that can polymerize monomers into polymer. An “anionic ligand” is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. A “neutral donor ligand” is a neutrally charged ligand which donates one or more pairs of electrons to a metal ion.

[0062] A metallocene catalyst is defined as an organometallic compound with at least one π -bound cyclopentadienyl moiety or substituted cyclopentadienyl moiety (such as substituted or unsubstituted Cp, Ind, or Flu) and more frequently two (or three) π -bound cyclopentadienyl moieties or substituted cyclopentadienyl moieties (such as substituted or unsubstituted Cp, Ind, or Flu). (Cp = cyclopentadienyl, Ind= indenyl, Flu=fluorenyl).

[0063] For purposes of the present disclosure, in relation to catalyst compounds, the term “substituted” means that a hydrogen group has been replaced with a hydrocarbyl group, a heteroatom, or a heteroatom containing group. For example, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group.

[0064] “Catalyst productivity” is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising W g of catalyst (cat), over a period of time of T hours; and may be expressed by the following formula: $P/(T \times W)$ and expressed in units of $\text{gP/gcat} \cdot \text{hr}^{-1}$. “Conversion” is the amount of monomer that is converted to polymer product, and is reported as mol% and is calculated based on the polymer yield and the amount of monomer fed into the reactor. “Catalyst activity” is a measure of the level of activity of the catalyst and is reported as the mass of product polymer (P) produced per mole (or mmol) of

catalyst (cat) used (kgP/molcat or gP/mmolCat), and catalyst activity can also be expressed per unit of time, for example, per hour (hr), e.g., (Kg/mmol h).

[0065] For purposes herein an "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound comprising carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have a "propylene" content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from propylene in the polymerization reaction and the derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer.

[0066] For purposes herein a "polymer" has two or more of the same or different monomer ("mer") units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. "Different" in reference to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, copolymer, as used herein, can include terpolymers and the like. An oligomer is typically a polymer having a low molecular weight, such as Mn of less than 25,000 g/mol, or less than 2,500 g/mol, or a low number of mer units, such as 75 mer units or less or 50 mer units or less. An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer comprising at least 50 mole% ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer comprising at least 50 mole% propylene derived units, and so on.

[0067] As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity index (PDI), is defined to be Mw divided by Mn.

[0068] The term "continuous" means a system that operates without interruption or cessation for a period of time, such as where reactants are continually fed into a reaction zone and products are continually or regularly withdrawn without stopping the reaction in the reaction zone. For example, a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

[0069] A “solution polymerization” means a polymerization process in which the polymerization is conducted in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are typically not turbid as described in Oliveira, J. V. et al. (2000) “High-Pressure Phase Equilibria for Polypropylene-Hydrocarbon Systems,” *Ind. Eng. Chem. Res.*, v.39, pp. 4627-4633.

[0070] A bulk polymerization means a polymerization process in which the monomers and/or comonomers being polymerized are used as a solvent or diluent using little or no inert solvent or diluent. A small fraction of inert solvent might be used as a carrier for catalyst and scavenger. A bulk polymerization system contains less than about 25 wt% of inert solvent or diluent, such as less than about 10 wt%, such as less than about 1 wt%, such as 0 wt%.

Description

[0071] The present disclosure relates to activator compounds that can be used in olefin polymerization processes. For example, the present disclosure provides activators, catalyst systems comprising catalyst compounds and activators, and methods for polymerizing olefins using said catalyst systems. In the present disclosure, activators are described that feature ammonium or phosphonium groups with long-chain aliphatic hydrocarbyl groups for improved solubility of the activator in aliphatic solvents, as compared to conventional activator compounds.

[0072] The present disclosure relates to activator compounds that can be used in olefin polymerization processes. For example, the present disclosure provides ammonium borate activators, catalyst systems comprising ammonium borate activators, and methods for polymerizing olefins using ammonium borate activators. In the present disclosure, activators are described that feature ammonium groups with long-chain aliphatic hydrocarbyl groups for improved solubility of the activator in aliphatic solvents, as compared to conventional activator compounds. Useful borate groups of the present disclosure include fluoronaphthyl borates. It has been discovered that activators of the present disclosure having fluoronaphthyl borate anions have improved solubility in aliphatic solvents, as compared to conventional activator compounds. Activators of the present disclosure can provide polyolefins having a weight average molecular weight (Mw) of about 100,000 g/mol or greater and a melt temperature (Tm) of about 110°C or greater. Further, activators having a cation having at least one methyl group,

and optionally at least one C₁₀ to C₅₀ linear alkyl group can provide enhanced activity for polymer production.

[0073] In another aspect, the present disclosure relates to polymer compositions obtained from the catalyst systems and processes set forth herein. The components of the catalyst systems according to the present disclosure and used in the polymerization processes of the present disclosure, as well as the resulting polymers, are described in more detail herein below.

[0074] The present disclosure relates to a catalyst system comprising a transition metal compound and an activator compound of formula (I) or (AI), to the use of an activator compound of formula (I) or (AI) for activating a transition metal compound in a catalyst system for polymerizing olefins, and to processes for polymerizing olefins, the process comprising contacting under polymerization conditions one or more olefins with a catalyst system comprising a transition metal compound and an activator compound of formula (I) or (AI).

[0075] The present disclosure also relates to processes for polymerizing olefins comprising contacting, under polymerization conditions, one or more olefins with a catalyst system comprising a transition metal compound and an activator compound of formula (I) or (AI). The weight average molecular weight of the polymer formed can increase with increasing monomer conversion at a given reaction temperature.

[0076] The activator compounds of formula (I) and (AI) will be further illustrated below. Any combinations of cations and non-coordinating anions disclosed herein are suitable to be used in the processes of the present disclosure and are thus incorporated herein.

Non-Coordinating Anion (NCA) Activators

[0077] Noncoordinating anion (NCA) means an anion either that does not coordinate to the catalyst metal cation or that does coordinate to the metal cation, but only weakly. The term NCA is also defined to include multicomponent NCA-containing activators, such as N,N-diocetadecylanilinium tetrakis(perfluoronaphthyl)borate, that contain an acidic cationic group and the non-coordinating anion. The term NCA is also defined to include neutral Lewis acids, such as tris(pentafluoronaphthyl)boron, that can react with a catalyst to form an activated species by abstraction of an anionic group. An NCA coordinates weakly enough that a neutral Lewis base, such as an olefinically or acetylenically unsaturated monomer can displace it from the catalyst center. Any metal or metalloid that can form a compatible, weakly coordinating complex may be used or contained in the noncoordinating anion. Suitable metals can include aluminum, gold, and platinum. Suitable metalloids can include boron, aluminum, phosphorus,

and silicon. The term non-coordinating anion activator includes neutral activators, ionic activators, and Lewis acid activators.

[0078] “Compatible” non-coordinating anions can be those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with the present disclosure are those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization.

10 Activators

[0079] The present disclosure provides activators, such as ammonium or phosphonium metallate or metalloid activator compounds, comprising ammonium or phosphonium groups with long-chain aliphatic hydrocarbyl groups combined with metallate or metalloid anions, such as borates or aluminates. When an activator of the present disclosure is used with a catalyst compound (such as a group 4 metallocene compound) in an olefin polymerization, a polymer can be formed having a higher molecular weight and melt temperature than polymers formed using comparative activators. Likewise, when an activator of the present disclosure where R¹ is methyl is used with a group 4 metallocene catalyst in an olefin polymerization, the catalyst system activity is substantially better than comparative activators, and can form polymers having a higher molecular weight and/or melt temperature vs. polymers formed using comparative activators. In addition, it has been discovered that activators of the present disclosure are soluble in aliphatic solvent.

[0080] In one or more embodiments, a 20 wt% mixture of the compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C, preferably a 30 wt% mixture of the compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C.

[0081] In embodiments of the invention, the activators described herein have a solubility of more than 10 mM (or more than 20 mM, or more than 50 mM) at 25°C (stirred 2 hours) in methylcyclohexane.

[0082] In embodiments of the invention, the activators described herein have a solubility of more than 1 mM (or more than 10 mM, or more than 20 mM) at 25°C (stirred 2 hours) in isohexane.

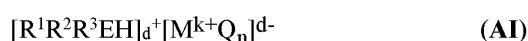
[0083] In embodiments of the invention, the activators described herein have a solubility of more than 10 mM (or more than 20 mM, or more than 50 mM) at 25°C (stirred 2 hours) in methylcyclohexane and a solubility of more than 1 mM (or more than 10 mM, or more than 20 mM) at 25°C (stirred 2 hours) in isohexane.

- 5 [0084] The present disclosure relates to a catalyst system comprising a transition metal compound and an activator compound as described herein, to the use of such activator compounds for activating a transition metal compound in a catalyst system for polymerizing olefins, and to processes for polymerizing olefins, the process comprising contacting under polymerization conditions one or more olefins with a catalyst system comprising a transition
- 10 metal compound and such activator compounds, where aromatic solvents, such as toluene, are absent (e.g. present at zero mol%, alternately present at less than 1 mol%, preferably the catalyst system, the polymerization reaction and/or the polymer produced are free of “detectable aromatic hydrocarbon solvent,” such as toluene. For purposes of the present disclosure, “detectable aromatic hydrocarbon solvent” means 0.1 mg/m² or more as determined
- 15 by gas phase chromatography. For purposes of the present disclosure, “detectable toluene” means 0.1 mg/m² or more as determined by gas phase chromatography.

[0085] The polyolefins produced herein preferably contain 0 ppm (alternately less than 1 ppm) of aromatic hydrocarbon. Preferably, the polyolefins produced herein contain 0 ppm (alternately less than 1 ppm) of toluene.

- 20 [0086] The catalyst systems used herein preferably contain 0 ppm (alternately less than 1 ppm) of aromatic hydrocarbon. Preferably, the catalyst systems used herein contain 0 ppm (alternately less than 1 ppm) of toluene.

[0087] This invention further relates to activator compounds represented by Formula (AI):



- 25 wherein: E is nitrogen or phosphorous, preferably nitrogen;
d is 1, 2 or 3; k is 1, 2, or 3 (preferably 3); n is 1, 2, 3, 4, 5, or 6 (preferably 4, 5 or 6); n - k = d (preferably d is 1, 2 or 3; k is 3; n is 4, 5, or 6, preferably when M is B, n is 4);
R¹ is an optionally substituted C₁-C₂₀ (or C₁ to C₁₀, or C₁-C₆, or C₁-C₄, or C₁-C₂, or C₁) linear alkyl group;
- 30 each of R² and R³ is independently an optionally substituted C₁-C₄₀ linear alkyl group (such as a C₆ to C₄₀ linear alkyl group, or a C₁₀ to C₃₀ linear alkyl group) or a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbonyl group (such as a C₆ to C₄₀ aryl group or linear

alkyl group, a C₁₂ to C₃₀ aryl group or linear alkyl group, or a C₁₀ to C₂₀ aryl group or linear alkyl group), an optionally substituted alkoxy group, an optionally substituted silyl group, a halogen (Br, Cl, I, F, etc.), or a halogen containing group (such as bromoalkyl or bromoaryl), wherein R¹, R², and R³ together comprise 15 or more carbon atoms (such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 38 or more carbon atoms, such as 40 or more carbon atoms, such as 15 to 100 carbon atoms, such as 25 to 75 carbon atoms);

M is an element selected from group 13 of the Periodic Table of the Elements, preferably boron or aluminum; and

each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical, provided that when Q is a fluorophenyl group, then R² is not a C₁-C₄₀ linear alkyl group, preferably R² is not an optionally substituted C₁-C₄₀ linear alkyl group (alternately when Q is a substituted phenyl group, then R² is not a C₁-C₄₀ linear alkyl group, preferably R² is not an optionally substituted C₁-C₄₀ linear alkyl group). Preferably, when Q is a fluorophenyl group (alternately when Q is a substituted phenyl group), then R² is a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group (such as a C₆ to C₄₀ aryl group or linear alkyl group, a C₁₂ to C₃₀ aryl group or linear alkyl group, or a C₁₀ to C₂₀ aryl group or linear alkyl group), an optionally substituted alkoxy group, or an optionally substituted silyl group. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 30 carbon atoms, more preferably each Q is a fluorinated aryl (such as phenyl or naphthyl) group, and most preferably each Q is a perfluorinated aryl (such as phenyl or naphthyl) group.

Examples of suitable [M^{k+}Q_n]^{d-} also include diboron compounds as disclosed in US Patent No. 5,447,895, which is fully incorporated herein by reference. Preferably at least one Q is not substituted phenyl, preferably all Q are not substituted phenyl. Preferably at least one Q is not perfluorophenyl, preferably all Q are not perfluorophenyl.

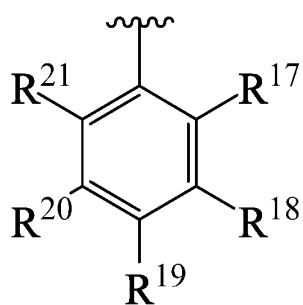
[0088] In some embodiments of the invention, R¹ is not methyl, R² is not C₁₈ alkyl and R³ is not C₁₈ alkyl, alternately R¹ is not methyl, R² is not C₁₈ alkyl and R³ is not C₁₈ alkyl and at least one Q is not substituted phenyl, preferably all Q are not substituted phenyl.

[0089] In embodiments, the the meta and para substituents are, independently, an optionally substituted **linear alkyl group** (such as n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl,

- n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl, n-tetracosyl, n-pentacosyl, n-hexacosyl, n-heptacosyl, n-octacosyl, n-nonacosyl, or n-tricontyl), an optionally substituted silyl group, such as a **trialkylsilyl group**, where each alkyl is independently an
- 5 optionally substituted C₁ to C₂₀ alkyl (such as trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, trihexylsilyl, triheptylsilyl, trioctylsilyl, trinonylsilyl, tridecylsilyl, triundecylsilyl, tridodecylsilyl, tri-tridecylsilyl, tri-tetradecylsilyl, tri-pentadecylsilyl, tri-hexadecylsilyl, tri-heptadecylsilyl, tri-octadecylsilyl, tri-nonadecylsilyl, tri-icosylsilyl), or an optionally substituted **alkoxy group** (such as -OR*, where R* is an optionally substituted C₁
- 10 to C₂₀ alkyl or aryl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, phenyl, phenyl alkyl (such as methyl phenyl, propyl phenyl, etc.), naphthyl, or anthracenyl), a **halogen** (such as Br or Cl) or a **halogen containing group** (such as bromomethyl, bromophenyl, and the like).
- 15 **[0090]** In embodiments, the meta-substituted phenyl is methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, n-tricontylphenyl, dimethylphenyl, diethylphenyl, di-n-propylphenyl, di-n-butylphenyl, di-n-pentylphenyl, di-n-hexylphenyl, di-n-heptylphenyl, di-n-octylphenyl, di-n-nonylphenyl, di-n-decylphenyl, di-n-undecylphenyl, di-n-dodecylphenyl, di-n-tridecylphenyl, di-n-tetradecylphenyl, di-n-pentadecylphenyl, di-n-hexadecylphenyl, di-n-heptadecylphenyl, di-n-octadecylphenyl, di-n-nonadecylphenyl, di-n-icosylphenyl, di-n-henicosylphenyl, di-n-docosylphenyl, di-n-tricosylphenyl, di-n-tetracosylphenyl, di-n-pentacosylphenyl, di-n-hexacosylphenyl, di-n-heptacosylphenyl, di-n-octacosylphenyl, di-n-nonacosylphenyl, and di-n-tricontylphenyl. The two meta substituents may be the same or different.
- 25 **[0091]** In embodiments, the para-substituted phenyl is methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-
- 30

octadecylphenyl, n-nonadecylphenyl, n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, or n-tricontylphenyl.

- 5 **[0092]** In embodiments, the meta- and/or para-substituted phenyl group is represented by the formula:



- 10 , where R^{17} and R^{21} are hydrogen, and each of R^{18} , R^{19} , and R^{20} is independently selected from hydrogen, C_1 - C_{40} hydrocarbyl or C_1 - C_{40} substituted hydrocarbyl, halogen, or a halogen-containing group (provided that at least one of R^{18} , R^{19} , and R^{20} is not H, alternately at least two of R^{18} , R^{19} , and R^{20} are not H), or a combination thereof.

- [0093]** Preferably, R^{17} and R^{21} are hydrogen, and each of R^{18} , R^{19} , and R^{20} is selected from the group consisting of hydrogen, C_1 to C_{40} linear alkyl or C_1 - C_{40} substituted linear alkyl (provided that at least one of R^{18} , R^{19} , and R^{20} is not H, alternately at least two of R^{18} , R^{19} , and R^{20} are not H, alternately all three of R^{18} , R^{19} , and R^{20} are not H).

- 15 **[0094]** Preferably, R^{17} and R^{21} are H, and one, two, or three of R^{18} , R^{19} , and R^{20} are selected from the group consisting of H, **a linear alkyl group** (such as n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl, n-tetracosyl, n-pentacosyl, n-hexacosyl, n-heptacosyl, n-octacosyl, n-nonacosyl, or n-tricontyl), **an**
 20 **optionally substituted trialkylsilyl group**, where each alkyl is independently a C_1 to C_{20} optionally substituted alkyl (such as trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, trihexylsilyl, triheptylsilyl, trioctylsilyl, trinonylsilyl, tridecylsilyl, triundecylsilyl, tridodecylsilyl, tri-tridecylsilyl, tri-tetradecylsilyl, tri-pentadecylsilyl, tri-hexadecylsilyl, tri-heptadecylsilyl, tri-octadecylsilyl, tri-nonadecylsilyl, tri-icosylsilyl), **a halogen** (such as Br, Cl, or F), or **an optionally substituted alkoxy group** (such as $-OR^*$, where R^* is a C_1 to C_{20} optionally substituted alkyl or aryl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl,

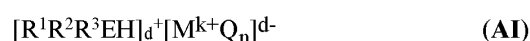
octadecyl, nonadecyl, icosyl, phenyl, phenyl alkyl (such as methyl phenyl, propyl phenyl, etc.), naphthyl, or anthracene), provided that at least one of R^{18} , R^{19} , and R^{20} is not H, alternately at least two of R^{18} , R^{19} , and R^{20} are not H, alternately all three of R^{18} , R^{19} , and R^{20} are not H).

[0095] In embodiments, R^1 is methyl, R^2 is a C_1 to C_{40} linear alkyl group (such as a C_6 to C_{40} linear alkyl, or C_{10} to C_{30} linear alkyl), and R^3 is a para-substituted phenyl group, wherein the para substituent is, independently, an optionally substituted C_1 to C_{40} hydrocarbyl group (such as a C_6 to C_{40} aryl group or linear alkyl group, a C_{12} to C_{30} aryl group or linear alkyl group, or a C_{10} to C_{20} aryl group or linear alkyl group), an optionally substituted alkoxy group, an optionally substituted silyl group, a halogen, or a halogen containing group.

[0096] In embodiments, R^1 is methyl, R^2 is n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, or n-icosyl, and R^3 is methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, or n-icosylphenyl.

[0097] In embodiments of any activator formula herein, each R^2 and/or R^3 may be independently optionally substituted with at least one of halide, C_1 - C_{50} alkyl, C_5 - C_{50} aryl, C_6 - C_{35} arylalkyl, or C_6 - C_{35} alkylaryl, provided that substituted R^2 and R^3 groups are not branched alkyl groups (as defined above).

[0098] In at least one embodiment of the invention, the activator is represented by Formula (I) or (AI):



wherein:

M is a group 13 atom, preferably B or Al;

d is 1, 2 or 3; k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4), $n - k = d$ (preferably d is 1, 2 or 3; k is 3; n is 4, 5, or 6, preferably when M is B, n is 4);

E is nitrogen or phosphorous, preferably nitrogen;

each of R^1 , R^2 , and R^3 is independently a C_1 - C_{40} linear alkyl, a C_5 - C_{22} -aryl, a C_7 to C_{30} arylalkyl (where the alkyl has from 1 to 10 carbon atoms and the aryl has from 6 to 20 carbon atoms), or a five-, six- or seven-membered heterocyclyl comprising at least one atom selected from N, P, O and S, wherein each of R^1 , R^2 , and R^3 is optionally substituted by halogen, wherein

R² optionally bonds with R⁵ to independently form a five-, six- or seven-membered ring, preferably wherein, R¹, R², and R³ together comprise 15 or more carbon atoms, such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 38 or more carbon atoms, such as 40 or more carbon atoms. In at least one embodiment, R¹ and R² are independently C₁-C₂₂-alkyl, substituted C₁-C₂₂-alkyl, unsubstituted phenyl, or substituted phenyl (in at least one embodiment, each of R¹, R² and R³ is independently selected from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, and n-icosyl);

each of R⁴, R⁵, R⁶, and R⁷ is independently naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is naphthyl substituted with from one to seven fluorine atoms, preferably at least one R⁴, R⁵, R⁶, and R⁷ is not substituted phenyl, preferably all of R⁴, R⁵, R⁶, and R⁷ are not substituted phenyl; and

each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 30 carbon atoms, more preferably each Q is a fluorinated aryl (such as phenyl or naphthyl) group, and most preferably each Q is a perfluorinated aryl (such as phenyl or naphthyl) group. In preferred embodiments of the invention, at least one Q is not substituted phenyl, such as perfluorophenyl, preferably all Q are not substituted phenyl, such as perfluorophenyl.

[0099] In at least one embodiment of the invention, an activator is an ionic ammonium or phosphonium borate represented by Formula (I):



wherein:

E is nitrogen or phosphorous;

R¹ is a C₁-C₄₀ linear alkyl,

each of R², and R³ is independently C₁-C₄₀ linear alkyl, C₅-C₂₂-aryl, C₅ to C₅₀ arylalkyl where the alkyl has from 1 to 30 (or 1 to 10) carbon atoms and the aryl has from 6 to 20 carbon atoms, or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from N, P, O and S, wherein each of R¹, R², and R³ is optionally substituted by halogen, wherein R² optionally bonds with R⁵ to independently form a five-, six- or seven-membered ring,

preferably wherein, R¹, R², and R³ together comprise 15 or more carbon atoms, such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms and each of R⁴, R⁵, R⁶, and R⁷ is independently each

5 a fluorinated hydrocarbyl group having 1 to 30 carbon atoms, more preferably each of R⁴, R⁵, R⁶, and R⁷ is independently is a fluorinated aryl (such as phenyl or naphthyl) group, and most preferably each of R⁴, R⁵, R⁶, and R⁷ is independently is a perfluorinated aryl (such as phenyl or naphthyl) group, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms, preferably at least one R⁴, R⁵, R⁶, and R⁷ is not substituted phenyl,

10 preferably all of R⁴, R⁵, R⁶, and R⁷ are not substituted phenyl. In a preferred embodiment, R¹ is not methyl, R² is not C18 and R³ is not C18. In a preferred embodiment, R¹ is not methyl, R² is not C18 and R³ is not C18 and at least one R⁴, R⁵, R⁶, and R⁷ is not substituted phenyl, preferably all of R⁴, R⁵, R⁶, and R⁷ are not substituted phenyl.

[0100] This invention also relates to activator compounds represented by Formula (I):



wherein:

E is nitrogen or phosphorous;

each of R¹, R², and R³ is independently C₁-C₄₀ linear alkyl, C₅-C₅₀-aryl, wherein each of R¹, R², and R³ is independently unsubstituted or substituted with at least one of halide, C₁-C₅₀ alkyl, C₅-C₅₀ aryl, C₆-C₃₅ arylalkyl, or C₆-C₃₅ alkylaryl, wherein R¹, R², and R³ together

20 comprise 15 or more carbon atoms, such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms, and each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with

25 from one to seven fluorine atoms.

[0101] In a preferred aspect, the activator is an ionic ammonium borate represented by Formula (I):



wherein:

30 E is nitrogen or phosphorous;

R¹ is a methyl group;

R² is C₆-C₅₀ aryl which is optionally substituted with at least one of halide, C₁-C₃₅ alkyl, C₅-C₁₅ aryl, C₆-C₃₅ arylalkyl, and C₆-C₃₅ alkylaryl;

R³ is C₁-C₄₀ linear alkyl or C₅-C₄₂-aryl which is optionally substituted with at least one of halide, C₁-C₃₅ alkyl, C₅-C₁₅ aryl, C₆-C₃₅ arylalkyl, and C₆-C₃₅ alkylaryl, wherein R² optionally bonds with R³ to independently form a five-, six- or seven-membered ring, and R² and R³ together comprise 20 or more carbon atoms, such as 21 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms, and

each of R⁴, R⁵, R⁶, and R⁷ is independently naphthyl or substituted naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is naphthyl substituted with from one to seven fluorine atoms.

[0102] In any embodiment of formula (I) or (AI), R² is unsubstituted phenyl or substituted phenyl. In at least one embodiment, R² is phenyl, methyl phenyl, n-butyl phenyl, n-octadecyl-phenyl, or an isomer thereof, preferably R² is meta or para substituted phenyl, such as meta- or para- substituted alkyl substituted phenyl. In at least one embodiment, R³ is independently selected from C₁ to C₃₀ linear alkyl, such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, and n-icosyl.

[0103] In any embodiment of formula (I) or (AI), each of R⁴, R⁵, R⁶, and R⁷ is independently naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is naphthyl substituted with one, two, three, four, five, six or seven fluorine atoms.

[0104] In any embodiment of formula (I) or (AI), preferably at least one R⁴, R⁵, R⁶, and R⁷ is not substituted phenyl, preferably all of R⁴, R⁵, R⁶, and R⁷ are not substituted phenyl. In a preferred embodiment, R¹ is not methyl, R² is not C₁₈ and R³ is not C₁₈.

[0105] In any embodiment of formula (I) or (AI), preferably all Q or all of R⁴, R⁵, R⁶, and R⁷ are not perfluoroaryl, such as perfluorophenyl.

[0106] In any embodiment of formula (I) or (AI), all of R⁴, R⁵, R⁶, and R⁷ are naphthyl, wherein at least one, two, three, or four of R⁴, R⁵, R⁶, and R⁷ is/are substituted with one, two, three, four, five, six or seven fluorine atoms.

[0107] In any embodiment described herein, preferably each of R⁴, R⁵, R⁶, and R⁷ is independently a naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms, preferably seven fluorine atoms.

[0108] In at least one embodiment, R⁴ is independently naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms.

[0109] In any embodiment described herein, each of R⁴, R⁵, R⁶, and R⁷ is independently each a fluorinated hydrocarbyl group having 1 to 30 carbon atoms, more preferably each of R⁴, R⁵, R⁶, and R⁷ is independently is a fluorinated aryl (such as phenyl, biphenyl, [(C₆H₃(C₆H₅)₂)₄B], or naphthyl) group, and most preferably each of R⁴, R⁵, R⁶, and R⁷ is independently is a perfluorinated aryl (such as bi-phenyl, [(C₆H₃(C₆H₅)₂)₄B], or naphthyl) group, preferably at least one R⁴, R⁵, R⁶, and R⁷ is not perfluorophenyl.

[0110] In any embodiment of this invention, when Q is a fluorophenyl group, then R² is not an optionally substituted C₁-C₂₀ linear alkyl group.

[0111] In at least one embodiment, an activator is an ionic ammonium borate represented by Formula (I):



wherein:

E is nitrogen or phosphorous;

each of R¹, R², and R³ is independently C₁-C₄₀ linear alkyl, C₅-C₂₂-aryl, arylalkyl where the alkyl has from 1 to 10 carbon atoms and the aryl has from 6 to 20 carbon atoms, or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from N, P, O and S, wherein each of R¹, R², and R³ is optionally substituted by halogen, -NR', -OR' or -SiR'₃ (where R' is independently hydrogen or C₁-C₂₀ hydrocarbyl), wherein R² optionally bonds with R⁵ to independently form a five-, six- or seven-membered ring. R¹, R², and R³ together comprise 15 or more carbon atoms, such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms. In at least one embodiment, R¹ and R² are independently C₁-C₂₂-alkyl, substituted C₁-C₂₂-alkyl, unsubstituted phenyl, or substituted phenyl. In at least one embodiment, each of R¹, R² and R³ is independently selected from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-butadecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, and n-icosyl.

[0112] In at least one embodiment, each of R⁴, R⁵, R⁶, and R⁷ is independently aryl- or naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is naphthyl substituted with from one to seven fluorine atoms. In at least one embodiment, each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.

[0113] In at least one embodiment, each of R^4 , R^5 , R^6 , and R^7 is independently a naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms.

5 [0114] In at least one embodiment, R^4 is independently naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms, and each of R^5 , R^6 , and R^7 is independently phenyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, or five fluorine atoms or naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms.

10 [0115] The terms “cocatalyst” and “activator” are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds of the present disclosure by converting the neutral catalyst compound to a catalytically active catalyst compound cation.

15 [0116] Catalyst systems of the present disclosure may be formed by combining the catalysts with activators in any suitable manner, including by supporting them for use in slurry or gas phase polymerization. The catalyst systems may also be added to or generated in solution polymerization or bulk polymerization (in the monomer, i.e., little or no solvent).

20 [0117] Both the cation part of formulas (AI) and (I) as well as the anion part thereof, which is an NCA, will be further illustrated below. Any combinations of cations and NCAs disclosed herein are suitable to be used in the processes of the present disclosure and are thus incorporated herein.

Activators-The Cations

25 [0118] The cation component of the activators described herein (such as those of formulas (AI) and (I) above), is a protonated Lewis base that can be capable of protonating a moiety, such as an alkyl or aryl, from the transition metal compound. Thus, upon release of a neutral leaving group (e.g. an alkane resulting from the combination of a proton donated from the cationic component of the activator and an alkyl substituent of the transition metal compound) transition metal cation results, which is the catalytically active species.

30 [0119] In at least one embodiment of formula (I) or (AI), where the cation is $[R^1R^2R^3EH]^+$, E is nitrogen or phosphorous, and each of R^1 , R^2 , and R^3 is independently C_1 - C_{40} linear alkyl, C_5 - C_{22} -aryl, arylalkyl (where the alkyl has from 1 to 10 carbon atoms and the aryl has from 6 to 20 carbon atoms) or five-, six- or seven-membered heterocyclyl comprising at least one atom

selected from N, P, O and S, wherein each of R¹, R², and R³ is optionally substituted by halogen, -NR'₂, -OR' or -SiR'₃ (where each R' is independently hydrogen or C₁-C₂₀ hydrocarbyl), wherein R² optionally bonds with R⁵ to independently form a five-, six- or seven-membered ring. R¹, R², and R³ together comprise 15 or more carbon atoms, such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 37 or more carbon atoms, such as 40 or more carbon atoms, such as 45 or more carbon atoms. In at least one embodiment, R¹, R², and R³ are independently substituted or unsubstituted C₁-C₂₂ linear alkyl, or substituted or unsubstituted phenyl. In at least one embodiment, each of R¹, R² and R³ is independently selected from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, and n-icosyl. In at least one embodiment, each of R² and R³ is independently selected from methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, and n-icosylphenyl.

[0120] In a preferred embodiment, R¹ is methyl, R² is substituted phenyl, R³ is C₁₀ to C₃₀ linear alkyl. Preferably R² is not meta substituted phenyl.

[0121] In a preferred embodiment, R¹ is methyl, R² is C₁ to C₃₅ alkyl substituted phenyl (preferably ortho- or meta- substituted), R³ is C₁₀ to C₃₀ linear alkyl.

[0122] In a preferred embodiment, R¹ is methyl, R² is C₁ to C₃₅ alkyl substituted phenyl (preferably para substituted), R³ is C₁₀ to C₃₀ linear alkyl.

[0123] In a preferred embodiment, R¹ is methyl; R² is C₁ to C₃₅ alkyl substituted phenyl, such as methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, and n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, n-triacontylphenyl; and R³ is C₁₀ to C₃₀ linear alkyl, such as n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-

octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl; n-tetracosyl, n-pentacosyl; n-hexacosyl; n-heptacosyl, n-octacosyl, n-nonacosyl, n-triacontyl.

[0124] In a preferred embodiment, R^2 is C_1 to C_{35} alkyl substituted phenyl, such as methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, and n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, n-triacontylphenyl; and R^3 is C_{10} to C_{30} linear alkyl, such as n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl; n-tetracosyl, n-pentacosyl; n-hexacosyl; n-heptacosyl, n-octacosyl, n-nonacosyl, n-triacontyl.

[0125] In a preferred embodiment of formula (I), R^1 is methyl, R^2 is substituted phenyl, R^3 is C_{10} to C_{30} linear alkyl, and R^4 , R^5 , R^6 , R^7 are perfluoronaphthyl.

[0126] In a preferred embodiment of formula (AI), R^1 is methyl, R^2 is substituted phenyl, R^3 is C_{10} to C_{30} linear alkyl, E is nitrogen, and each Q is perfluoronaphthyl.

[0127] In a preferred embodiment, R^1 is methyl; R^2 is C_1 to C_{35} alkyl substituted phenyl, such as methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, and n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, n-triacontylphenyl; R^3 is C_{10} to C_{30} linear alkyl, such as n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl; n-tetracosyl, n-pentacosyl; n-hexacosyl; n-heptacosyl, n-octacosyl, n-nonacosyl, n-triacontyl; and each Q or each of R^4 , R^5 , R^6 , R^7 are perfluoronaphthyl.

[0128] In a preferred embodiment of the invention, R^1 is o-MePh, R^2 and R^3 are n-octadecyl.

[0129] In a preferred embodiment of the invention, R^1 is m-MePh, R^2 and R^3 are n-octadecyl.

[0130] In a preferred embodiment of the invention, R¹ is not para-alkylphenyl, such as p-MePh.

[0131] In a preferred embodiment of the invention, R¹ is Me, R² is n-octadecylaryl, and R³ is n-octadecyl.

5 [0132] In a preferred embodiment of the invention, R¹ is Me, R² is n-octadecylphenyl, and R³ is n-octadecyl.

[0133] In a preferred embodiment of the invention, R¹ is Me, R² is n-butylaryl, and R³ is n-octadecyl.

10 [0134] In a preferred embodiment of the invention, R¹ is Me, R² is n-butylphenyl, and R³ is n-octadecyl.

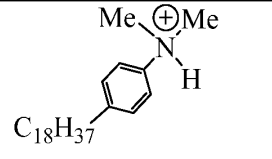
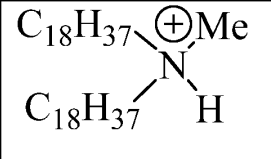
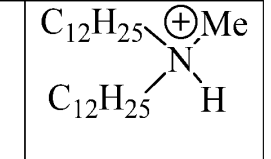
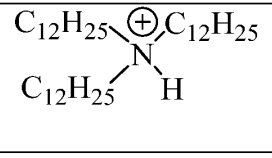
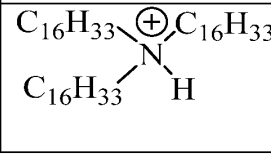
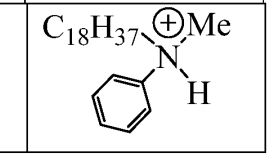
[0135] In a preferred embodiment of the invention, R¹ is n-decyl, R² is n-butylaryl, and R³ is n-decyl.

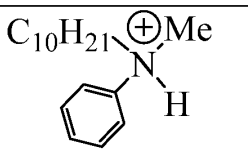
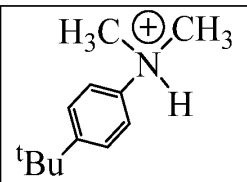
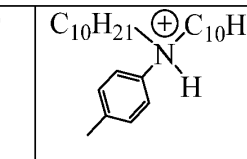
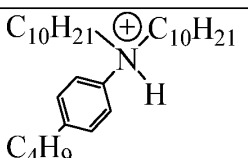
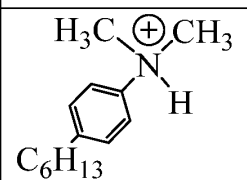
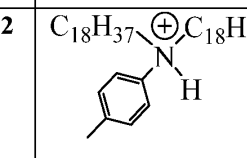
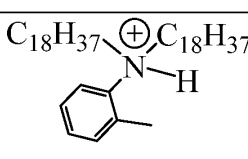
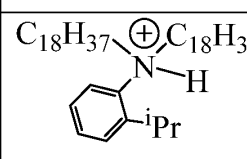
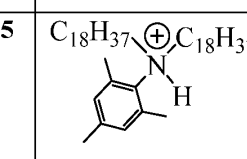
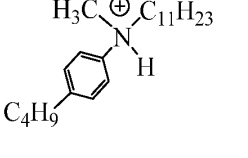
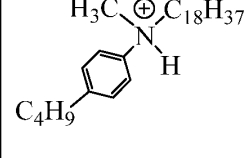
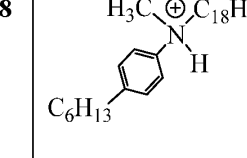
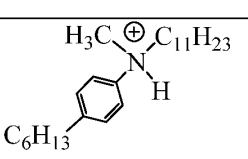
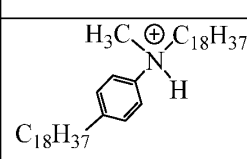
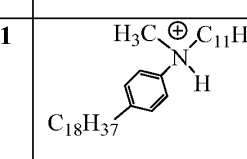
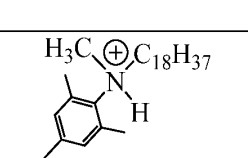
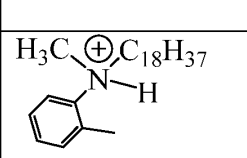
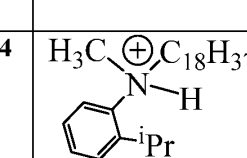
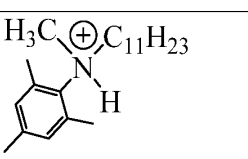
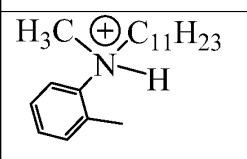
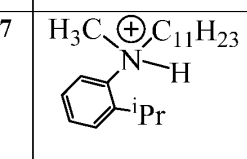
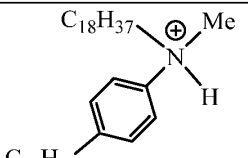
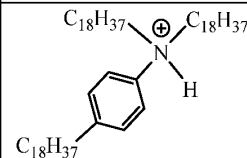
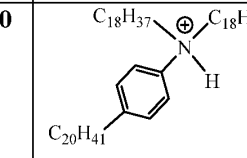
[0136] In a preferred embodiment of the invention, R¹ is n-decyl, R² is n-butylphenyl, and R³ is n-decyl.

15 [0137] In a preferred embodiment of the invention, R¹ is n-propyl, R² is p-methylphenyl, and R³ is n-octadecyl.

[0138] In a preferred embodiment of the invention, R¹, R² and R³ together comprise 20 or more carbon atoms, such as 21 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 37 or more carbon atoms, such as 40 or more carbon atoms, such as 45 or more carbon atoms, such as 15 to 100 carbon atoms, such as 25 to 75 carbon atoms, such as 38 to 70 carbon atoms.

[0139] In at least one embodiment, the cation is selected from the group consisting of:

1		2		3	
4		5		6	

7		8		9	
10		11		12	
13		14		15	
16		17		18	
19		20		21	
22		23		24	
25		26		27	
29		28		30	

31		32		33	
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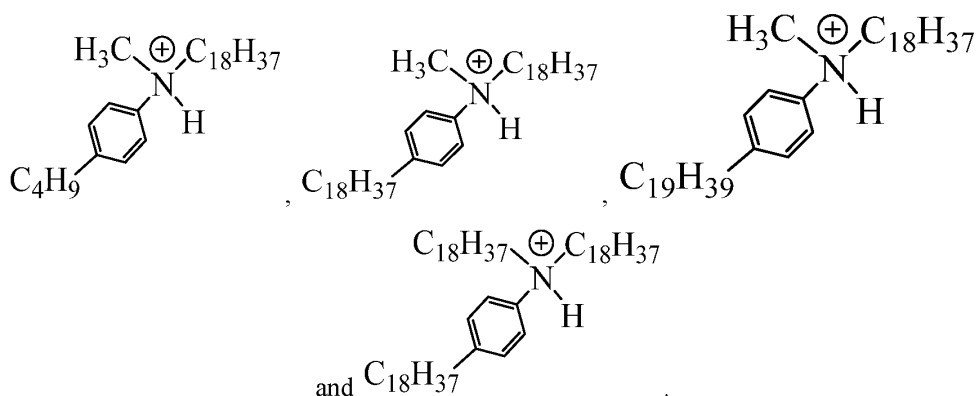
- [0140]** In at least one embodiment of formulas **(AI)** and **(I)**, E is nitrogen or phosphorous, R¹ is a methyl group; R² is C₆-C₄₀ aryl (such as substituted phenyl) and R³ is independently C₁-C₃₅ linear alkyl, C₅-C₄₀-aryl, wherein each of R² and R³ is independently unsubstituted or substituted with at least one of C₁-C₃₅ alkyl, C₅-C₃₀ aryl, C₆-C₃₀₅ arylalkyl, C₆-C₃₀ alkylaryl, halogen, wherein R² optionally bonds with R³ to independently form a five-, six- or seven-membered ring, wherein R², and R³ together comprise 20 or more carbon atoms; and optionally R¹, R², and R³ together comprise 21 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms. In at least one embodiment, R² is independently substituted C₁-C₂₂-alkyl, unsubstituted phenyl, or substituted phenyl. In at least one embodiment, R³ is independently selected from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, and n-icosyl.

- [0141]** Preferably, the cation is selected from the group consisting of:

16		17		18	
19		20		21	
22		23		24	
25		26		27	

29		28		30	
31		32		33	

[0142] Preferably the compound represented by formulas (AI) and (I) comprises a cation selected from the group consisting of:



Activators-The Anion

[0143] The anion component of the activators described herein includes those represented by the formula $[M^{k+}Q_n]^-$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4),
 10 (preferably k is 3; n is 4, 5, or 6, preferably when M is B, n is 4); M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more
 15 than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group, optionally having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a perfluorinated aryl group. Preferably at least one Q is not

substituted phenyl, such as perfluorophenyl, preferably all Q are not substituted phenyl, such as perfluorophenyl.

[0144] In a preferred embodiment of any embodiment of Formula (AI), when R¹ is methyl, R² is C18 and R³ is C18, then each Q is not perfluorophenyl.

- 5 **[0145]** In at least one embodiment, for the borate moiety ([BR⁴R⁵R⁶R⁷]⁻) of the activator represented by formula (I), each of R⁴, R⁵, R⁶, and R⁷ is independently aryl (such as naphthyl), wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms. In at least one embodiment, each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.

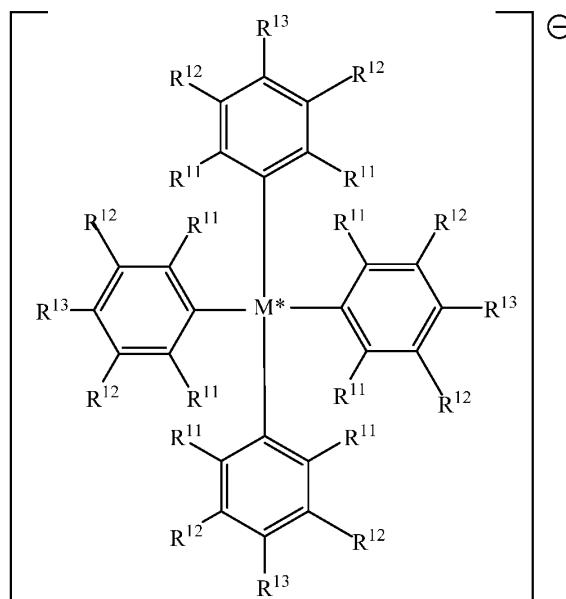
- 10 **[0146]** In at least one embodiment, each of R⁴, R⁵, R⁶, and R⁷ is independently naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms.

[0147] In a preferred embodiment of any embodiment of Formula (I), when R¹ is methyl, R² is C18 and R³ is C18, then each of R⁴, R⁵, R⁶, and R⁷ is not perfluorophenyl.

- 15 **[0148]** In at least one embodiment, R⁴ is independently naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms, and each of R⁵, R⁶, and R⁷ is independently phenyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, or five fluorine atoms or naphthyl comprising one fluorine atom, two fluorine atoms, three fluorine atoms, four fluorine atoms, five fluorine atoms, six fluorine atoms, or seven fluorine atoms.

[0149] In one embodiment, the borate activator comprises tetrakis(heptafluoronaphth-2-yl)borate.

- 20 **[0150]** Preferred anions for use in the non-coordinating anion activators described herein include those represented by Formula 7 below:

**Formula 7**

wherein:

M* is a group 13 atom, preferably B or Al, preferably B;

5 each R¹¹ is, independently, a halide, preferably a fluoride;

each R¹² is, independently, a halide, a C₆ to C₂₀ substituted aromatic hydrocarbyl group or a siloxy group of the formula –O–Si–R^a, where R^a is a C₁ to C₂₀ hydrocarbyl or hydrocarbylsilyl group, preferably R¹² is a fluoride or a perfluorinated phenyl group;

10 each R¹³ is a halide, a C₆ to C₂₀ substituted aromatic hydrocarbyl group or a siloxy group of the formula –O–Si–R^a, where R^a is a C₁ to C₂₀ hydrocarbyl or hydrocarbylsilyl group, preferably R¹³ is a fluoride or a C₆ perfluorinated aromatic hydrocarbyl group;

15 wherein R¹² and R¹³ can form one or more saturated or unsaturated, substituted or unsubstituted rings, preferably R¹² and R¹³ form a perfluorinated phenyl ring. Preferably the anion has a molecular weight of greater than 700 g/mol, and, preferably, at least three of the substituents on the M* atom each have a molecular volume of greater than 180 cubic Å.

[0151] "Molecular volume" is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing molecular volumes allows the substituent with the smaller molecular volume to be considered "less bulky" in comparison to the substituent with the larger molecular volume. Conversely, a substituent with a larger molecular volume may be considered "more bulky" than a substituent with a smaller molecular volume.

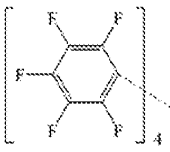
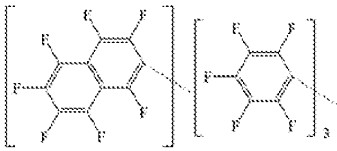
[0152] Molecular volume may be calculated as reported in Girolami, G. S. (1994) "A Simple "Back of the Envelope" Method for Estimating the Densities and Molecular Volumes of Liquids and Solids," *Journal of Chemical Education*, v.71(11), November 1994, pp. 962-964. Molecular volume (MV), in units of cubic Å, is calculated using the formula: $MV = 8.3V_s$, where V_s is the scaled volume. V_s is the sum of the relative volumes of the constituent atoms, and is calculated from the molecular formula of the substituent using Table A below of relative volumes. For fused rings, the V_s is decreased by 7.5% per fused ring. The Calculated Total MV of the anion is the sum of the MV per substituent, for example, the MV of perfluorophenyl is 183 Å³, and the Calculated Total MV for tetrakis(perfluorophenyl)borate is four times 183 Å³, or 732 Å³.

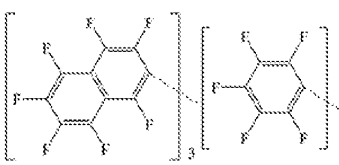
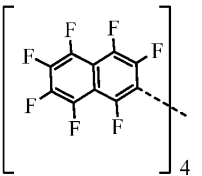
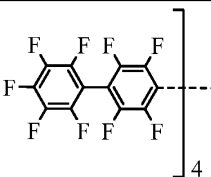
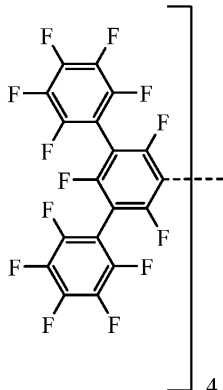
Table A

Element	Relative Volume
H	1
1 st short period, Li to F	2
2 nd short period, Na to Cl	4
1 st long period, K to Br	5
2 nd long period, Rb to I	7.5
3 rd long period, Cs to Bi	9

[0153] Exemplary anions useful herein and their respective scaled volumes and molecular volumes are shown in Table 2 below. The dashed bonds indicate bonding to boron.

Table 2

Ion	Structure of Boron Substituents	Molecular Formula of Each Substituent	V_s	MV Per subst. (Å ³)	Calculated Total MV (Å ³)
tetrakis(perfluorophenyl)borate		C ₆ F ₅	22	183	732
tris(perfluorophenyl)-(perfluoronaphthyl)borate		C ₆ F ₅ C ₁₀ F ₇	22 34	183 261	810

(perfluorophenyl)tris-(perfluoronaphthyl)borate		C_6F_5 $C_{10}F_7$	22 34	183 261	966
tetrakis(perfluoronaphthyl)borate		$C_{10}F_7$	34	261	1044
tetrakis(perfluorobiphenyl)borate		$C_{12}F_9$	42	349	1396
$[(C_6F_3(C_6F_5)_2)_4B]$		$C_{18}F_{13}$	62	515	2060

- [0154]** The activators may be added to a polymerization in the form of an ion pair using, for example, $[M2HTH]^+ [NCA]^-$ in which the di(hydrogenated tallow)methylamine (“M2HTH”) cation reacts with a basic leaving group on the transition metal complex to form a transition metal complex cation and $[NCA]^-$. Alternatively, the transition metal complex may be reacted with a neutral NCA precursor, such as $B(C_{10}F_7)_3$, which abstracts an anionic group from the complex to form an activated species. Useful activators include di(hydrogenated tallow)methylamine(perfluoronaphthyl)borate (i.e., $[M2HTH]B(C_{10}F_7)_4$) and di(octadecyl)tolylamine (perfluoronaphthyl)borate (i.e., $[DODTH]B(C_{10}F_7)_4$).
- [0155]** In at least one embodiment, the activators obtained in their salt form used for a borate activator compound are: Lithium tetrakis(heptafluoronaphthalen-2-yl)borate etherate (Li-BF28), N,N-Dimethylanilinium tetrakis(heptafluoronaphthalen-2-yl)borate (DMAH-

BF28), Sodium tetrakis(heptafluoronaphthalen-2-yl)borate (Na-BF28) and N,N-dimethylanilinium tetrakis(heptafluoronaphthalen-2-yl)borate (DMAH-BF28).

[0156] In at least one embodiment, an activator of the present disclosure, when combined with a group 4 metallocene catalyst compound to form an active olefin polymerization catalyst, produces a higher molecular weight polymer (e.g., Mw) than comparative activators that use other borate anions.

[0157] In at least one embodiment, an activator of the present disclosure where R¹ is methyl, when combined with a group 4 metallocene to form an active olefin polymerization catalyst, produces a higher molecular weight polymer (e.g., Mw) than comparative activators that use other borate anions.

[0158] The typical activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio is about a 1:1 molar ratio. Alternate preferred ranges include from 0.1:1 to 100:1, alternately from 0.5:1 to 200:1, alternately from 1:1 to 500:1 alternately from 1:1 to 1000:1. A particularly useful range is from 0.5:1 to 10:1, preferably 1:1 to 5:1.

[0159] It is also within the scope of the present disclosure that the catalyst compounds can be combined with combinations of alumoxanes and the activators described herein.

Synthesis

[0160] In at least one embodiment, the general synthesis of the activators can be performed using a two-step process. In the first step, an amine or phosphine is dissolved in a solvent (e.g. hexane, cyclohexane, methylcyclohexane, ether, dichloromethane, toluene) and an excess (e.g., 1.2 molar equivalents) of hydrogen chloride is added to form a chloride salt. This salt is typically isolated by filtration from the reaction medium and dried under reduced pressure. The isolated chloride is then heated to reflux with about one molar equivalent of an alkali metal metallate or metalloid (such as a borate or aluminate) in a solvent (e.g. cyclohexane, dichloromethane, methylcyclohexane) to form the desired borate or aluminate along with byproduct alkali metal chloride, the latter of which can typically be removed by filtration.

[0161] In at least one embodiment, the general synthesis of the ammonium borate activators can be performed using a two-step process. In the first step, an amine is dissolved in a solvent (e.g. hexane, cyclohexane, methylcyclohexane, ether, dichloromethane, toluene) and an excess (e.g., 1.2 molar equivalents) of hydrogen chloride is added to form an ammonium chloride salt. This salt is typically isolated by filtration from the reaction medium and dried under reduced pressure. The isolated ammonium chloride is then heated to reflux with about one molar equivalent of an alkali metal borate in a solvent (e.g. cyclohexane, dichloromethane,

methylcyclohexane) to form the ammonium borate along with byproduct alkali metal chloride, the latter of which can typically be removed by filtration.

[0162] In at least one embodiment, an activator of the present disclosure is soluble in an aliphatic solvent at a concentration of about 10mM or greater, such as about 20mM or greater, 5 such as about 30mM or greater, such as about 50mM or greater, such as about 75mM or greater, such as about 100mM or greater, such as about 200mM or greater, such as about 300mM or greater. In at least one embodiment, an activator of the present disclosure dissolves in isohexane or methylcyclohexane at 25°C to form a homogeneous solution of at least 10 mM concentration.

10 [0163] In at least one embodiment, the solubility of the borate or aluminate activators of the present disclosure in aliphatic hydrocarbon solvents increases with the number of aliphatic carbons in the cation group (i.e., the ammonium or the phosphonium). In at least one embodiment, a solubility of at least 10mM is achieved with an activator having an ammonium or phosphonium group of about 21 aliphatic carbon atoms or more, such as about 25 aliphatic 15 carbons atoms or more, such as about 35 carbon atoms or more.

[0164] In at least one embodiment, the solubility of the ammonium borate activators of the present disclosure in aliphatic hydrocarbon solvents increases with the number of aliphatic carbons in the ammonium group. In at least one embodiment, a solubility of at least 10mM is achieved with an activator having an ammonium group of about 21 aliphatic carbon atoms or 20 more, such as about 25 aliphatic carbons atoms or more, such as about 35 carbon atoms or more.

[0165] Useful aliphatic hydrocarbon solvent can be isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, 25 and mixtures thereof. In at least one embodiment, aromatics are present in the solvent at less than 1 wt%, such as less than 0.5 wt%, such as at 0 wt% based upon the weight of the solvents. The activators of the present disclosure can be dissolved in one or more additional solvents. Additional solvent includes ethereal, halogenated and *N,N*-dimethylformamide solvents.

[0166] In at least one embodiment, the aliphatic solvent is isohexane and/or 30 methylcyclohexane.

Optional Scavengers or Co-Activators

[0167] In addition to these activator compounds, scavengers or co-activators may be used. Aluminum alkyl or organoaluminum compounds which may be utilized as scavengers or co-

activators include, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, and diethyl zinc.

[0168] In at least one embodiment, little or no scavenger is used in the process to produce the ethylene polymer. Scavenger (such as trialkyl aluminum) can be present at zero mol%,
5 alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, such as less than 50:1, such as less than 15:1, such as less than 10:1.

Transition Metal Catalyst Compounds

[0169] Any transition metal compound capable of catalyzing a reaction, such as a polymerization reaction, upon activation with an activator as described above is suitable for
10 use in polymerization processes of the present disclosure. Transition metal compounds known as metallocenes are exemplary catalyst compounds according to the present disclosure.

[0170] In at least one embodiment, the present disclosure provides a catalyst system comprising a catalyst compound having a metal atom. The catalyst compound can be a metallocene catalyst compound. The metal can be a Group 3 through Group 12 metal atom,
15 such as Group 3 through Group 10 metal atoms, or lanthanide Group atoms. The catalyst compound having a Group 3 through Group 12 metal atom can be monodentate or multidentate, such as bidentate, tridentate, or tetradentate, where a heteroatom of the catalyst, such as phosphorous, oxygen, nitrogen, or sulfur is chelated to the metal atom of the catalyst. Non-limiting examples include bis(phenolate)s. In at least one embodiment, the Group 3 through
20 Group 12 metal atom is selected from Group 5, Group 6, Group 8, or Group 10 metal atoms. In at least one embodiment, a Group 3 through Group 10 metal atom is selected from Cr, Sc, Ti, Zr, Hf, V, Nb, Ta, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni. In at least one embodiment, a metal atom is selected from Groups 4, 5, and 6 metal atoms. In at least one embodiment, a metal atom is a Group 4 metal atom selected from Ti, Zr, or Hf. The oxidation state of the
25 metal atom can range from 0 to +7, for example +1, +2, +3, +4, or +5, for example +2, +3, or +4.

Metallocene Catalyst Compounds

[0171] A "metallocene" catalyst compound is preferably a transition metal catalyst compound having one, two or three, typically one or two, substituted or unsubstituted
30 cyclopentadienyl ligands (such as substituted or unsubstituted Cp, Ind or Flu) bound to the transition metal. Metallocene catalyst compounds as used herein include metallocenes comprising Group 3 to Group 12 metal complexes, such as, Group 4 to Group 6 metal complexes, for example, Group 4 metal complexes. The metallocene catalyst compound of

catalyst systems of the present disclosure may be unbridged metallocene catalyst compounds represented by the formula: $\text{Cp}^{\text{A}}\text{Cp}^{\text{B}}\text{M}'\text{X}'_{\text{n}}$, wherein each Cp^{A} and Cp^{B} is independently selected from cyclopentadienyl ligands (for example, Cp, Ind, or Flu) and ligands isolobal to cyclopentadienyl, one or both Cp^{A} and Cp^{B} may contain heteroatoms, and one or both Cp^{A} and Cp^{B} may be substituted by one or more R'' groups; M' is selected from Groups 3 through 12 atoms and lanthanide Group atoms; X' is an anionic leaving group; n is 0 or an integer from 1 to 4; each R'' is independently selected from alkyl, substituted alkyl, heteroalkyl, alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, aryloxy, alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, ether, and thioether.

[0172] In at least one embodiment, each Cp^{A} and Cp^{B} is independently selected from cyclopentadienyl, indenyl, fluorenyl, indacenyl, tetrahydroindenyl, cyclopentaphenanthrenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7-H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated and substituted versions thereof. Each Cp^{A} and Cp^{B} may independently be indenyl or tetrahydroindenyl.

[0173] The metallocene catalyst compound may be a bridged metallocene catalyst compound represented by the formula: $\text{Cp}^{\text{A}}(\text{T})\text{Cp}^{\text{B}}\text{M}'\text{X}'_{\text{n}}$, wherein each Cp^{A} and Cp^{B} is independently selected from cyclopentadienyl ligands (for example, Cp, Ind, or Flu) and ligands isolobal to cyclopentadienyl, where one or both Cp^{A} and Cp^{B} may contain heteroatoms, and one or both Cp^{A} and Cp^{B} may be substituted by one or more R'' groups; M' is selected from Groups 3 through 12 atoms and lanthanide Group atoms, preferably Group 4; X' is an anionic leaving group; n is 0 or an integer from 1 to 4; (T) is a bridging group selected from divalent alkyl, divalent substituted alkyl, divalent heteroalkyl, divalent alkenyl, divalent substituted alkenyl, divalent heteroalkenyl, divalent alkynyl, divalent substituted alkynyl, divalent heteroalkynyl, divalent alkoxy, divalent aryloxy, divalent alkylthio, divalent arylthio, divalent aryl, divalent substituted aryl, divalent heteroaryl, divalent aralkyl, divalent aralkylene, divalent alkaryl, divalent alkarylene, divalent haloalkyl, divalent haloalkenyl, divalent haloalkynyl, divalent heteroalkyl, divalent heterocycle, divalent heteroaryl, a divalent heteroatom-containing group, divalent hydrocarbyl, divalent substituted hydrocarbyl, divalent

heterohydrocarbyl, divalent silyl, divalent boryl, divalent phosphino, divalent phosphine, divalent amino, divalent amine, divalent ether, divalent thioether. R" is selected from alkyl, substituted alkyl, heteroalkyl, alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, aryloxy, alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, germanium, ether, and thioether.

[0174] In at least one embodiment, each of Cp^A and Cp^B is independently selected from cyclopentadienyl, indenyl, fluorenyl, cyclopentaphenanthrenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7-H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated, and substituted versions thereof, preferably cyclopentadienyl, n-propylcyclopentadienyl, indenyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, and n-butylcyclopentadienyl. Each Cp^A and Cp^B may independently be indenyl or tetrahydroindenyl.

[0175] (T) is a bridging group containing at least one Group 13, 14, 15, or 16 element, in particular boron or a Group 14, 15 or 16 element, preferably (T) is O, S, NR', or SiR'₂, where each R' is independently hydrogen or C₁-C₂₀ hydrocarbyl.

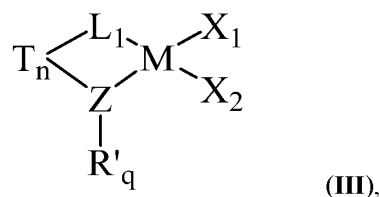
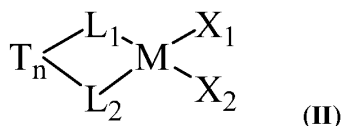
[0176] In another embodiment, the metallocene catalyst compound is represented by the formula:



where Cp is independently a substituted or unsubstituted cyclopentadienyl ligand (for example, substituted or unsubstituted Cp, Ind, or Flu) or substituted or unsubstituted ligand isolobal to cyclopentadienyl; M is a Group 4 transition metal; G is a heteroatom group represented by the formula JR*_z where J is N, P, O or S, and R* is a linear, branched, or cyclic C₁-C₂₀ hydrocarbyl; z is 1 or 2; T is a bridging group; y is 0 or 1; X is a leaving group; m=1, n= 1, 2 or 3, q=0, 1, 2 or 3, and the sum of m+n+q is equal to the coordination number of the transition metal.

[0177] In at least one embodiment, J is N, and R* is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, cyclooctyl, cyclododecyl, decyl, undecyl, dodecyl, adamantyl or an isomer thereof.

[0178] In at least one embodiment, the catalyst compound is represented by formula (II) or formula (III):



wherein in each of formula (II) and formula (III):

M is the metal center, and is a Group 4 metal, such as titanium, zirconium or hafnium, such as zirconium or hafnium when L₁ and L₂ are present and titanium when Z is present;

n is 0 or 1;

T is an optional bridging group which, if present, is a bridging group containing at least one Group 13, 14, 15, or 16 element, in particular boron or a Group 14, 15 or 16 element (preferably T is selected from dialkylsilyl, diarylsilyl, dialkylmethyl, ethylenyl (—CH₂—CH₂—) or hydrocarbylethylenyl wherein one, two, three or four of the hydrogen atoms in ethylenyl are substituted by hydrocarbyl, where hydrocarbyl can be independently C₁ to C₁₆ alkyl or phenyl, tolyl, xylyl and the like), and when T is present, the catalyst represented can be in a racemic or a meso form;

L₁ and L₂ are independently cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, optionally substituted, that are each bonded to M, or L₁ and L₂ are independently cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, which are optionally substituted, in which any two adjacent substituents on L¹ and L² are optionally joined to form a substituted or unsubstituted, saturated, partially unsaturated, or aromatic cyclic or polycyclic substituent;

Z is nitrogen, oxygen, sulfur, or phosphorus (preferably nitrogen);

q is 1 or 2 (preferably q is 1 when Z is N);

R' is a cyclic, linear or branched C₁ to C₄₀ alkyl or substituted alkyl group;

X₁ and X₂ are, independently, hydrogen, halogen, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, silylcarbyl radicals, substituted silylcarbyl radicals, germylcarbyl radicals, or substituted germylcarbyl radicals; or X₁ and X₂ are joined and bound to the metal atom to form a

metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.

[0179] Preferably, T in any formula herein is present and is a bridging group containing at least one Group 13, 14, 15, or 16 element, in particular a Group 14 element. Examples of suitable bridging groups include P(=S)R', P(=Se)R', P(=O)R', R'₂C, R'₂Si, R'₂Ge, R'₂CCR', R'₂CCR'₂CR', R'₂CCR'₂CR'₂CR', R'C=CR', R'C=CR'CR', R'₂CCR'=CR'CR', R'C=CR'CR'=CR', R'C=CR'CR'₂CR', R'₂CSiR', R'₂SiSiR', R'₂SiOSiR', R'₂CSiR'₂CR', R'₂SiCR'₂SiR', R'C=CR'SiR', R'₂CGeR', R'₂GeGeR', R'₂CGeR'₂CR', R'₂GeCR'₂GeR', R'₂SiGeR', R'C=CR'GeR', R'B, R'₂C-BR', R'₂C-BR'-CR', R'₂C-O-CR', R'₂CR'₂C-O-CR'₂CR', R'₂C-O-CR'₂CR', R'₂C-O-CR'=CR', R'₂C-S-CR', R'₂CR'₂C-S-CR'₂CR', R'₂C-S-CR'₂CR', R'₂C-S-CR'=CR', R'₂C-Se-CR', R'₂CR'₂C-Se-CR'₂CR', R'₂C-Se-CR'₂CR', R'₂C-Se-CR'=CR', R'₂C-N=CR', R'₂C-NR'-CR', R'₂C-NR'-CR'₂CR', R'₂C-NR'-CR'=CR', R'₂CR'₂C-NR'-CR'₂CR', R'₂C-P=CR', R'₂C-PR'-CR', O, S, Se, Te, NR', PR', AsR', SbR', O-O, S-S, R'N-NR', R'P-PR', O-S, O-NR', O-PR', S-NR', S-PR', and R'N-PR' where R' is hydrogen or a C₁-C₂₀ containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl substituent and optionally two or more adjacent R' may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent. Preferred examples for the bridging group T include CH₂, CH₂CH₂, SiMe₂, SiPh₂, SiMePh, Si(CH₂)₃, Si(CH₂)₄, O, S, NPh, PPh, NMe, PMe, NEt, NPr, NBu, PEt, PPr, Me₂SiOSiMe₂, and PBu.

[0180] In a preferred embodiment of the invention in any embodiment of any formula described herein, T is represented by the formula R^a₂J or (R^a₂J)₂, where J is C, Si, or Ge, and each R^a is, independently, hydrogen, halogen, C₁ to C₂₀ hydrocarbyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl) or a C₁ to C₂₀ substituted hydrocarbyl, and two R^a can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system. Preferably, T is a bridging group comprising carbon or silica, such as dialkylsilyl, preferably T is selected from CH₂, CH₂CH₂, C(CH₃)₂, SiMe₂, SiPh₂, SiMePh, silylcyclobutyl (Si(CH₂)₃), (Ph)₂C, (p-(Et)₃SiPh)₂C, Me₂SiOSiMe₂, and cyclopentasilylene (Si(CH₂)₄).

[0181] In at least one embodiment, the catalyst compound has a symmetry that is C₂ symmetrical.

[0182] The metallocene catalyst component may comprise any combination of any “embodiment” described herein.

[0183] Suitable metallocenes useful herein include, but are not limited to, the metallocenes disclosed and referenced in the US patents cited above, as well as those disclosed and referenced in US Patents 7,179,876; 7,169,864; 7,157,531; 7,129,302; 6,995,109; 6,958,306; 6,884,748; 6,689,847; US Patent publication 2007/0055028, and published PCT Applications WO 97/22635; WO 00/699/22; WO 01/30860; WO 01/30861; WO 02/46246; WO 02/50088; WO 04/026921; and WO 06/019494, all fully incorporated herein by reference. Additional catalysts suitable for use herein include those referenced in US Patents 6,309,997; 6,265,338; US Patent publication 2006/019925, and the following articles: Resconi, L. et al. (2000) “Selectivity in Propene Polymerization with Metallocene Catalysts,” *Chem. Rev.*, v.100(4), pp. 1253-1346; Gibson, V. C. et al. (2003) “Advances in Non-Metallocene Olefin Polymerization Catalysis,” *Chem. Rev.*, v.103(1), pp. 283-316; *Chem Eur. J.* 2006, v.12, p. 7546; Nakayama, Y et al. (2004), “Olefin Polymerization Behavior of bis(phenoxy-imine) Zr, Ti, and V complexes with MgCl₂-based Cocatalysts,” *J. Mol. Catalysis A: Chemical*, v.213, pp. 141-150; Nakayama, Y. et al. (2005), Propylene Polymerization Behavior of Fluorinated Bis(phenoxy-imine) Ti Complexes with an MgCl₂-Based Compound (MgCl₂-Supported Ti-Based Catalysts),” *Macromol. Chem. Phys.*, v.206(18), pp. 1847-1852; and Matsui, S. et al. (2001) “A Family of Zirconium Complexes Having Two Phenoxy-Imine Chelate Ligands for Olefin Polymerization,” *J. Am. Chem. Soc.*, v.123(28), pp. 6847-6856.

[0184] Exemplary metallocene compounds useful herein are include:

bis(cyclopentadienyl)zirconium dichloride,
bis(n-butylcyclopentadienyl)zirconium dichloride,
bis(n-butylcyclopentadienyl)zirconium dimethyl,
bis(pentamethylcyclopentadienyl)zirconium dichloride,
bis(pentamethylcyclopentadienyl)zirconium dimethyl,
bis(pentamethylcyclopentadienyl)hafnium dichloride,
bis(pentamethylcyclopentadienyl)zirconium dimethyl,
bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride,
bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dimethyl,
bis(1-methyl-3-n-butylcyclopentadienyl)hafnium dichloride,
bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dimethyl,
bis(indenyl)zirconium dichloride, bis(indenyl)zirconium dimethyl,

- bis(tetrahydro-1-indenyl)zirconium dichloride,
 bis(tetrahydro-1-indenyl)zirconium dimethyl,
 (n-propyl cyclopentadienyl, pentamethyl cyclopentadienyl)zirconium dichloride, and
 (n-propyl cyclopentadienyl, pentamethyl cyclopentadienyl)zirconium dimethyl.
- 5 **[0185]** In at least one embodiment, the catalyst compound may be selected from:
 dimethylsilylbis(tetrahydroindenyl)MX_n,
 dimethylsilyl bis(2-methylindenyl)MX_n,
 dimethylsilyl bis(2-methylfluorenyl)MX_n,
 dimethylsilyl bis(2-methyl-5,7-propylindenyl)MX_n,
 10 dimethylsilyl bis(2-methyl-4-phenylindenyl)MX_n,
 dimethylsilyl bis(2-ethyl-5-phenylindenyl)MX_n,
 dimethylsilyl bis(2-methyl-4-biphenylindenyl)MX_n,
 dimethylsilylene bis(2-methyl-4-carbazolylindenyl)MX_n,
rac-dimethylsilyl-bis-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-methyl-1H-
 15 benz(f)indene)MX_n,
 diphenylmethylenecyclopentadienyl(fluorenyl)MX_n,
 bis(methylcyclopentadienyl)MX_n,
rac-dimethylsilylbis(2-methyl,3-propyl indenyl)MX_n,
 dimethylsilylbis(indenyl)MX_n,
 20 *Rac-meso*-diphenylsilyl-bis(n-propylcyclopentadienyl)MX_n,
 1, 1'-bis(4-trimethylsilylphenyl)methylene-(cyclopentadienyl)(3,8-di-tertiary-butyl-1-
 fluorenyl)MX_n (bridge is considered the 1 position),
 bis-trimethylsilylphenyl-methylene(cyclopentadienyl)(di-*t*-butylfluorenyl)MX_n,
 bis-trimethylsilylphenyl-methylene(cyclopentadienyl)(fluorenyl)MX_n,
 25 bisphenylmethylenecyclopentadienyl(dimethylfluorenyl)MX_n,
 bis(n-propylcyclopentadienyl)MX_n,
 bis(n-butylcyclopentadienyl)MX_n,
 bis(n-pentylcyclopentadienyl)MX_n,
 (n-propyl cyclopentadienyl)(n-butylcyclopentadienyl)MX_n,
 30 bis[(2-trimethylsilyl)ethyl]cyclopentadienyl]MX_n,
 bis(trimethylsilyl cyclopentadienyl)MX_n,
 dimethylsilylbis(n-propylcyclopentadienyl)MX_n,
 dimethylsilylbis(n-butylcyclopentadienyl)MX_n,

- bis(1-n-propyl-2-methylcyclopentadienyl)MX_n,
 (n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)MX_n,
 bis(1-methyl, 3-n-butyl cyclopentadienyl)MX_n,
 bis(indenyl)MX_n,
- 5 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)MX_n,
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)MX_n,
 μ -(CH₃)₂Si(cyclopentadienyl)(1-adamantylamido)MX_n,
 μ -(CH₃)₂Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)MX_n,
 μ -(CH₃)₂(tetramethylcyclopentadienyl)(1-adamantylamido)MX_n,
- 10 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-adamantylamido)MX_n,
 μ -(CH₃)₂C(tetramethylcyclopentadienyl)(1-adamantylamido)MX_n,
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-tertbutylamido)MX_n,
 μ -(CH₃)₂Si(fluorenyl)(1-tertbutylamido)MX_n,
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)MX_n,
- 15 μ -(C₆H₅)₂C(tetramethylcyclopentadienyl)(1-cyclododecylamido)MX_n,
 μ -(CH₃)₂Si(η^5 -2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(tertbutylamido)MX_n,
 where M is selected from Ti, Zr, and Hf; where X is selected from the group consisting of
 halogens, hydrides, C₁₋₁₂ alkyls, C₂₋₁₂ alkenyls, C₆₋₁₂ aryls, C₇₋₂₀ alkylaryls, C₁₋₁₂ alkoxys, C₆₋₁₆
 aryloxys, C₇₋₁₈ alkylaryloxys, C₁₋₁₂ fluoroalkyls, C₆₋₁₂ fluoroaryls, and C₁₋₁₂ heteroatom-
 20 containing hydrocarbons, substituted derivatives thereof, and combinations thereof, and where
 n is zero or an integer from 1 to 4, preferably X is selected from halogens (such as bromide,
 fluoride, chloride), or C₁ to C₂₀ alkyls (such as methyl, ethyl, propyl, butyl, and pentyl) and n
 is 1 or 2, preferably 2.

[0186] In other embodiments of the invention, the catalyst is one or more of:

- 25 bis(1-methyl, 3-n-butyl cyclopentadienyl) M(R)₂;
 dimethylsilyl bis(indenyl)M(R)₂;
 bis(indenyl)M(R)₂;
 dimethylsilyl bis(tetrahydroindenyl)M(R)₂;
 bis(n-propylcyclopentadienyl)M(R)₂;
- 30 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)M(R)₂;
 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)M(R)₂;
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)M(R)₂;
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)M(R)₂;

- μ -(CH₃)₂Si(cyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 5 μ -(CH₃)₂C(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-tertbutylamido)M(R)₂;
 μ -(CH₃)₂Si(fluorenyl)(1-tertbutylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)₂;
 μ -(C₆H₅)₂C(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)₂;
 10 μ -(CH₃)₂Si(η^5 -2,6,6-trimethyl-1,5,6,7-tetrahydro-*s*-indacen-1-yl)(tertbutylamido)M(R)₂;
 where M is selected from Ti, Zr, and Hf, and R is selected from halogen or C₁ to C₅ alkyl.
- [0187]** In preferred embodiments of the invention, the catalyst compound is one or more of:
- dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl;
 15 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl;
 dimethylsilyl (tetramethylcyclopentadienyl)(*t*-butylamido)titanium dimethyl;
 dimethylsilyl (tetramethylcyclopentadienyl)(*t*-butylamido)titanium dimethyl;
 μ -(CH₃)₂Si(cyclopentadienyl)(1-adamantylamido)titanium dimethyl;
 μ -(CH₃)₂Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)titanium dimethyl;
 20 μ -(CH₃)₂(tetramethylcyclopentadienyl)(1-adamantylamido)titanium dimethyl;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-adamantylamido)titanium dimethyl;
 μ -(CH₃)₂C(tetramethylcyclopentadienyl)(1-adamantylamido)titanium dimethyl;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-tertbutylamido)titanium dimethyl;
 μ -(CH₃)₂Si(fluorenyl)(1-tertbutylamido)titanium dimethyl;
 25 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)titanium dimethyl;
 μ -(C₆H₅)₂C(tetramethylcyclopentadienyl)(1-cyclododecylamido)titanium dimethyl; and/or
 μ -(CH₃)₂Si(η^5 -2,6,6-trimethyl-1,5,6,7-tetrahydro-*s*-indacen-1-yl)(tertbutylamido)titanium dimethyl.
- [0188]** In at least one embodiment, the catalyst is *rac*-dimethylsilyl-bis(indenyl)hafnium dimethyl and or 1, 1'-bis(4-triethylsilylphenyl)methylene-(cyclopentadienyl)(3,8-di-tertiary-butyl-1-fluorenyl)hafnium dimethyl.
- [0189]** In at least one embodiment, the catalyst compound is one or more of:
- bis(1-methyl, 3-*n*-butyl cyclopentadienyl)hafnium dimethyl,

- bis(1-methyl, 3-n-butyl cyclopentadienyl)zirconium dimethyl,
 dimethylsilyl bis(indenyl)zirconium dimethyl,
 dimethylsilyl bis(indenyl)hafnium dimethyl,
 bis(indenyl)zirconium dimethyl,
 5 bis(indenyl)hafnium dimethyl,
 dimethylsilyl bis(tetrahydroindenyl)zirconium dimethyl,
 bis(n-propylcyclopentadienyl)zirconium dimethyl,
 dimethylsilyl bis(tetrahydroindenyl)hafnium dimethyl,
 dimethylsilyl bis(2-methylindenyl)zirconium dimethyl,
 10 dimethylsilyl bis(2-methylfluorenyl)zirconium dimethyl,
 dimethylsilyl bis(2-methylindenyl)hafnium dimethyl,
 dimethylsilyl bis(2-methylfluorenyl)hafnium dimethyl,
 dimethylsilyl bis(2-methyl-5,7-propylindenyl) zirconium dimethyl,
 dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl,
 15 dimethylsilyl bis(2-ethyl-5-phenylindenyl) zirconium dimethyl,
 dimethylsilyl bis(2-methyl-4-biphenylindenyl) zirconium dimethyl,
 dimethylsilylene bis(2-methyl-4-carbazolylindenyl) zirconium dimethyl,
rac-dimethylsilyl-bis-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-methyl-1H-benz(f)indene)hafnium dimethyl,
 20 diphenylmethane (cyclopentadienyl)(fluorenyl)hafnium dimethyl,
 bis(methylcyclopentadienyl)zirconium dimethyl,
rac-dimethylsilyl bis(2-methyl,3-propyl indenyl)hafnium dimethyl,
 dimethylsilyl bis(indenyl)hafnium dimethyl,
 dimethylsilyl bis(indenyl)zirconium dimethyl,
 25 dimethyl *rac*-dimethylsilyl-bis-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-methyl-1H-benz(f)indene)hafnium dimethyl,
Rac-meso-diphenylsilyl-bis(n-propylcyclopentadienyl)hafnium dimethyl,
 1, 1'-bis(4-triethylsilylphenyl)methylene-(cyclopentadienyl)(3,8-di-tertiary-butyl-1-fluorenyl)hafnium X_n (bridge is considered the 1 position),
 30 bis-trimethylsilylphenyl-methylene(cyclopentadienyl)(di-t-butylfluorenyl)hafnium dimethyl,
 bis-trimethylsilylphenyl-methylene(cyclopentadienyl)(fluorenyl)hafnium dimethyl,
 bisphenylmethane(cyclopentadienyl)(dimethylfluorenyl)hafnium dimethyl,
 bis(n-propylcyclopentadienyl)hafnium dimethyl,

- bis(n-butylcyclopentadienyl)hafnium dimethyl,
 bis(n-pentylcyclopentadienyl)hafnium dimethyl,
 (n-propyl cyclopentadienyl)(n-butylcyclopentadienyl)hafnium dimethyl,
 bis[(2-trimethylsilyl)ethyl]cyclopentadienyl]hafnium dimethyl,
 5 bis(trimethylsilyl cyclopentadienyl)hafnium dimethyl,
 dimethylsilylbis(n-propylcyclopentadienyl)hafnium dimethyl,
 dimethylsilylbis(n-butylcyclopentadienyl)hafnium dimethyl,
 bis(1-n-propyl-2-methylcyclopentadienyl)hafnium dimethyl, and
 (n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)hafnium dimethyl,
 10 bis(n-propylcyclopentadienyl)hafnium dimethyl,
 bis(n-butylcyclopentadienyl)hafnium dimethyl,
 bis(n-pentylcyclopentadienyl)hafnium dimethyl,
 (n-propyl cyclopentadienyl)(n-butylcyclopentadienyl)hafnium dimethyl,
 bis[(2-trimethylsilyl)ethyl]cyclopentadienyl]hafnium dimethyl,
 15 bis(trimethylsilyl cyclopentadienyl)hafnium dimethyl,
 dimethylsilylbis(n-propylcyclopentadienyl)hafnium dimethyl,
 dimethylsilylbis(n-butylcyclopentadienyl)hafnium dimethyl,
 bis(1-n-propyl-2-methylcyclopentadienyl)hafnium dimethyl,
 (n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)hafnium dimethyl, and
 20 dimethylsilyl(3-n-propylcyclopentadienyl)(tetramethylcyclopentadienyl)zirconium dimethyl.

Non-Metallocene Catalyst Compounds

- [0190]** Transition metal complexes for polymerization processes can include any olefin polymerization catalyst. Suitable catalyst components may include “non-metallocene complexes” that are defined to be transition metal complexes that do not feature a
 25 cyclopentadienyl anion or substituted cyclopentadienyl anion donors (e.g., cyclopentadienyl, fluorenyl, indenyl, methylcyclopentadienyl). Examples of families of non-metallocene complexes that may be suitable can include late transition metal pyridylbisimines (e.g., US 7,087,686), group 4 pyridyldiamidos (e.g., US 7,973,116), quinolinyldiamidos (e.g., US Pub. No. 2018/0002352 A1), pyridylamididos (e.g., US 7,087,690), phenoxyimines (e.g., Makio,
 30 H. et al. (2009) “Development and Application of FI Catalysts for Olefin Polymerization: Unique Catalysis and Distinctive Polymer Formation,” *Accounts of Chemical Research*, v.42(10), pp. 1532-1544), and bridged bi-aromatic complexes (e.g., US 7,091,292), the disclosures of which are incorporated herein by reference.

[0191] Catalyst complexes that are suitable for use in combination with the activators described herein include: pyridyldiamido complexes; quinolinyldiamido complexes; phenoxyimine complexes; bisphenolate complexes; cyclopentadienyl-amidinate complexes; and iron pyridyl bis(imine) complexes or any combination thereof, including any combination
5 with metallocene complexes.

[0192] The term “pyridyldiamido complex” or “pyridyldiamide complex” or “pyridyldiamido catalyst” or “pyridyldiamide catalyst” refers to a class of coordination complexes described in US Pat. No. 7,973,116B2, US 2012/0071616A1, US 2011/0224391A1, US 2011/0301310A1, US 2015/0141601A1, US 6,900,321 and US 8,592,615 that feature a
10 dianionic tridentate ligand that is coordinated to a metal center through one neutral Lewis basic donor atom (e.g., a pyridine group) and a pair of anionic amido or phosphido (i.e., deprotonated amine or phosphine) donors. In these complexes the pyridyldiamido ligand is coordinated to the metal with the formation of one five membered chelate ring and one seven membered chelate ring. It is possible for additional atoms of the pyridyldiamido ligand to be coordinated
15 to the metal without affecting the catalyst function upon activation; an example of this could be a cyclometalated substituted aryl group that forms an additional bond to the metal center.

[0193] The term “quinolinyldiamido complex” or “quinolinyldiamido catalyst” or “quinolinyldiamide complex” or “quinolinyldiamide catalyst” refers to a related class of pyridyldiamido complex/catalyst described in US 2018/0002352 where a quinolinyly moiety is
20 present instead of a pyridyl moiety.

[0194] The term “phenoxyimine complex” or “phenoxyimine catalyst” refers to a class of coordination complexes described in EP 0874005 that feature a monoanionic bidentate ligand that is coordinated to a metal center through one neutral Lewis basic donor atom (e.g., an imine moiety) and an anionic aryloxy (i.e., deprotonated phenoxy) donor. Typically two of these
25 bidentate phenoxyimine ligands are coordinated to a group 4 metal to form a complex that is useful as a catalyst component.

[0195] The term “bisphenolate complex” or “bisphenolate catalyst” refers to a class of coordination complexes described in US 6,841,502, WO2017/004462, and WO2006/020624 that feature a dianionic tetradentate ligand that is coordinated to a metal center through two
30 neutral Lewis basic donor atoms (e.g., oxygen bridge moieties) and two anionic aryloxy (i.e., deprotonated phenoxy) donors.

[0196] The term “cyclopentadienyl-amidinate complex” or “cyclopentadienyl-amidinate catalyst” refers to a class of coordination complexes described in US 8,188,200 that typically

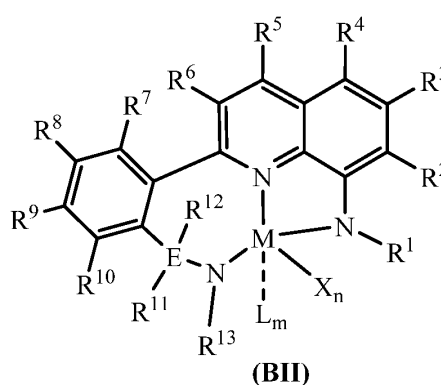
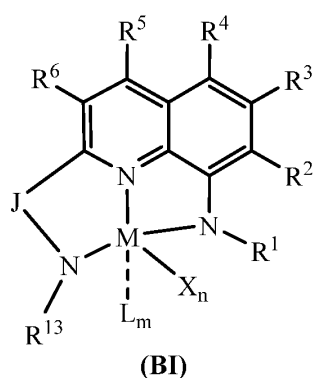
feature a group 4 metal bound to a cyclopentadienyl anion, a bidentate amidinate anion, and a couple of other anionic groups.

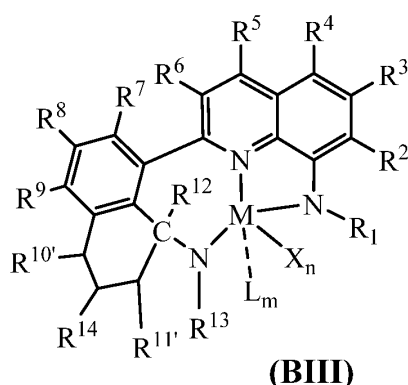
[0197] The term “iron pyridyl bis(imine) complex” refers to a class of iron coordination complexes described in US 7,087,686 that typically feature an iron metal center coordinated to a neutral, tridentate pyridyl bis(imine) ligand and two other anionic ligands.

[0198] Non-metallocene complexes can include iron complexes of tridentate pyridylbisimine ligands, zirconium and hafnium complexes of pyridylamido ligands, zirconium and hafnium complexes of tridentate pyridyldiamido ligands, zirconium and hafnium complexes of tridentate quinolinyldiamido ligands, zirconium and hafnium complexes of bidentate phenoxyimine ligands, and zirconium and hafnium complexes of bridged bi-aromatic ligands.

[0199] Suitable non-metallocene complexes can include zirconium and hafnium non-metallocene complexes. In at least one embodiment, non-metallocene complexes for the present disclosure include group 4 non-metallocene complexes including two anionic donor atoms and one or two neutral donor atoms. Suitable non-metallocene complexes for the present disclosure include group 4 non-metallocene complexes including an anionic amido donor. Suitable non-metallocene complexes for the present disclosure include group 4 non-metallocene complexes including an anionic aryloxy donor atom. Suitable non-metallocene complexes for the present disclosure include group 4 non-metallocene complexes including two anionic aryloxy donor atoms and two additional neutral donor atoms.

[0200] A catalyst compounds can be a quinolinyldiamido (QDA) transition metal complex represented by Formula (BI), such as by Formula (BII), such as by Formula (BIII):





wherein:

M is a group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal, such as a group 4 metal;

J is group including a three-atom-length bridge between the quinoline and the amido
5 nitrogen, such as a group containing up to 50 non-hydrogen atoms;

E is carbon, silicon, or germanium;

X is an anionic leaving group, (such as a hydrocarbyl group or a halogen);

L is a neutral Lewis base;

R¹ and R¹³ are independently selected from the group including of hydrocarbyls,
10 substituted hydrocarbyls, and silyl groups;

R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R^{10'}, R¹¹, R^{11'}, R¹², and R¹⁴ are independently
hydrogen, hydrocarbyl, alkoxy, silyl, amino, aryloxy, substituted hydrocarbyl, halogen, or
phosphino;

n is 1 or 2;

15 m is 0, 1, or 2, where

n+m is not greater than 4; and

any two R groups (e.g., R¹ & R², R² & R³, R¹⁰ and R¹¹, etc.) may be joined to form
a substituted hydrocarbyl, unsubstituted hydrocarbyl, substituted heterocyclic, or unsubstituted
heterocyclic, saturated or unsaturated ring, where the ring has 5, 6, 7, or 8 ring atoms and where

20 substitutions on the ring can join to form additional rings;

any two X groups may be joined together to form a dianionic group;

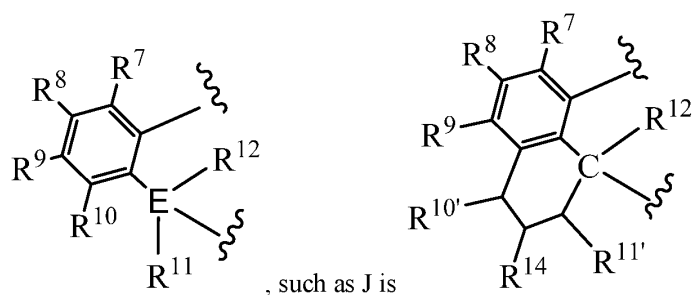
any two L groups may be joined together to form a bidentate Lewis base; and

any X group may be joined to an L group to form a monoanionic bidentate group.

[0201] In at least one embodiment, M is a group 4 metal, such as zirconium or hafnium,
25 such as M is hafnium.

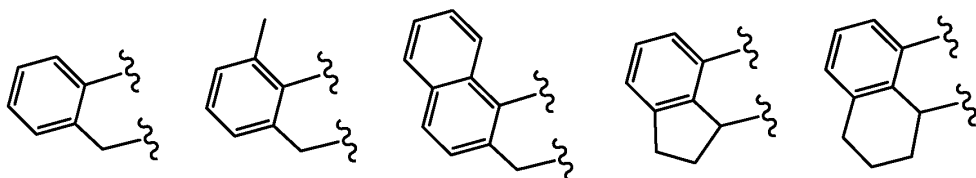
[0202] Representative non-metallocene transition metal compounds usable for forming poly(α -olefin)s of the present disclosure also include tetrabenzyl zirconium, tetra bis(trimethylsilylmethyl) zirconium, oxotris(trimethylsilylmethyl) vanadium, tetrabenzyl hafnium, tetrabenzyl titanium, bis(hexamethyl disilazido)dimethyl titanium, tris(trimethyl silyl methyl) niobium dichloride, and tris(trimethylsilylmethyl) tantalum dichloride.

[0203] In at least one embodiment, J is an aromatic substituted or unsubstituted hydrocarbyl having from 3 to 30 non-hydrogen atoms, such as J is represented by the formula:



where R^7 , R^8 , R^9 , R^{10} , $R^{10'}$, R^{11} , $R^{11'}$, R^{12} , R^{14} and E are as defined above, and any two R groups (e.g., R^7 & R^8 , R^8 & R^9 , R^9 & R^{10} , R^{10} & R^{11} , etc.) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms (such as 5 or 6 atoms), and said ring may be saturated or unsaturated (such as partially unsaturated or aromatic), such as J is an arylalkyl (such as arylmethyl, etc.) or dihydro-1H-indenyl, or tetrahydronaphthalenyl group.

[0204] In at least one embodiment, J is selected from the following structures:



where $\sim$ indicates connection to the complex.

[0205] In at least one embodiment, E is carbon.

[0206] X may be an alkyl (such as alkyl groups having 1 to 10 carbons, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof), aryl, hydride, alkylsilane, fluoride, chloride, bromide, iodide, triflate, carboxylate, amido (such as NMe_2), or alkylsulfonate.

[0207] In at least one embodiment, L is an ether, amine or thioether.

[0208] In at least one embodiment, R^7 and R^8 are joined to form a six-membered aromatic ring with the joined R^7/R^8 group being $-\text{CH}=\text{CHCH}=\text{CH}-$.

[0209] R^{10} and R^{11} may be joined to form a five-membered ring with the joined $R^{10}R^{11}$ group being $-\text{CH}_2\text{CH}_2-$.

5 [0210] In at least one embodiment, R^{10} and R^{11} are joined to form a six-membered ring with the joined $R^{10}R^{11}$ group being $-\text{CH}_2\text{CH}_2\text{CH}_2-$.

[0211] R^1 and R^{13} may be independently selected from phenyl groups that are variously substituted with between zero to five substituents that include F, Cl, Br, I, CF_3 , NO_2 , alkoxy, dialkylamino, aryl, and alkyl groups having 1 to 10 carbons, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof.

[0212] In at least one embodiment, the QDA transition metal complex represented by the Formula (BII) above where:

M is a group 4 metal (such hafnium);

E is selected from carbon, silicon, or germanium (such as carbon);

15 X is an alkyl, aryl, hydride, alkylsilane, fluoride, chloride, bromide, iodide, triflate, carboxylate, amido, alkoxo, or alkylsulfonate;

L is an ether, amine, or thioether;

R^1 and R^{13} are independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups (such as aryl);

20 R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , and R^{12} are independently hydrogen, hydrocarbyl, alkoxy, silyl, amino, aryloxy, substituted hydrocarbyls, halogen, and phosphino;

n is 1 or 2;

m is 0, 1, or 2;

n+m is from 1 to 4;

25 two X groups may be joined together to form a dianionic group;

two L groups may be joined together to form a bidentate Lewis base;

an X group may be joined to an L group to form a monoanionic bidentate group;

R^7 and R^8 may be joined to form a ring (such as an aromatic ring, a six-membered aromatic ring with the joined R^7R^8 group being $-\text{CH}=\text{CHCH}=\text{CH}-$); and

30 R^{10} and R^{11} may be joined to form a ring (such as a five-membered ring with the joined $R^{10}R^{11}$ group being $-\text{CH}_2\text{CH}_2-$, a six-membered ring with the joined $R^{10}R^{11}$ group being $-\text{CH}_2\text{CH}_2\text{CH}_2-$).

[0213] In at least one embodiment of Formula (BI), (BII), and (BIII), R⁴, R⁵, and R⁶ are independently selected from the group including hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁴ and R⁵ and/or R⁵ and R⁶) are joined to form a substituted hydrocarbyl, unsubstituted hydrocarbyl, unsubstituted heterocyclic ring or substituted heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings.

[0214] In at least one embodiment of Formula (BI), (BII), and (BIII), R⁷, R⁸, R⁹, and R¹⁰ are independently selected from the group including hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁷ and R⁸ and/or R⁹ and R¹⁰) may be joined to form a saturated, substituted hydrocarbyl, unsubstituted hydrocarbyl, unsubstituted heterocyclic ring or substituted heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings.

[0215] In at least one embodiment of Formula (BI), (BII), and (BIII), R² and R³ are each, independently, selected from the group including hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R² and R³ may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R² and R³ may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings.

[0216] In at least one embodiment of Formula (BI), (BII), and (BIII), R¹¹ and R¹² are each, independently, selected from the group including hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R¹¹ and R¹² may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R¹¹ and R¹² may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings, or R¹¹ and R¹⁰ may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings.

[0217] In at least one embodiment of Formula (BI), (BII), and (BIII), R¹ and R¹³ are independently selected from phenyl groups that are variously substituted with between zero to five substituents that include F, Cl, Br, I, CF₃, NO₂, alkoxy, dialkylamino, aryl, and alkyl

groups having 1 to 10 carbons, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof.

[0218] In at least one embodiment of Formula (BII), suitable R^{12} -E- R^{11} groups include CH_2 , CMe_2 , $SiMe_2$, $SiEt_2$, $SiPr_2$, $SiBu_2$, $SiPh_2$, $Si(aryl)_2$, $Si(alkyl)_2$, $CH(aryl)$, $CH(Ph)$,
 5 $CH(alkyl)$, and $CH(2\text{-isopropylphenyl})$, where alkyl is a C_1 to C_{40} alkyl group (such as C_1 to C_{20} alkyl, such as one or more of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and isomers thereof), aryl is a C_5 to C_{40} aryl group (such as a C_6 to C_{20} aryl group, such as phenyl or substituted phenyl, such as phenyl, 2-isopropylphenyl, or 2-tertbutylphenyl).

10 [0219] In at least one embodiment of Formula (BIII), R^{11} , R^{12} , R^9 , R^{14} , and R^{10} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^{10} and R^{14} , and/or R^{11} and R^{14} , and/or R^9 and R^{10}) may be joined to form a saturated, substituted hydrocarbyl, unsubstituted hydrocarbyl, unsubstituted heterocyclic ring or substituted
 15 heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings.

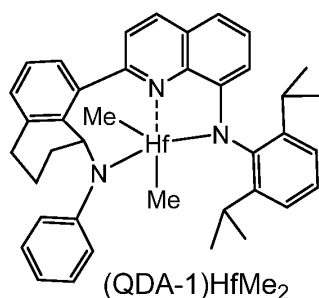
[0220] The R groups above (i.e., any of R^2 to R^{14}) and other R groups mentioned hereafter may contain from 1 to 30, such as 2 to 20 carbon atoms, such as from 6 to 20 carbon atoms. The R groups above (i.e., any of R^2 to R^{14}) and other R groups mentioned hereafter, may be
 20 independently selected from the group including hydrogen, methyl, ethyl, phenyl, isopropyl, isobutyl, trimethylsilyl, and $-CH_2-Si(Me)_3$.

[0221] In at least one embodiment, the quinolinyldiamide complex is linked to one or more additional transition metal complex, such as a quinolinyldiamide complex or another suitable non-metallocene, through an R group in such a fashion as to make a bimetallic, trimetallic, or
 25 multimetallic complex that may be used as a catalyst component for olefin polymerization. The linker R-group in such a complex may contain 1 to 30 carbon atoms.

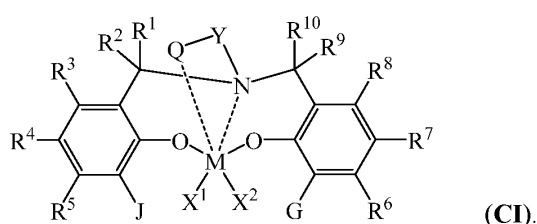
[0222] In at least one embodiment, E is carbon and R^{11} and R^{12} are independently selected from phenyl groups that are substituted with 0, 1, 2, 3, 4, or 5 substituents selected from the group consisting of F, Cl, Br, I, CF_3 , NO_2 , alkoxy, dialkylamino, hydrocarbyl, and substituted
 30 hydrocarbyl groups with from one to ten carbons.

[0223] In at least one embodiment of Formula (BII) or (BIII), R^{11} and R^{12} are independently selected from hydrogen, methyl, ethyl, phenyl, isopropyl, isobutyl, $-CH_2-Si(Me)_3$, and trimethylsilyl.

- [0224] In at least one embodiment of Formula (BII), and (BIII), R^7 , R^8 , R^9 , and R^{10} are independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, phenyl, cyclohexyl, fluoro, chloro, methoxy, ethoxy, phenoxy, $-\text{CH}_2\text{-Si}(\text{Me})_3$, and trimethylsilyl.
- [0225] In at least one embodiment of Formula (BI), (BII), and (BIII), R^2 , R^3 , R^4 , R^5 , and R^6 are independently selected from the group consisting of hydrogen, hydrocarbyls, alkoxy, silyl, amino, substituted hydrocarbyls, and halogen.
- [0226] In at least one embodiment of Formula (BIII), R^{10} , R^{11} and R^{14} are independently selected from hydrogen, methyl, ethyl, phenyl, isopropyl, isobutyl, $-\text{CH}_2\text{-Si}(\text{Me})_3$, and trimethylsilyl.
- 10 [0227] In at least one embodiment of Formula (BI), (BII), and (BIII), each L is independently selected from Et_2O , MeOtBu , Et_3N , PhNMe_2 , MePh_2N , tetrahydrofuran, and dimethylsulfide.
- [0228] In at least one embodiment of Formula (BI), (BII), and (BIII), each X is independently selected from methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, 15 phenyl, hydrido, chloro, fluoro, bromo, iodo, dimethylamido, diethylamido, dipropylamido, and diisopropylamido.
- [0229] In at least one embodiment of Formula (BI), (BII), and (BIII), R^1 is 2,6-diisopropylphenyl, 2,4,6-triisopropylphenyl, 2,6-diisopropyl-4-methylphenyl, 2,6-diethylphenyl, 2-ethyl-6-isopropylphenyl, 2,6-bis(3-pentyl)phenyl, 20 2,6-dicyclopentylphenyl, or 2,6-dicyclohexylphenyl.
- [0230] In at least one embodiment of Formula (BI), (BII), and (BIII), R^{13} is phenyl, 2-methylphenyl, 2-ethylphenyl, 2-propylphenyl, 2,6-dimethylphenyl, 2-isopropylphenyl, 4-methylphenyl, 3,5-dimethylphenyl, 3,5-di-tert-butylphenyl, 4-fluorophenyl, 3-methylphenyl, 4-dimethylaminophenyl, or 2-phenylphenyl.
- 25 [0231] In at least one embodiment of Formula (BII), J is dihydro-1H-indenyl and R^1 is 2,6-dialkylphenyl or 2,4,6-trialkylphenyl.
- [0232] In at least one embodiment of Formula (BI), (BII), and (BIII), R^1 is 2,6-diisopropylphenyl and R^{13} is a hydrocarbyl group containing 1, 2, 3, 4, 5, 6, or 7 carbon atoms.
- 30 [0233] An exemplary catalyst used for polymerizations of the present disclosure is (QDA-1)HfMe₂, as described in US Pub. No. 2018/0002352 A1.

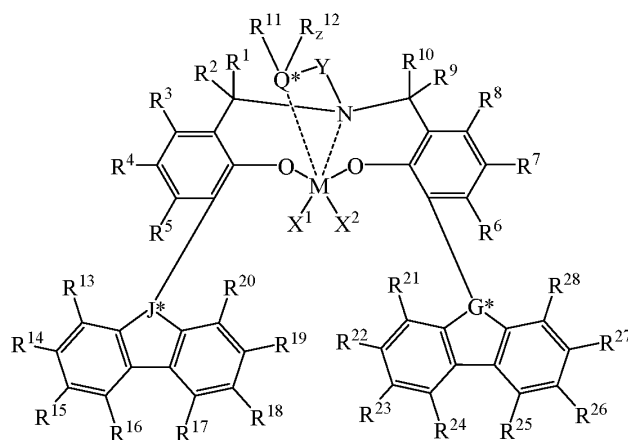


[0234] In at least one embodiment, the catalyst compound is a bis(phenolate) catalyst compound represented by Formula (CI):

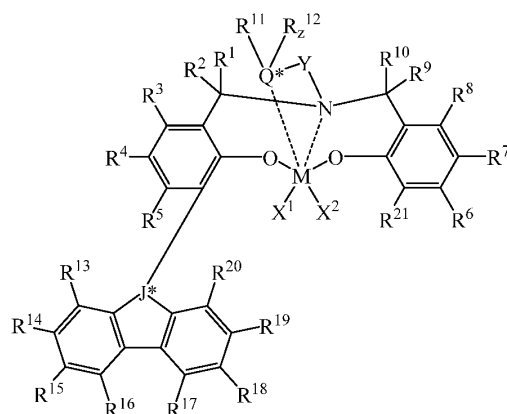


- 5 M is a Group 4 metal, such as Hf or Zr. X¹ and X² are independently a univalent C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or X¹ and X² join together to form a C₄-C₆₂ cyclic or polycyclic ring structure. R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or two or more of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, or R¹⁰ are joined together to form a C₄-C₆₂ cyclic or polycyclic ring structure, or a combination thereof; Q is a neutral donor group; J is heterocycle, a substituted or unsubstituted C₇-C₆₀ fused polycyclic group, where at least one ring is aromatic and where at least one ring, which may or may not be aromatic, has at least five ring atoms; G is as defined for J or may be hydrogen, C₂-C₆₀ hydrocarbyl, C₁-C₆₀ substituted hydrocarbyl, or may independently form a C₄-C₆₀ cyclic or polycyclic ring structure with R⁶, R⁷, or R⁸ or a combination thereof; Y is divalent C₁-C₂₀ hydrocarbyl or divalent C₁-C₂₀ substituted hydrocarbyl or (-Q-Y-) together form a heterocycle; and heterocycle may be aromatic and/or may have multiple fused rings.

[0235] In at least one embodiment, the catalyst compound represented by Formula (CI) is represented by Formula (CII) or Formula (CIII):



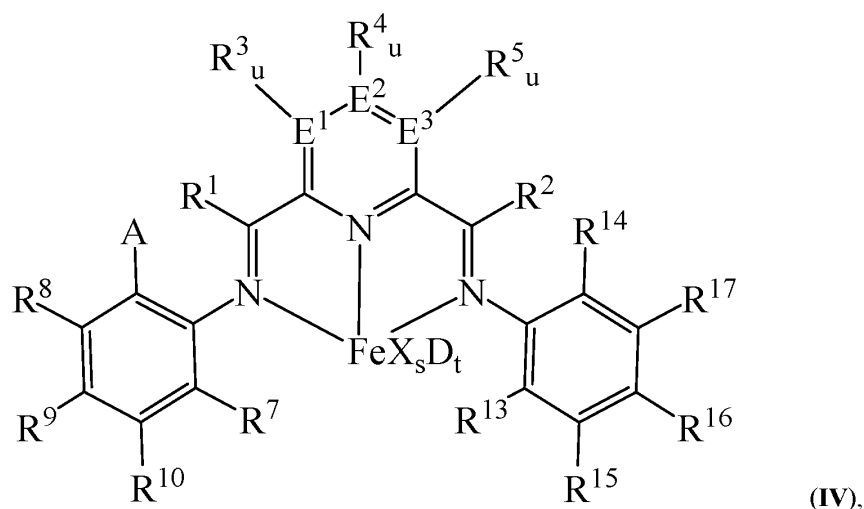
(CII), or



(CIII).

- M is Hf, Zr, or Ti. X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , and Y are as defined for Formula (CI). R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , and R^{28} is independently a hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a functional group comprising elements from Groups 13 to 17, or two or more of R^1 , 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} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , and R^{28} may independently join together to form a C₄-C₆₂ cyclic or polycyclic ring structure, or a combination thereof; R^{11} and R^{12} may join together to form a five- to eight-membered heterocycle; Q* is a group 15 or 16 atom; z is 0 or 1; J* is CRⁿ or N, and G* is CRⁿ or N, where Rⁿ is C₁-C₂₀ hydrocarbyl or carbonyl-containing C₁-C₂₀ hydrocarbyl; and z = 0 if Q* is a group 16 atom, and z = 1 if Q* is a group 15 atom.

[0236] In at least one embodiment the catalyst is an iron complex represented by formula (IV):



wherein:

A is chlorine, bromine, iodine, -CF₃ or -OR¹¹;

each of R¹ and R² is independently hydrogen, C₁-C₂₂-alkyl, C₂-C₂₂-alkenyl, C₆-C₂₂-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O and S;

wherein each of R¹ and R² is optionally substituted by halogen, -NR¹², -OR¹¹ or -SiR¹²;

wherein R¹ optionally bonds with R³, and R² optionally bonds with R⁵, in each case to independently form a five-, six- or seven-membered ring;

R⁷ is a C₁-C₂₀ alkyl;

each of R³, R⁴, R⁵, R⁸, R⁹, R¹⁰, R¹⁵, R¹⁶, and R¹⁷ is independently hydrogen, C₁-C₂₂-alkyl, C₂-C₂₂-alkenyl, C₆-C₂₂-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, -NR¹², -OR¹¹, halogen, -SiR¹² or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O, and S;

wherein R³, R⁴, R⁵, R⁷, R⁸, R⁹, R¹⁰, R¹⁵, R¹⁶, and R¹⁷ are optionally substituted by halogen, -NR¹², -OR¹¹ or -SiR¹²;

wherein R³ optionally bonds with R⁴, R⁴ optionally bonds with R⁵, R⁷ optionally bonds with R¹⁰, R¹⁰ optionally bonds with R⁹, R⁹ optionally bonds with R⁸, R¹⁷ optionally bonds with R¹⁶, and R¹⁶ optionally bonds with R¹⁵, in each case to independently form a five-, six- or

seven-membered carbocyclic or heterocyclic ring, the heterocyclic ring comprising at least one atom from the group consisting of N, P, O and S;

R^{13} is C_1 - C_{20} -alkyl bonded with the aryl ring via a primary or secondary carbon atom;

R^{14} is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$, or C_1 - C_{20} -alkyl bonded with the aryl
5 ring;

each R^{11} is independently hydrogen, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or $-SiR^{12}_3$, wherein R^{11} is optionally substituted by halogen, or two R^{11} radicals optionally bond to form a five- or six-membered ring;

10 each R^{12} is independently hydrogen, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or two R^{12} radicals optionally bond to form a five- or six-membered ring;

each of E^1 , E^2 , and E^3 is independently carbon, nitrogen or phosphorus;

each u is independently 0 if E^1 , E^2 , and E^3 is nitrogen or phosphorus and is 1 if E^1 , E^2 ,
15 and E^3 is carbon;

each X is independently fluorine, chlorine, bromine, iodine, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{10} -alkenyl, C_6 - C_{20} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, $-NR^{18}_2$, $-OR^{18}$, $-SR^{18}$, $-SO_3R^{18}$, $-OC(O)R^{18}$, $-CN$, $-SCN$, β -diketonate, $-CO$, $-BF_4^-$, $-PF_6^-$ or bulky non-coordinating anions, and the radicals X can be
20 bonded with one another;

each R^{18} is independently hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or $-SiR^{19}_3$, wherein R^{18} can be substituted by halogen or nitrogen- or oxygen-containing groups and two R^{18} radicals optionally bond to form a five- or six-membered ring;

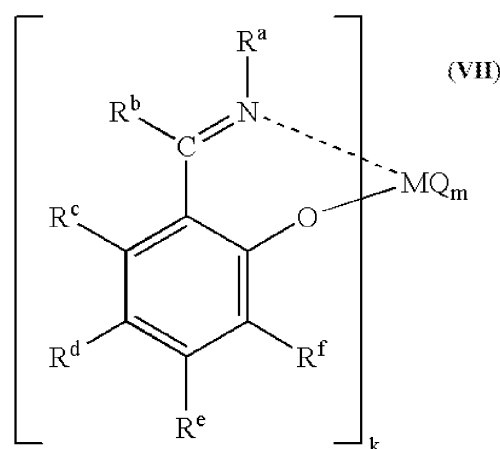
25 each R^{19} is independently hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl or arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, wherein R^{19} can be substituted by halogen or nitrogen- or oxygen-containing groups or two R^{19} radicals optionally bond to form a five- or six-membered ring;

s is 1, 2, or 3;

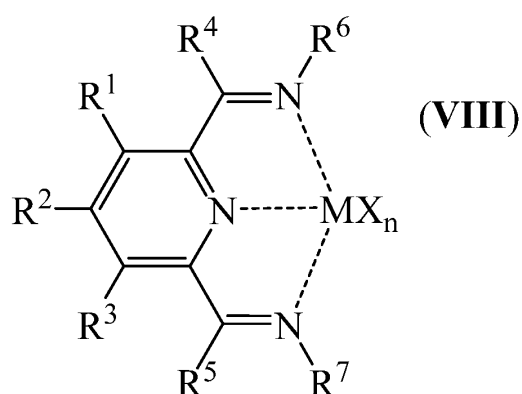
30 D is a neutral donor; and

t is 0 to 2.

[0237] In another embodiment, the catalyst is a phenoxyimine compound represented by the formula (VII):



- wherein M represents a transition metal atom selected from the groups 3 to 11 metals in the periodic table; k is an integer of 1 to 6; m is an integer of 1 to 6; R^a to R^f may be the same or different from one another and each represent a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residue, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, among which 2 or more groups may be bound to each other to form a ring; when k is 2 or more, R^a groups, R^b groups, R^c groups, R^d groups, R^e groups, or R^f groups may be the same or different from one another, one group of R^a to R^f contained in one ligand and one group of R^a to R^f contained in another ligand may form a linking group or a single bond, and a heteroatom contained in R^a to R^f may coordinate with or bind to M; m is a number satisfying the valence of M; Q represents a hydrogen atom, a halogen atom, an oxygen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group; when m is 2 or more, a plurality of groups represented by Q may be the same or different from one another, and a plurality of groups represented by Q may be mutually bound to form a ring.
- [0238] In another embodiment, the catalyst is a bis(imino)pyridyl of the formula (VIII):



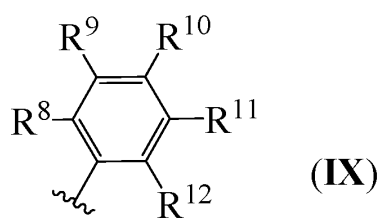
wherein:

M is Co or Fe; each X is an anion; n is 1, 2 or 3, so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe or Co atom present in

5 (VIII);

R¹, R² and R³ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R⁴ and R⁵ are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

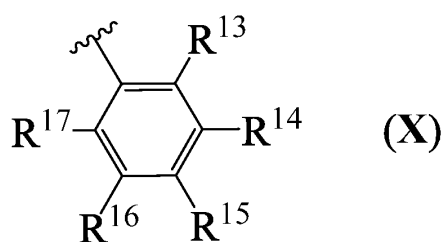


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R⁶ is formula (IX):

, and

R⁷ is formula (X):



R⁸ and R¹³ are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;

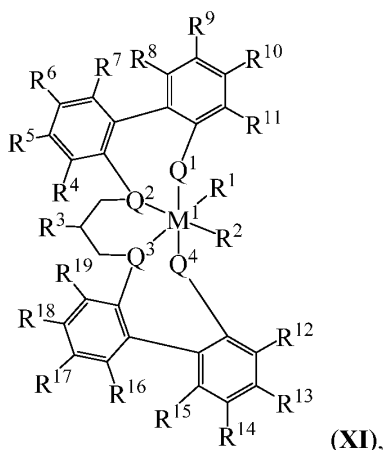
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R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} that are adjacent to one another, together may form a ring.

- 5 [0239] In at least one embodiment, the catalyst compound is represented by the formula (XI):



M^1 is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten. In at least one embodiment, M^1 is zirconium.

- 10 [0240] Each of Q^1 , Q^2 , Q^3 , and Q^4 is independently oxygen or sulfur. In at least one embodiment, at least one of Q^1 , Q^2 , Q^3 , and Q^4 is oxygen, alternately all of Q^1 , Q^2 , Q^3 , and Q^4 are oxygen.

- [0241] R^1 and R^2 are independently hydrogen, halogen, hydroxyl, hydrocarbyl, or substituted hydrocarbyl (such as C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, C_6 - C_{20} aryl, C_6 - C_{10} aryloxy, C_2 - C_{10} alkenyl, C_2 - C_{40} alkenyl, C_7 - C_{40} arylalkyl, C_7 - C_{40} alkylaryl, C_8 - C_{40} arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen). R^1 and R^2 can be a halogen selected from fluorine, chlorine, bromine, or iodine. Preferably, R^1 and R^2 are chlorine.

- 20 [0242] Alternatively, R^1 and R^2 may also be joined together to form an alkanediyl group or a conjugated C_4 - C_{40} diene ligand which is coordinated to M^1 . R^1 and R^2 may also be identical or different conjugated dienes, optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the dienes having up to 30 atoms not counting hydrogen and/or forming a π -complex with M^1 .

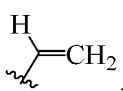
[0243] Exemplary groups suitable for R¹ and or R² can include 1,4-diphenyl, 1,3-butadiene, 1,3-pentadiene, 2-methyl 1,3-pentadiene, 2,4-hexadiene, 1-phenyl, 1,3-pentadiene, 1,4-dibenzyl, 1,3-butadiene, 1,4-ditolyl-1,3-butadiene, 1,4-bis (trimethylsilyl)-1,3-butadiene, and 1,4-dinaphthyl-1,3-butadiene. R¹ and R² can be identical and are C₁-C₃ alkyl or alkoxy, C₆-C₁₀ aryl or aryloxy, C₂-C₄ alkenyl, C₇-C₁₀ arylalkyl, C₇-C₁₂ alkylaryl, or halogen.

[0244] Each of R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, and R¹⁹ is independently hydrogen, halogen, C₁-C₄₀ hydrocarbyl or C₁-C₄₀ substituted hydrocarbyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen), -NR', -SR', -OR, -OSiR'₃, -PR'₂, where each R' is hydrogen, halogen, C₁-C₁₀ alkyl, or C₆-C₁₀ aryl, or one or more of R⁴ and R⁵, R⁵ and R⁶, R⁶ and R⁷, R⁸ and R⁹, R⁹ and R¹⁰, R¹⁰ and R¹¹, R¹² and R¹³, R¹³ and R¹⁴, R¹⁴ and R¹⁵, R¹⁶ and R¹⁷, R¹⁷ and R¹⁸, and R¹⁸ and R¹⁹ are joined to form a saturated ring, unsaturated ring, substituted saturated ring, or substituted unsaturated ring. In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl. Preferably, R¹¹ and R¹² are C₆-C₁₀ aryl such as phenyl or naphthyl optionally substituted with C₁-C₄₀ hydrocarbyl, such as C₁-C₁₀ hydrocarbyl. Preferably, R⁶ and R¹⁷ are C₁-C₄₀ alkyl, such as C₁-C₁₀ alkyl.

[0245] In at least one embodiment, each of R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, and R¹⁹ is independently hydrogen or C₁-C₄₀ hydrocarbyl. In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl. Preferably, each of R⁶ and R¹⁷ is C₁-C₄₀ hydrocarbyl and R⁴, R⁵, R⁷, R⁸, R⁹, R¹⁰, R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁸, and R¹⁹ is hydrogen. In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl.

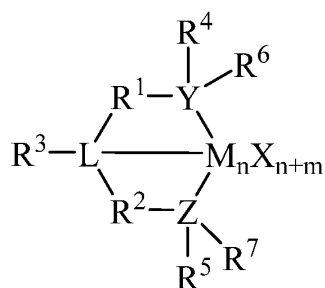
[0246] R^3 is a C₁-C₄₀ unsaturated alkyl or substituted C₁-C₄₀ unsaturated alkyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen).

[0247] Preferably, R^3 is a hydrocarbyl comprising a vinyl moiety. As used herein, “vinyl” and “vinyl moiety” are used interchangeably and include a terminal alkene, e.g., represented

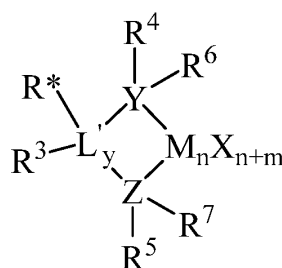
by the structure . Hydrocarbyl of R^3 may be further substituted (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen). Preferably, R^3 is C₁-C₄₀ unsaturated alkyl that is vinyl or substituted C₁-C₄₀ unsaturated alkyl that is vinyl. R^3 can be represented by the structure $-R'CH=CH_2$ where R' is C₁-C₄₀ hydrocarbyl or C₁-C₄₀ substituted hydrocarbyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen). In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl.

[0248] In at least one embodiment, R^3 is 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl, 1-nonenyl, or 1-decenyl.

[0249] In at least one embodiment, the catalyst is a Group 15-containing metal compound represented by Formulas (XII) or (XIII):



(XII)



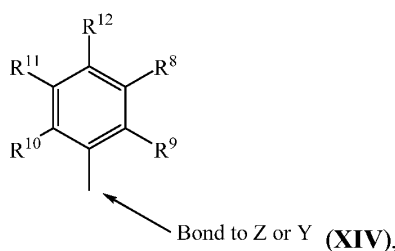
(XIII),

wherein M is a Group 3 to 12 transition metal or a Group 13 or 14 main group metal, a Group 4, 5, or 6 metal. In many embodiments, M is a Group 4 metal, such as zirconium, titanium, or hafnium. Each X is independently a leaving group, such as an anionic leaving group. The leaving group may include a hydrogen, a hydrocarbyl group, a heteroatom, a halogen, or an alkyl; y is 0 or 1 (when y is 0 group L' is absent). The term 'n' is the oxidation state of M. In various embodiments, n is +3, +4, or +5. In many embodiments, n is +4. The term 'm' represents the formal charge of the YZL or the YZL' ligand, and is 0, -1, -2 or -3 in various embodiments. In many embodiments, m is -2. L is a Group 15 or 16 element, such as nitrogen or oxygen; L' is a Group 15 or 16 element or Group 14 containing group, such as carbon, silicon or germanium. Y is a Group 15 element, such as nitrogen or phosphorus. In many embodiments, Y is nitrogen. Z is a Group 15 element, such as nitrogen or phosphorus. In many embodiments, Z is nitrogen. R¹ and R² are, independently, a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus. In many embodiments, R¹ and R² are a C₂ to C₂₀ alkyl, aryl or aralkyl group, such as a C₂ to C₂₀ linear, branched or cyclic alkyl group, or a C₂ to C₂₀ hydrocarbon group. R¹ and R² may also be interconnected to each other. R³ may be absent or may be a hydrocarbon group, a hydrogen, a halogen, a heteroatom containing group. In many embodiments, R³ is absent, for example, if L is an oxygen, or a hydrogen, or a linear, cyclic, or branched alkyl group having 1 to 20 carbon atoms. R⁴ and R⁵ are independently an alkyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic aralkyl group, a substituted cyclic aralkyl group, or multiple ring system, often having up to 20 carbon atoms. In many embodiments, R⁴ and R⁵ have between 3 and 10 carbon atoms, or are a C₁ to C₂₀ hydrocarbon group, a C₁ to C₂₀ aryl group or a C₁ to C₂₀ aralkyl group, or a heteroatom containing group. R⁴ and R⁵ may be interconnected to each other. R⁶ and R⁷ are independently absent, hydrogen, an alkyl group, halogen, heteroatom, or a hydrocarbyl group, such as a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms. In many

embodiments, R^6 and R^7 are absent. R^* may be absent, or may be a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group.

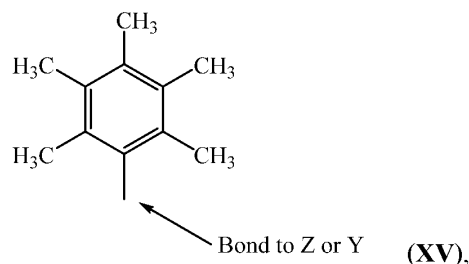
[0250] By "formal charge of the YZL or YZL' ligand," it is meant the charge of the entire ligand absent the metal and the leaving groups X. By " R^1 and R^2 may also be interconnected" it is meant that R^1 and R^2 may be directly bound to each other or may be bound to each other through other groups. By " R^4 and R^5 may also be interconnected" it is meant that R^4 and R^5 may be directly bound to each other or may be bound to each other through other groups. An alkyl group may be linear, branched alkyl radicals, alkenyl radicals, alkynyl radicals, cycloalkyl radicals, aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxy carbonyl radicals, carbomoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. An aralkyl group is defined to be a substituted aryl group.

[0251] In one or more embodiments, R^4 and R^5 are independently a group represented by structure (XIV):



wherein R^8 to R^{12} are each independently hydrogen, a C_1 to C_{40} alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms. In many embodiments, R^8 to R^{12} are a C_1 to C_{20} linear or branched alkyl group, such as a methyl, ethyl, propyl, or butyl group. Any two of the R groups may form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic. In one embodiment R^9 , R^{10} and R^{12} are independently a methyl, ethyl, propyl, or butyl group (including all isomers). In another embodiment, R^9 , R^{10} and R^{12} are methyl groups, and R^8 and R^{11} are hydrogen.

[0252] In one or more embodiments, R^4 and R^5 are both a group represented by structure (XV):



wherein M is a Group 4 metal, such as zirconium, titanium, or hafnium. In at least one embodiment, M is zirconium. Each of L, Y, and Z may be a nitrogen. Each of R¹ and R² may be -CH₂-CH₂-. R³ may be hydrogen, and R⁶ and R⁷ may be absent.

5 [0253] In preferred embodiments, the catalyst compounds described in PCT/US2018/051345, filed September 17, 2018 may be used with the activators described herein, particularly the catalyst compounds described at Page 16 to Page 32 of the application as filed.

[0254] In some embodiments, a co-activator is combined with the catalyst compound (such as halogenated catalyst compounds described above) to form an alkylated catalyst compound. 10 Organoaluminum compounds which may be utilized as co-activators include, for example, trialkyl aluminum compounds, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, and the like, or alumoxanes.

[0255] In some embodiments, two or more different catalyst compounds are present in the catalyst system used herein. In some embodiments, two or more different catalyst compounds 15 are present in the reaction zone where the process(es) described herein occur. When two transition metal compound based catalysts are used in one reactor as a mixed catalyst system, the two transition metal compounds are preferably chosen such that the two are compatible. A simple screening method such as by ¹H or ¹³C NMR, known to those of ordinary skill in the art, can be used to determine which transition metal compounds are compatible. It is preferable 20 to use the same activator for the transition metal compounds, however, two different activators can be used in combination. If one or more transition metal compounds contain an anionic ligand as a leaving group which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane or other alkyl aluminum is typically contacted with the transition metal 25 compounds prior to addition of the non-coordinating anion activator.

[0256] The two transition metal compounds (pre-catalysts) may be used in any ratio. Preferred molar ratios of (A) transition metal compound to (B) transition metal compound fall within the range of (A:B) 1:1000 to 1000:1, alternatively 1:100 to 500:1, alternatively 1:10 to

200:1, alternatively 1:1 to 100:1, and alternatively 1:1 to 75:1, and alternatively 5:1 to 50:1. The particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired. In a particular embodiment, when using the two pre-catalysts, where both are activated with the same activator, useful mole percents, based upon
5 the molecular weight of the pre-catalysts, are 10 to 99.9% A to 0.1 to 90%B, alternatively 25 to 99% A to 0.5 to 50% B, alternatively 50 to 99% A to 1 to 25% B, and alternatively 75 to 99% A to 1 to 10%B.

Support Materials

[0257] In embodiments herein, the catalyst system may comprise a support material. In at
10 least one embodiment, the support material is a porous support material, for example, talc, or inorganic oxides. Other support materials include zeolites, clays, organoclays, or any other suitable organic or inorganic support material and the like, or mixtures thereof.

[0258] In at least one embodiment, the support material is an inorganic oxide. Suitable inorganic oxide materials for use in catalyst systems herein include Groups 2, 4, 13, and 14
15 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be used, for example, functionalized polyolefins, such as polypropylene. Supports include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations
20 of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania, and the like. Support materials include Al_2O_3 , ZrO_2 , SiO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{TiO}_2$, silica clay, silicon oxide/clay, or mixtures thereof.

[0259] The support material, such as an inorganic oxide, can have a surface area of from
25 $10 \text{ m}^2/\text{g}$ to $700 \text{ m}^2/\text{g}$, pore volume in the range of from 0.1 cc/g to 4.0 cc/g and average particle size in the range of from $5 \text{ }\mu\text{m}$ to $500 \text{ }\mu\text{m}$. In at least one embodiment, the surface area of the support material is in the range of from $50 \text{ m}^2/\text{g}$ to $500 \text{ m}^2/\text{g}$, pore volume of from 0.5 cc/g to 3.5 cc/g and average particle size of from $10 \text{ }\mu\text{m}$ to $200 \text{ }\mu\text{m}$. In at least one embodiment, the surface area of the support material is in the range is from $100 \text{ m}^2/\text{g}$ to $400 \text{ m}^2/\text{g}$, pore volume from 0.8 cc/g to 3.0 cc/g and average particle size is from $5 \text{ }\mu\text{m}$ to $100 \text{ }\mu\text{m}$. The average pore
30 size of the support material useful in the present disclosure is in the range of from $10 \text{ }\text{\AA}$ to $1000 \text{ }\text{\AA}$, such as $50 \text{ }\text{\AA}$ to $500 \text{ }\text{\AA}$, such as $75 \text{ }\text{\AA}$ to $350 \text{ }\text{\AA}$. In some embodiments, the support material is a high surface area, amorphous silica (surface area= $300 \text{ m}^2/\text{gm}$; pore volume of $1.65 \text{ cm}^3/\text{gm}$). Exemplary silicas are marketed under the tradenames of DAVISON 952 or

DAVISON 955 by the Davison Chemical Division of W.R. Grace and Company. In other embodiments DAVISON 948 is used.

[0260] The support material should be dry, that is, substantially free of absorbed water. Drying of the support material can be effected by heating or calcining at 100°C to 1,000°C, such as at least about 600°C. When the support material is silica, it is heated to at least 200°C, such as 200°C to 850°C, such as at about 600°C; and for a time of 1 minute to about 100 hours, from 12 hours to 72 hours, or from 24 hours to 60 hours. The calcined support material should have at least some reactive hydroxyl (OH) groups to produce supported catalyst systems of the present disclosure. The calcined support material is then contacted with at least one polymerization catalyst comprising at least one catalyst compound and an activator.

[0261] The support material, having reactive surface groups, typically hydroxyl groups, is slurried in a non-polar solvent and the resulting slurry is contacted with a solution of a catalyst compound and an activator. In some embodiments, the slurry of the support material is first contacted with the activator for a period of time in the range of from 0.5 hours to 24 hours, from 2 hours to 16 hours, or from 4 hours to 8 hours. The solution of the catalyst compound is then contacted with the isolated support/activator. In some embodiments, the supported catalyst system is generated *in situ*. In at least one embodiment, the slurry of the support material is first contacted with the catalyst compound for a period of time in the range of from 0.5 hours to 24 hours, from 2 hours to 16 hours, or from 4 hours to 8 hours. The slurry of the supported catalyst compound is then contacted with the activator solution.

[0262] The mixture of the catalyst, activator and support is heated to 0°C to 70°C, such as to 23°C to 60°C, such as at room temperature. Contact times typically range from 0.5 hours to 24 hours, from 2 hours to 16 hours, or from 4 hours to 8 hours.

[0263] Suitable non-polar solvents are materials in which all of the reactants used herein, *e.g.*, the activator, and the catalyst compound, are at least partially soluble and which are liquid at room temperature. Non-limiting example non-polar solvents are alkanes, such as isopentane, hexane, n-heptane, octane, nonane, and decane, cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene, and ethylbenzene.

[0264] In at least one embodiment, the support material comprises a support material treated with an electron-withdrawing anion. The support material can be silica, alumina, silica-alumina, silica-zirconia, alumina-zirconia, aluminum phosphate, heteropolytungstates, titania, magnesia, boria, zinc oxide, mixed oxides thereof, or mixtures thereof; and the electron-

withdrawing anion is selected from fluoride, chloride, bromide, phosphate, triflate, bisulfate, sulfate, or any combination thereof.

[0265] The electron-withdrawing component used to treat the support material can be any component that increases the Lewis or Brønsted acidity of the support material upon treatment (as compared to the support material that is not treated with at least one electron-withdrawing anion). In at least one embodiment, the electron-withdrawing component is an electron-withdrawing anion derived from a salt, an acid, or other compound, such as a volatile organic compound, that serves as a source or precursor for that anion. Electron-withdrawing anions can be sulfate, bisulfate, fluoride, chloride, bromide, iodide, fluorosulfate, fluoroborate, phosphate, fluorophosphate, trifluoroacetate, triflate, fluoro-zirconate, fluorotitanate, phosphotungstate, or mixtures thereof, or combinations thereof. An electron-withdrawing anion can be fluoride, chloride, bromide, phosphate, triflate, bisulfate, or sulfate, or any combination thereof, at least one embodiment of this disclosure. In at least one embodiment, the electron-withdrawing anion is sulfate, bisulfate, fluoride, chloride, bromide, iodide, fluorosulfate, fluoroborate, phosphate, fluorophosphate, trifluoroacetate, triflate, fluoro-zirconate, fluorotitanate, or combinations thereof.

[0266] Thus, for example, the support material suitable for use in the catalyst systems of the present disclosure can be one or more of fluorided alumina, chlorided alumina, bromided alumina, sulfated alumina, fluorided silica-alumina, chlorided silica-alumina, bromided silica-alumina, sulfated silica-alumina, fluorided silica-zirconia, chlorided silica-zirconia, bromided silica-zirconia, sulfated silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or combinations thereof. In at least one embodiment, the activator-support can be, or can comprise, fluorided alumina, sulfated alumina, fluorided silica-alumina, sulfated silica-alumina, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or combinations thereof. In another embodiment, the support material includes alumina treated with hexafluorotitanic acid, silica-coated alumina treated with hexafluorotitanic acid, silica-alumina treated with hexafluorozirconic acid, silica-alumina treated with trifluoroacetic acid, fluorided boria-alumina, silica treated with tetrafluoroboric acid, alumina treated with tetrafluoroboric acid, alumina treated with hexafluorophosphoric acid, or combinations thereof. Further, any of these activator-supports optionally can be treated with a metal ion.

[0267] Nonlimiting examples of cations suitable for use in the present disclosure in the salt of the electron-withdrawing anion include ammonium, trialkyl ammonium, tetraalkyl ammonium, tetraalkyl phosphonium, H^+ , $[H(OEt_2)_2]^+$, or combinations thereof.

[0268] Further, combinations of one or more different electron-withdrawing anions, in varying proportions, can be used to tailor the specific acidity of the support material to a desired level. Combinations of electron-withdrawing components can be contacted with the support material simultaneously or individually, and in any order that provides a desired chemically-treated support material acidity. For example, in at least one embodiment, two or more electron-withdrawing anion source compounds in two or more separate contacting steps.

[0269] In at least one embodiment of the present disclosure, one example of a process by which a chemically-treated support material is prepared is as follows: a selected support material, or combination of support materials, can be contacted with a first electron-withdrawing anion source compound to form a first mixture; such first mixture can be calcined and then contacted with a second electron-withdrawing anion source compound to form a second mixture; the second mixture can then be calcined to form a treated support material. In such a process, the first and second electron-withdrawing anion source compounds can be either the same or different compounds.

[0270] The method by which the oxide is contacted with the electron-withdrawing component, typically a salt or an acid of an electron-withdrawing anion, can include gelling, co-gelling, impregnation of one compound onto another, or combinations thereof. Following a contacting method, the contacted mixture of the support material, electron-withdrawing anion, and optional metal ion, can be calcined.

[0271] According to another embodiment of the present disclosure, the support material can be treated by a process comprising: (i) contacting a support material with a first electron-withdrawing anion source compound to form a first mixture; (ii) calcining the first mixture to produce a calcined first mixture; (iii) contacting the calcined first mixture with a second electron-withdrawing anion source compound to form a second mixture; and (iv) calcining the second mixture to form the treated support material.

Polymer Processes

[0272] In embodiments herein, the present disclosure provides polymerization processes where monomer (such as propylene or ethylene), and optionally comonomer, are contacted with a catalyst system comprising an activator and at least one catalyst compound, as described

above. The catalyst compound and activator may be combined in any order, and are combined typically prior to contacting with the monomer.

[0273] In at least one embodiment, a polymerization process includes a) contacting one or more olefin monomers with a catalyst system comprising: i) an activator and ii) a catalyst compound of the present disclosure. The activator is a non-coordination anion activator. The one or more olefin monomers may be propylene and/or ethylene and the polymerization process further comprises heating the one or more olefin monomers and the catalyst system to 70°C or more to form propylene polymers or ethylene polymers, such as propylene polymers.

[0274] Monomers useful herein include substituted or unsubstituted C₂ to C₄₀ alpha olefins, such as C₂ to C₂₀ alpha olefins, such as C₂ to C₁₂ alpha olefins, such as ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In at least one embodiment, the monomer comprises propylene and an optional comonomers comprising one or more propylene or C₄ to C₄₀ olefins, such as C₄ to C₂₀ olefins, such as C₆ to C₁₂ olefins. The C₄ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₄ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups. In at least one embodiment, the monomer comprises propylene and an optional comonomers comprising one or more C₃ to C₄₀ olefins, such as C₄ to C₂₀ olefins, such as C₆ to C₁₂ olefins. The C₃ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₃ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups.

[0275] Exemplary C₂ to C₄₀ olefin monomers and optional comonomers include propylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, such as hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, such as norbornene, norbornadiene, and dicyclopentadiene.

[0276] In at least one embodiment, one or more dienes are present in the polymer produced herein at up to 10 wt%, such as at 0.00001 to 1.0 wt%, such as 0.002 to 0.5 wt%, such as 0.003 to 0.2 wt%, based upon the total weight of the composition. In some embodiments, 500 ppm

or less of diene is added to the polymerization, such as 400 ppm or less, such as 300 ppm or less. In other embodiments at least 50 ppm of diene is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

[0277] Diene monomers include any hydrocarbon structure, such as C₄ to C₃₀, having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). The diene monomers can be selected from alpha, omega-diene monomers (*i.e.* di-vinyl monomers). The diolefin monomers are linear di-vinyl monomers, such as those containing from 4 to 30 carbon atoms. Examples of dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (Mw less than 1000 g/mol). Cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

[0278] Polymerization processes of the present disclosure can be carried out in any suitable manner. Any suitable suspension, homogeneous, bulk, solution, slurry, or gas phase polymerization process can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Homogeneous polymerization processes and slurry processes can be performed. (A useful homogeneous polymerization process is one where at least 90 wt% of the product is soluble in the reaction media.) A bulk homogeneous process can be used. (An example bulk process is one where monomer concentration in all feeds to the reactor is 70 volume % or more.) Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene). In at least one embodiment, the process is a slurry polymerization process. As used herein the term “slurry polymerization process” means a polymerization process where a supported catalyst is employed and monomers are polymerized on the supported catalyst particles. At least 95 wt% of polymer products derived from the supported catalyst are in granular form as solid particles (not dissolved in the diluent).

[0279] Suitable diluents/solvents for polymerization include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (Isopar™); perhalogenated hydrocarbons, such as perfluorinated C₄-C₁₀ alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In at least one embodiment, the solvent is not aromatic, such that aromatics are present in the solvent at less than 1 wt%, such as less than 0.5 wt%, such as less than 0 wt% based upon the weight of the solvents.

[0280] In at least one embodiment, the feed concentration of the monomers and comonomers for the polymerization is 60 vol% solvent or less, such as 40 vol% or less, such as 20 vol% or less, based on the total volume of the feedstream. The polymerization can be performed in a bulk process.

[0281] Polymerizations can be performed at any temperature and/or pressure suitable to obtain the desired polymers, such as ethylene and or propylene polymers. Typical temperatures and/or pressures include a temperature in the range of from 0°C to 300°C, such as 20°C to 200°C, such as 35°C to 150°C, such as 40°C to 120°C, such as 45°C to 80°C, for example about 74°C, and at a pressure in the range of from 0.35 MPa to 10 MPa, such as 0.45 MPa to 6 MPa, such as 0.5 MPa to 4 MPa.

[0282] In a typical polymerization, the run time of the reaction is up to 300 minutes, such as in the range of from 5 to 250 minutes, such as 10 to 120 minutes.

[0283] In at least one embodiment, hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa), such as from 0.01 to 25 psig (0.07 to 172 kPa), such as 0.1 to 10 psig (0.7 to 70 kPa).

[0284] In at least one embodiment, the activity of the catalyst is from 50 gP/mmolCat/hour to 200,000 gP/mmolCat/hr, such as from 10,000 gP/mmolCat/hr to 150,000 gP/mmolCat/hr, such as from 40,000 gP/mmolCat/hr to 100,000 gP/mmolCat/hr, such as about 50,000 gP/mmolCat/hr or more, such as 70,000 gP/mmolCat/hr or more. In at least one embodiment, the conversion of olefin monomer is at least 10%, based upon polymer yield and the weight of

the monomer entering the reaction zone, such as 20% or more, such as 30% or more, such as 50% or more, such as 80% or more.

[0285] In at least one embodiment, a catalyst system of the present disclosure is capable of producing a polyolefin. In at least one embodiment, a polyolefin is a homopolymer of ethylene or propylene or a copolymer of ethylene such as a copolymer of ethylene having from 0.1 to 25 wt% (such as from 0.5 to 20 wt%, such as from 1 to 15 wt%, such as from 5 to 17 wt%) of ethylene with the remainder balance being one or more C₃ to C₂₀ olefin comonomers (such as C₃ to C₁₂ alpha-olefin, such as propylene, butene, hexene, octene, decene, dodecene, such as propylene, butene, hexene, octene). A polyolefin can be a copolymer of propylene such as a copolymer of propylene having from 0.1 to 25 wt% (such as from 0.5 to 20 wt%, such as from 1 to 15 wt%, such as from 3 to 10 wt%) of propylene and from 99.9 to 75 wt% of one or more of C₂ or C₄ to C₂₀ olefin comonomer (such as ethylene or C₄ to C₁₂ alpha-olefin, such as butene, hexene, octene, decene, dodecene, such as ethylene, butene, hexene, octene).

[0286] In at least one embodiment, a catalyst system of the present disclosure is capable of producing polyolefins, such as polypropylene (e.g., iPP) or ethylene-octene copolymers, having an Mw from 40,000 to 1,500,000, such as from 70,000 to 1,000,000, such as from 90,000 to 500,000, such as from 90,000 to 250,000, such as from 90,000 to 200,000, such as from 90,000 to 110,000.

[0287] In at least one embodiment, a catalyst system of the present disclosure is capable of producing polyolefins, such as polypropylene (e.g., iPP) or ethylene-octene copolymers, having an Mn from 5,000 to 1,000,000, such as from 20,000 to 160,000, such as from 30,000 to 70,000, such as from 40,000 to 70,000. In at least one embodiment, a catalyst system of the present disclosure is capable of producing propylene polymers having an Mw/Mn value from 1 to 10, such as from 1.5 to 9, such as from 2 to 7, such as from 2 to 4, such as from 2.5 to 3, for example about 2.

[0288] In at least one embodiment, a catalyst system of the present disclosure is capable of producing polyolefins, such as polypropylene (e.g., iPP) or ethylene-octene, ethylene-propylene, or ethylene-butene copolymers, having a melting temperature (T_m) of less than 140°C, or 100°C to 150°C, such as 110°C to 140°C, such as 120°C to 135°C, such as 130°C to 135°C.

[0289] In at least one embodiment, little or no scavenger is used in the process to produce polymer, such as propylene polymer. Scavenger (such as trialkyl aluminum) can be present at

zero mol%, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, such as less than 50:1, such as less than 15:1, such as less than 10:1.

[0290] In at least one embodiment, the polymerization: 1) is conducted at temperatures of 0 to 300°C (such as 25 to 150°C, such as 40 to 120°C, such as 70 to 110°C, such as 85 to 100°C); 2) is conducted at a pressure of atmospheric pressure to 10 MPa (such as 0.35 to 10 MPa, such as from 0.45 to 6 MPa, such as from 0.5 to 4 MPa); 3) is conducted in an aliphatic hydrocarbon solvent (such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, where aromatics are present in the solvent at less than 1 wt%, such as less than 0.5 wt%, such as at 0 wt% based upon the weight of the solvents); and 4) the productivity of the catalyst compound is at least 30,000 gP/mmolCat/hr (such as at least 50,000 gP/mmolCat/hr, such as at least 60,000 gP/mmolCat/hr, such as at least 80,000 gP/mmolCat/hr, such as at least 100,000 gP/mmolCat/hr).

[0291] In at least one embodiment, the catalyst system used in the polymerization comprises no more than one catalyst compound. A "reaction zone" also referred to as a "polymerization zone" is a vessel where polymerization takes place, for example a batch reactor. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in both a batch reactor and a continuous reactor, each polymerization stage is considered as a separate polymerization zone. In at least one embodiment, the polymerization occurs in one reaction zone.

[0292] Other additives may also be used in the polymerization, as desired, such as one or more scavengers, promoters, modifiers, chain transfer agents (such as diethyl zinc), hydrogen, or aluminum alkyls. Useful chain transfer agents are typically alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C₁-C₈ aliphatic radical, such as methyl, ethyl, propyl, butyl, phenyl, hexyl, octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

30 Gas phase polymerization

[0293] Generally, in a fluidized gas bed process used for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the

fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See, for example, US Pat. Nos. 4,543,399; 4,588,790; 5,028,670; 5,317,036; 5,352,749; 5,405,922; 5,436,304; 5,453,471; 5,462,999; 5,616,661; and 5,668,228; all of which are fully incorporated herein by reference.)

Slurry phase polymerization

[0294] A slurry polymerization process generally operates between 1 to about 50 atmosphere pressure range (15 psi to 735 psi, 103 kPa to 5068 kPa) or even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which monomer and comonomers, along with catalysts, are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent used in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, such as a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used, the process must be operated above the reaction diluent critical temperature and pressure. For example, a hexane or an isobutane medium is employed.

[0295] In at least one embodiment, a polymerization process is a particle form polymerization, or a slurry process, where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance US Pat. No. 3,248,179 which is fully incorporated herein by reference. The temperature in the particle form process can be from about 85°C to about 110°C. Two example polymerization methods for the slurry process are those using a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in US Pat. No. 4,613,484, which is herein fully incorporated by reference.

[0296] In another embodiment, the slurry process is carried out continuously in a loop reactor. The catalyst, as a slurry in isohexane or as a dry free flowing powder, is injected regularly to the reactor loop, which is itself filled with circulating slurry of growing polymer particles in a diluent of isohexane containing monomer and optional comonomer. Hydrogen, optionally, may be added as a molecular weight control. (In one embodiment hydrogen is

added from 50 ppm to 500 ppm, such as from 100 ppm to 400 ppm, such as 150 ppm to 300 ppm.)

[0297] The reactor may be maintained at a pressure of 2,000 kPa to 5,000 kPa, such as from 3,620 kPa to 4,309 kPa, and at a temperature of from about 60°C to about 120°C depending on the desired polymer melting characteristics. Reaction heat is removed through the loop wall since much of the reactor is in the form of a double-jacketed pipe. The slurry is allowed to exit the reactor at regular intervals or continuously to a heated low pressure flash vessel, rotary dryer and a nitrogen purge column in sequence for removal of the isohexane diluent and all unreacted monomer and comonomer. The resulting hydrocarbon free powder is then compounded for use in various applications.

[0298] Other additives may also be used in the polymerization, as desired, such as one or more scavengers, promoters, modifiers, chain transfer agents (such as diethyl zinc), reducing agents, oxidizing agents, hydrogen, aluminum alkyls, or silanes.

[0299] Useful chain transfer agents are typically alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C₁-C₈ hydrocarbyl, such as methyl, ethyl, propyl, butyl, penyl, hexyl octyl or an isomer thereof). Examples can include diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Solution polymerization

[0300] A solution polymerization is a polymerization process in which the polymer is dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are typically not turbid as described in Oliveira, J. V. et al. (2000) "High-Pressure Phase Equilibria for Polypropylene-Hydrocarbon Systems," *Ind. Eng. Chem. Res.*, v.39, pp. 4627-4633. Generally solution polymerization involves polymerization in a continuous reactor in which the polymer formed and the starting monomer and catalyst materials supplied, are agitated to reduce or avoid concentration gradients and in which the monomer acts as a diluent or solvent or in which a hydrocarbon is used as a diluent or solvent. Suitable processes typically operate at temperatures from about 0°C to about 250°C, such as about 10°C to about 150°C, such as about 40°C to about 140°C, such as about 50°C to about 120°C, and at pressures of about 0.1 MPa or more, such as 2 MPa or more. The upper pressure limit is not critically constrained but typically can be about 200 MPa or less, such as 120 MPa or less. Temperature

control in the reactor can generally be obtained by balancing the heat of polymerization and with reactor cooling by reactor jackets or cooling coils to cool the contents of the reactor, auto refrigeration, pre-chilled feeds, vaporization of liquid medium (diluent, monomers or solvent) or combinations of all three. Adiabatic reactors with pre-chilled feeds can also be used. The
5 purity, type, and amount of solvent can be optimized for the maximum catalyst productivity for a particular type of polymerization. The solvent can be also introduced as a catalyst carrier. The solvent can be introduced as a gas phase or as a liquid phase depending on the pressure and temperature. Advantageously, the solvent can be kept in the liquid phase and introduced as a liquid. Solvent can be introduced in the feed to the polymerization reactors.

10 Polyolefin Products

[0301] The present disclosure also provides compositions of matter which can be produced by the methods described herein.

[0302] In at least one embodiment, a polyolefin is a propylene homopolymer, an ethylene homopolymer or an ethylene copolymer, such as propylene-ethylene and/or ethylene-
15 alphaolefin (such as C₄ to C₂₀) copolymer (such as an ethylene-hexene copolymer or an ethylene-octene copolymer). A polyolefin can have an Mw/Mn of greater than 1 to 4 (such as greater than 1 to 3).

[0303] In at least one embodiment, a polyolefin is a homopolymer of ethylene or propylene or a copolymer of ethylene such as a copolymer of ethylene having from 0.1 to 25 wt% (such
20 as from 0.5 to 20 wt%, such as from 1 to 15 wt%, such as from 5 to 17 wt%) of ethylene with the remainder balance being one or more C₃ to C₂₀ olefin comonomers (such as C₃ to C₁₂ alpha-olefin, such as propylene, butene, hexene, octene, decene, dodecene, such as propylene, butene, hexene, octene). A polyolefin can be a copolymer of propylene such as a copolymer of propylene having from 0.1 to 25 wt% (such as from 0.5 to 20 wt%, such as from 1 to 15 wt%,
25 such as from 3 to 10 wt%) of propylene and from 99.9 to 75 wt% of one or more of C₂ or C₄ to C₂₀ olefin comonomer (such as ethylene or C₄ to C₁₂ alpha-olefin, such as butene, hexene, octene, decene, dodecene, such as ethylene, butene, hexene, octene).

[0304] In at least one embodiment, a polyolefin, such as a polypropylene (e.g., iPP) or an ethylene-octene copolymer, has an Mw from 40,000 to 1,500,000, such as from 70,000 to
30 1,000,000, such as from 90,000 to 500,000, such as from 90,000 to 250,000, such as from 90,000 to 200,000, such as from 90,000 to 110,000.

[0305] In at least one embodiment, a polyolefin, such as a polypropylene (e.g., iPP) or an ethylene-octene copolymer, has an Mn from 5,000 to 1,000,000, such as from 20,000 to

160,000, such as from 30,000 to 70,000, such as from 40,000 to 70,000. In at least one embodiment, a polyolefin, such as a polypropylene (e.g., iPP) or an ethylene-octene copolymer, has an Mw/Mn value from 1 to 10, such as from 1.5 to 9, such as from 2 to 7, such as from 2 to 4, such as from 2.5 to 3, for example about 2.

- 5 **[0306]** In at least one embodiment, a polyolefin, such as a polypropylene (e.g., iPP) or an ethylene-octene copolymer, has a melt temperature (T_m) of from 100°C to 150°C, such as 110°C to 140°C, such as 120°C to 135°, such as 130°C to 135°C.

[0307] In at least one embodiment, a polymer of the present disclosure has a $g'vis$ of greater than 0.9, such as greater than 0.92, such as greater than 0.95.

- 10 **[0308]** In at least one embodiment, the polymer is an ethylene copolymer, and the comonomer is octene, at a comonomer content of from 1 wt% to 18 wt% octene, such as from 5 wt% to 15 wt%, such as from 8 wt% to 13 wt%, such as from 9 wt% to 12 wt%.

- [0309]** In at least one embodiment, the polymer produced herein has a unimodal or multimodal molecular weight distribution as determined by Gel Permeation Chromatography (GPC). By “unimodal” is meant that the GPC trace has one peak or inflection point. By “multimodal” is meant that the GPC trace has at least two peaks or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versa).

- [0310]** In at least one embodiment, the polymer produced herein has a composition distribution breadth index (CDBI) of 50% or more, such as 60% or more, such as 70 % or more. CDBI is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO1993/03093, published February 18, 1993, specifically columns 7 and 8 as well as in Wild, L. et al. (1982) “Determinatino of Branching Distributions in Polyethylene and Ethylene Copolymers,” *J. Poly. Sci., Poly. Phys. Ed.*, v.20(3), pp. 441-455; and US Patent No. 5,008,204, including that fractions having a weight average molecular weight (M_w) below 15,000 are ignored when determining CDBI.

- [0311]** Copolymer of the present disclosure can have a reversed comonomer index. The reversed-co-monomer index (RCI_m) is computed from x_2 (mol% co-monomer C_3 , C_4 , C_6 , C_8 , etc.), as a function of molecular weight, where x_2 is obtained from the following expression in which n is the number of carbon atoms in the comonomer (3 for C_3 , 4 for C_4 , 6 for C_6 , etc.):

$$x_2 = -\frac{200 w_2}{-100 n - 2 w_2 + n w_2}$$

[0312] Then the molecular-weight distribution, $W(z)$ where $z = \log_{10} M$, is modified to $W'(z)$ by setting to 0 the points in W that are less than 5% of the maximum of W ; this is to effectively remove points for which the S/N in the composition signal is low. Also, points of W' for molecular weights below 2000 gm/mole are set to 0. Then W' is renormalized so that

$$1 = \int_{-\infty}^{\infty} W' dz$$

and a modified weight-average molecular weight (M_w') is calculated over the effectively reduced range of molecular weights as follows:

$$M_w' = \int_{-\infty}^{\infty} 10^z * W' dz$$

The RCI,m is then computed as:

$$RCI,m = \int_{-\infty}^{\infty} x^2 (10^z - M_w') W' dz$$

[0313] A reversed-co-monomer index (RCI,w) is also defined on the basis of the weight fraction co-monomer signal ($w_2/100$) and is computed as follows:

$$RCI,w = \int_{-\infty}^{\infty} \frac{w_2}{100} (10^z - M_w') W' dz$$

[0314] Note that in the above definite integrals the limits of integration are the widest possible for the sake of generality; however, in reality the function is only integrated over a finite range for which data is acquired, considering the function in the rest of the non-acquired range to be 0. Also, by the manner in which W' is obtained, it is possible that W' is a discontinuous function, and the above integrations need to be done piecewise.

[0315] Three co-monomer distribution ratios are also defined on the basis of the % weight (w_2) comonomer signal, denoted as CDR-1,w, CDR-2,w, and CDR-3,w, as follows:

$$\begin{aligned} CDR-1,w &= \frac{w_2(M_z)}{w_2(M_w)} \\ CDR-2,w &= \frac{w_2(M_z)}{w_2\left(\frac{M_w + M_n}{2}\right)} \\ CDR-3,w &= \frac{w_2\left(\frac{M_z + M_w}{2}\right)}{w_2\left(\frac{M_w + M_n}{2}\right)} \end{aligned}$$

where $w_2(M_w)$ is the % weight co-monomer signal corresponding to a molecular weight of M_w , $w_2(M_z)$ is the % weight co-monomer signal corresponding to a molecular weight of M_z , $w_2[(M_w+M_n)/2]$ is the % weight co-monomer signal corresponding to a molecular weight of $(M_w+M_n)/2$, and $w_2[(M_z+M_w)/2]$ is the % weight co-monomer signal corresponding to a molecular weight of $M_z+M_w/2$, where M_w is the weight-average molecular weight, M_n is the number-average molecular weight, and M_z is the z-average molecular weight.

[0316] Accordingly, the co-monomer distribution ratios can be also defined utilizing the % mole co-monomer signal, CDR-1,m, CDR-2,m, CDR-3,m, as:

$$\begin{aligned} \text{CDR-1,m} &= \frac{x_2(M_z)}{x_2(M_w)} \\ \text{CDR-2,m} &= \frac{x_2(M_z)}{x_2\left(\frac{M_w + M_n}{2}\right)} \\ \text{CDR-3,m} &= \frac{x_2\left(\frac{M_z + M_w}{2}\right)}{x_2\left(\frac{M_w + M_n}{2}\right)} \end{aligned}$$

where $x_2(M_w)$ is the % mole co-monomer signal corresponding to a molecular weight of M_w , $x_2(M_z)$ is the % mole co-monomer signal corresponding to a molecular weight of M_z , $x_2[(M_w+M_n)/2]$ is the % mole co-monomer signal corresponding to a molecular weight of $(M_w+M_n)/2$, and $x_2[(M_z+M_w)/2]$ is the % mole co-monomer signal corresponding to a molecular weight of $M_z+M_w/2$, where M_w is the weight-average molecular weight, M_n is the number-average molecular weight, and M_z is the z-average molecular weight.

[0317] In at least one embodiment of the present disclosure, the polymer produced by the processes described herein includes ethylene and one or more comonomers and the polymer has: 1) an RCI,m of 30 or more (alternatively from 30 to 250).

Molecular Weight, Comonomer Composition and Long Chain Branching Determination by Polymer Char GPC-IR Hyphenated with Multiple Detectors

[0318] The distribution and the moments of molecular weight (M_w , M_n , M_w/M_n , etc.), the comonomer content (C_2 , C_3 , C_6 , etc.) and the long chain branching (g') are determined by using a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a multiple-channel band-filter based Infrared detector IR5, an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10 μ m Mixed-B LS columns are used to provide polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB

mixture is filtered through a 0.1 μm Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 mL/min and the nominal injection volume is 200 μL . The whole system including transfer lines, columns, detectors are contained in an oven maintained at 145°C. Given amount of polymer sample is weighed and sealed in a standard vial with 80 μL flow marker (Heptane) added to it. After loading the vial in the autosampler, polymer is automatically dissolved in the instrument with 8 mL added TCB solvent. The polymer is dissolved at 160°C with continuous shaking for about 1 hour for most PE samples or 2 hour for PP samples. The TCB densities used in concentration calculation are 1.463 g/ml at room temperature and 1.284 g/ml at 145°C. The sample solution concentration is from 0.2 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples.

[0319] The concentration (c), at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal intensity (I), using the following equation:

$$c = \beta I$$

where β is the mass constant determined with PE or PP standards. The mass recovery is calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume.

[0320] The conventional molecular weight (IR MW) is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10M. The MW at each elution volume is calculated with following equation;

$$\log M = \frac{\log(K_{PS}/K)}{a+1} + \frac{a_{PS}+1}{a+1} \log M_{PS}$$

where the variables with subscript "PS" stands for polystyrene while those without a subscript are for the test samples. In this method, $a_{PS} = 0.67$ and $K_{PS} = 0.000175$ while a and K are calculated as described in the published in literature (Sun, T. et al. (2001) "Effect of Short Chain Branching on the Coil Dimensions of Polyolefins in Dilute Solutions," *Macromolecules*, v34(19), pp. 6812-6820), except that for purposes of this invention and claims thereto, $\alpha = 0.695$ and $K = 0.000579$ for linear ethylene polymers, $\alpha = 0.705$ and $K = 0.0002288$ for linear propylene polymers, $\alpha = 0.695 + (0.01 * (\text{wt. fraction propylene}))$ and $K = 0.000579 - (0.0003502 * (\text{wt. fraction propylene}))$ for ethylene-propylene copolymers. Concentrations are

expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity (hence K in the Mark–Houwink equation) is expressed in dL/g unless otherwise noted.

[0321] The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH₂ and CH₃ channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR such as EMCC commercial grades about LLDPE, Vistamaxx, ICP, etc.

[0322] The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (*M*) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, *Light Scattering from Polymer Solutions*, Academic Press, 1971):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c$$

Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , *c* is the polymer concentration determined from the IR5 analysis, *A*₂ is the second virial coefficient. *P*(θ) is the form factor for a monodisperse random coil, and *K*_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where *N*_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system.

The refractive index, *n* = 1.500 for TCB at 145°C and λ = 665 nm.

[0323] A high temperature Agilent (or Viscotek Corporation) viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$[\eta] = \eta_s / c$$

where *c* is concentration and was determined from the IR5 broadband channel output. The viscosity MW at each point is calculated from the below equation:

$$M = K_{PS} M^{\alpha_{PS} + 1} / [\eta]$$

[0324] The branching index (g'_{vis}) is calculated using the output of the GPC-IR5-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{avg}$, of the sample is calculated by:

$$[\eta]_{avg} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

where the summations are over the chromatographic slices, i , between the integration limits.

- 5 The branching index g'_{vis} is defined as:

$$g'_{vis} = \frac{[\eta]_{avg}}{kM_v^\alpha}$$

M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis. The K/a are for the reference linear polymers are as described above.

- [0325] All the concentration is expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g unless otherwise noted.

[0326] All molecular weights are reported in g/mol unless otherwise noted.

- [0327] Differential Scanning Calorimetry (DSC-Procedure-2). Melting Temperature, T_m , is measured by differential scanning calorimetry ("DSC") using a DSCQ200 unit. The sample is first equilibrated at 25°C and subsequently heated to 220°C using a heating rate of 10°C/min (first heat). The sample is held at 220°C for 3 min. The sample is subsequently cooled down to -100°C with a constant cooling rate of 10°C/min (first cool). The sample is equilibrated at -100°C before being heated to 220°C at a constant heating rate of 10°C/min (second heat). The exothermic peak of crystallization (first cool) is analyzed using the TA Universal Analysis software and the corresponding to 10°C/min cooling rate is determined. The endothermic peak of melting (second heat) is also analyzed using the TA Universal Analysis software and the peak melting temperature (T_m) corresponding to 10°C/min heating rate is determined. In the event of conflict between the DSC Procedure-1 and DSC procedure-2, DSC procedure-2 is used.

Blends

- 25 [0328] In another embodiment, the polymer (such as the polyethylene or polypropylene) produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic

acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene.

[0329] In at least one embodiment, the polymer (such as polyethylene or polypropylene) is present in the above blends, at from 10 to 99 wt%, based upon the weight of the polymers in the blend, such as 20 to 95 wt%, such as at least 30 to 90 wt%, such as at least 40 to 90 wt%, such as at least 50 to 90 wt%, such as at least 60 to 90 wt%, such as at least 70 to 90 wt%.

[0330] The blends described above may be produced by mixing the polymers of the present disclosure with one or more polymers (as described above), by connecting reactors together in series to make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

[0331] The blends may be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; and talc.

Films

[0332] One or more of the foregoing polymers, such as the foregoing polyethylenes, polypropylenes, or blends thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films.

5 These films may be formed by any number of well-known extrusion or coextrusion techniques, such as a blown bubble film processing technique, wherein the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially

10 oriented, or biaxially oriented to the same or different extents. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. The uniaxially orientation can be accomplished using typical cold drawing or hot drawing methods. Biaxial orientation can be accomplished using tenter frame equipment or a double bubble processes and may occur before or after the individual layers are brought

15 together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene then optionally the combination could be oriented even further. Typically the films are oriented in the Machine

20 Direction (MD) at a ratio of up to 15, such as between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15, such as 7 to 9. However, in at least one embodiment the film is oriented to the same extent in both the MD and TD directions.

[0333] The films may vary in thickness depending on the intended application; however, films of a thickness from 1 μm to 50 μm are usually suitable. Films intended for packaging are

25 usually from 10 μm to 50 μm thick. The thickness of the sealing layer is typically 0.2 μm to 50 μm. There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.

[0334] In at least one embodiment, one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, flame treatment, or microwave. In at

30 least one embodiment, one or both of the surface layers is modified by corona treatment.

[0335] This invention further relates to:

1. A compound represented by Formula (I):



wherein:

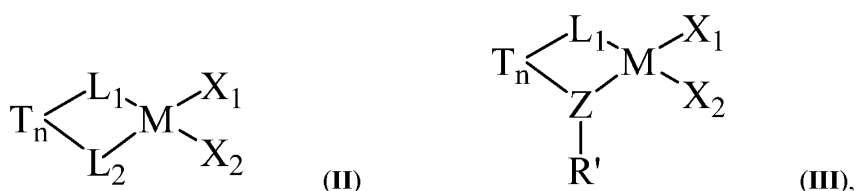
E is nitrogen or phosphorous;

each of R¹, R², and R³ is independently C₁-C₄₀ linear alkyl, C₅-C₂₂-aryl, wherein each of R¹, R², and R³ is independently unsubstituted or substituted with at least one of halide, C₁-C₁₀ alkyl, C₅-C₁₅ aryl, C₆-C₂₅ arylalkyl, and C₆-C₂₅ alkylaryl, wherein R¹, R², and R³ together comprise 15 or more carbon atoms;

each of R⁴, R⁵, R⁶, and R⁷ is naphthyl, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.

2. The compound of paragraph 1, wherein E is nitrogen.
- 10 3. The compound of paragraph 1 or paragraph 2, wherein at least one of R⁴, R⁵, R⁶, and R⁷ is substituted with seven fluorine atoms.
4. The compound of any of paragraphs 1 to 3, wherein each of R⁴, R⁵, R⁶, and R⁷ is substituted with from one to seven fluorine atoms.
5. The compound of any of paragraphs 1 to 4, wherein each of R⁴, R⁵, R⁶, and R⁷ is substituted with seven fluorine atoms.
- 15 6. The compound of any of paragraphs 1 to 5, wherein R¹, R², and R³ together comprise 17 or more carbon atoms.
7. The compound of any of paragraphs 1 to 6, wherein R¹, R², and R³ together comprise 20 or more carbon atoms.
- 20 8. The compound of any of paragraphs 1 to 7, wherein R¹, R², and R³ together comprise 25 or more carbon atoms.
9. The compound of any of paragraphs 1 to 8, wherein R¹, R², and R³ together comprise 35 or more carbon atoms.
10. The compound of any of paragraphs 1 to 9, wherein each of each of R¹, R², and R³ is independently C₁-C₄₀ linear alkyl, or C₅-C₂₂-aryl, wherein each of R¹, R², and R³ is independently unsubstituted or substituted with at least one C₁-C₁₀ alkyl.
- 25 11. The compound of any of paragraphs 1 to 10, wherein R¹ is C₁-C₁₀ alkyl and each of R² and R³ is C₁₀-C₄₀ alkyl.
12. The compound of any of paragraphs 1 to 11, wherein R¹ is methyl and each of R² and R³ is C₁₀-C₄₀ alkyl.
- 30 13. The compound of any of paragraphs 1 to 10, wherein R¹ is aryl C₅-C₂₂-aryl and each of each of R² and R³ is C₁-C₄₀ linear alkyl, wherein R¹ is unsubstituted or substituted with at least one C₁-C₁₀ alkyl.

14. The compound of paragraph 13, wherein R^1 is phenyl, R^2 methyl, and R^3 is C_{10} - C_{40} alkyl.
15. The compound of paragraph 1, wherein the compound represented by formula (I) comprises a cation selected from the group consisting of the cations n Table X.
- 5 16. A catalyst system comprising a catalyst and the activator compound of any of paragraphs 1 to 15.
17. The catalyst system of paragraph 16, further comprising a support material.
18. The catalyst system of paragraph 17, wherein the support material is selected from Al_2O_3 , ZrO_2 , SiO_2 , SiO_2/Al_2O_3 , SiO_2/TiO_2 , silica clay, silicon oxide/clay, or mixtures thereof.
- 10 19. The catalyst system of any of paragraphs 16 to 18, wherein the catalyst is represented by formula (II) or formula (III):



wherein in each of formula (II) and formula (III):

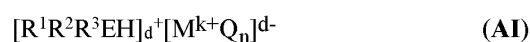
- M is the metal center, and is a Group 4 metal;
- 15 n is 0 or 1;
- T is an optional bridging group selected from dialkylsilyl, diarylsilyl, dialkylmethyl, ethylenyl or hydrocarbylethylenyl wherein one, two, three or four of the hydrogen atoms in ethylenyl are substituted by hydrocarbyl;
- Z is nitrogen, oxygen or phosphorus;
- 20 R' is a C_1 - C_{40} alkyl or substituted alkyl group, preferably a linear C_1 - C_{40} alkyl or substituted alkyl group;
- X₁ and X₂ are, independently, hydrogen, halogen, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, silylcarbyl radicals, substituted silylcarbyl radicals, germylcarbyl radicals, or substituted
- 25 germylcarbyl radicals; or both X₁ and X₂ are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.
20. The catalyst system of paragraph 19, wherein the catalyst is C₂ symmetrical.
21. The catalyst system of any of paragraphs 16 to 19, wherein the catalyst is rac-
- 30 dimethylsilyl-bis(indenyl)hafnium dimethyl.

22. The catalyst system of any of paragraphs 16 to 19, wherein the catalyst is one or more of:
- bis(1-methyl, 3-n-butyl cyclopentadienyl) M(R)₂;
dimethylsilyl bis(indenyl)M(R)₂;
- 5 bis(indenyl)M(R)₂;
dimethylsilyl bis(tetrahydroindenyl)M(R)₂;
bis(n-propylcyclopentadienyl)M(R)₂;
dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)M(R)₂;
dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)M(R)₂;
- 10 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)M(R)₂;
dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)M(R)₂;
 μ -(CH₃)₂Si(cyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
- 15 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂C(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-tertbutylamido)M(R)₂;
 μ -(CH₃)₂Si(fluorenyl)(1-tertbutylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)₂;
- 20 μ -(C₆H₅)₂C(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)₂;
 μ -(CH₃)₂Si(η^5 -2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(tertbutylamido)M(R)₂;
where M is selected from Ti, Zr, and Hf; and R is selected from halogen or C₁ to C₅ alkyl.
23. The catalyst system of paragraph 16, 17 or 18, wherein the catalyst is represented by the catalyst compound **(BI)**, **(BII)**, **(BIII)**, **(CI)**, **(CII)**, **(CIII)**, **(IV)**, **(VII)**, **(VIII)**, **(IX)**, **(X)**, **(XI)**, **(XII)**, **(XIII)**, **(XIV)**, or **(XV)**, as described herein.
24. A method of polymerizing olefins to produce at least one polyolefin, the method comprising: contacting at least one olefin with the catalyst system of any of paragraphs 16 to 23; and obtaining a polyolefin.
25. The method of paragraph 24, wherein the at least one olefin is propylene and the polyolefin is isotactic polypropylene.
- 30 26. A method of polymerizing olefins to produce at least one polyolefin, the method comprising: contacting two or more different olefins with the catalyst system of any of paragraphs 16 to 22; and obtaining a polyolefin.

27. The method of paragraph 26, wherein the two or more olefins are ethylene and propylene.
28. The method of paragraph 26 or 27, wherein the two or more olefins further comprise a diene.
- 5 29. The method of any of paragraphs 24-27, wherein the polyolefin has an Mw of from about 50,000 to about 300,000g/mol and a melt temperature of from about 120°C to about 140°C.
30. The method of paragraph 29, wherein the polyolefin has an Mw of from about 100,000 to about 300,000 and a melt temperature of from about 125°C to about 135°C.
- 10 31. The method of any of paragraphs 24 to 30, wherein the method is performed in gas phase or slurry phase.

[0336] This invention also relates to:

A1. A compound represented by Formula (AI):



15 wherein:

E is nitrogen or phosphorous;

d is 1, 2 or 3; k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6; n - k = d (preferably d is 1, 2 or 3; k is 3; n is 4, 5, or 6, preferably when M is B, n is 4);

20 R¹ is a C₁-C₂₀ (preferably C₁ to C₁₀) linear alkyl group; wherein R¹ is optionally substituted,

each of R² and R³ is independently an optionally substituted C₁-C₄₀ linear alkyl group or a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group, an optionally substituted alkoxy group, an optionally substituted silyl group, a halogen, or a halogen containing group,

25 wherein R¹, R², and R³ together comprise 15 or more carbon atoms (preferably 38 or more carbon atoms);

M is an element selected from group 13 of the Periodic Table of the Elements; and

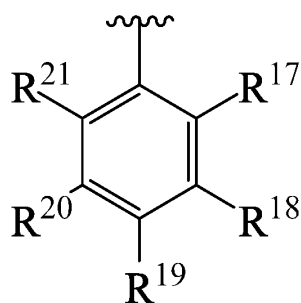
each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or

30 halosubstituted-hydrocarbyl radical, provided that when Q is a fluorophenyl group, then R² is not a C₁-C₄₀ linear alkyl group.

A2. The compound of Paragraph A1 wherein R¹ is C₁ to C₁₀ linear alkyl group, preferably methyl.

- A3. The compound of paragraph A1 or A2 wherein R² is a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group, an optionally substituted alkoxy group, an optionally substituted silyl group, a halogen or a halogen containing group.
- 5 A4. The compound of paragraph A1, A2, or A3 wherein R³ is an optionally substituted C₁-C₄₀ linear alkyl group.
- A5. The compound of paragraph A1 wherein R¹ is methyl; R² is a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group, an optionally substituted alkoxy group, an optionally substituted silyl group, a halogen or a halogen containing group; and R³ is an optionally substituted C₁-C₄₀ linear alkyl group.
- 10 A6. The compound of paragraph A1 wherein R¹ is methyl; R² is a meta- and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group; and R³ is an optionally substituted C₁-C₄₀ linear alkyl group.
- 15 A7. The compound of any of the above paragraphs A1 to A6, wherein R² is a para substituted phenyl selected from the group consisting of methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, and n-tricontylphenyl.
- 20 A8. The compound of any of paragraphs A1 to A6, wherein R² is a meta substituted phenyl having one or two meta substituents, which may be the same or different, where the substituents are independently selected from the group consisting of: methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, n-icosylphenyl, n-henicosylphenyl, n-docosylphenyl, n-tricosylphenyl, n-tetracosylphenyl, n-pentacosylphenyl, n-hexacosylphenyl, n-heptacosylphenyl, n-octacosylphenyl, n-nonacosylphenyl, n-tricontylphenyl.
- 30

A9. The compound of any of paragraph A1 to A5, wherein the meta- and/or para-substituted phenyl group is represented by the formula:



, where R^{17} and R^{21} are hydrogen, and each of R^{18} , R^{19} , and R^{20} is independently selected from hydrogen, C₁-C₄₀ hydrocarbyl or C₁-C₄₀ substituted hydrocarbyl, halogen, or a halogen-containing group.

A10. The compound of paragraph A9 wherein R^{17} and R^{21} are hydrogen, and one, two, or three of R^{18} , R^{19} , and R^{20} are selected from the group consisting of n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl, n-tetracosyl, n-pentacosyl, n-hexacosyl, n-heptacosyl, n-octacosyl, n-nonacosyl, n-tricontyl, trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, trihexylsilyl, triheptylsilyl, trioctylsilyl, trinonylsilyl, tridecylsilyl, triundecylsilyl, tridodecylsilyl, tri-tridecylsilyl, tri-tetradecylsilyl, tri-pentadecylsilyl, tri-hexadecylsilyl, tri-heptadecylsilyl, tri-octadecylsilyl, tri-nonadecylsilyl, tri-icosylsilyl, Br, Cl, F, methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy, tetradecoxy, pentadecoxy, hexadecoxy, heptadecoxy, octadecoxy, nonadecoxy, icosoxy, and phenoxy.

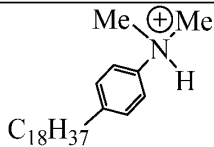
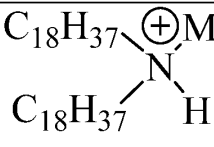
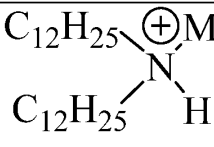
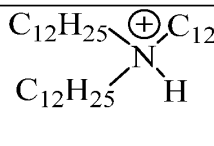
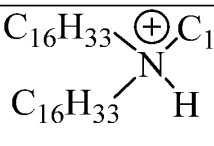
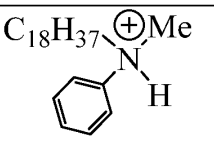
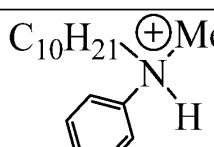
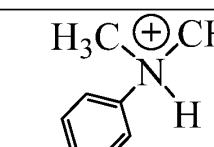
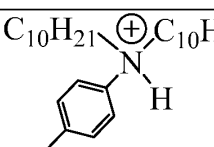
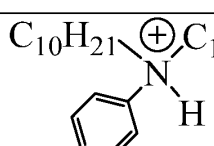
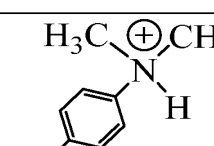
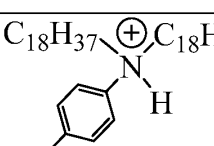
A11. The compound of paragraph A9 wherein R^1 is methyl and R^2 is a C₆ to C₄₀ linear alkyl group.

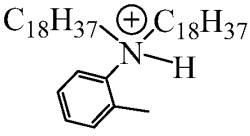
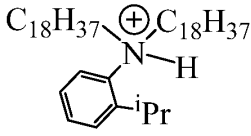
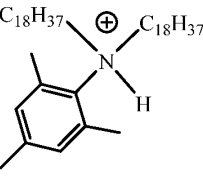
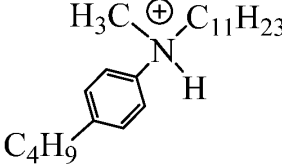
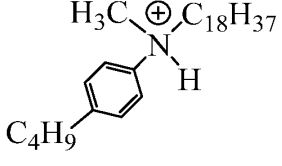
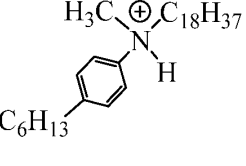
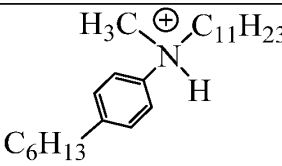
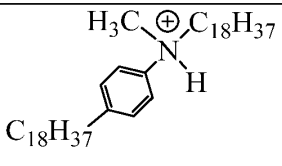
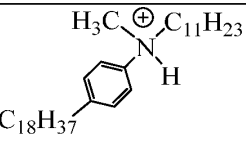
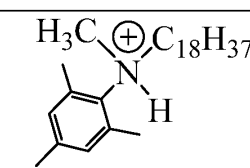
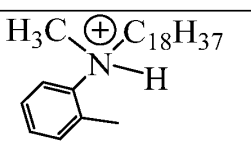
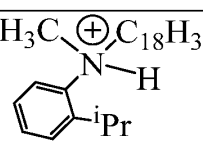
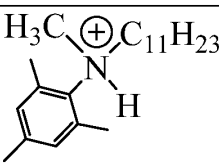
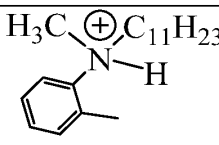
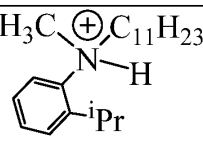
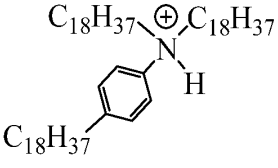
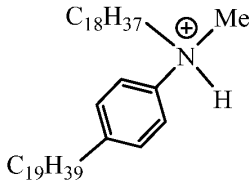
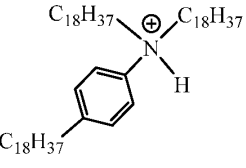
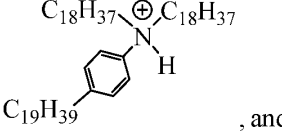
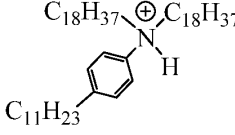
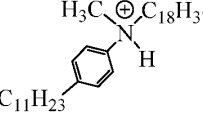
A12. The compound of paragraph A1 wherein, R^1 is methyl, R^2 is n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, or n-icosyl, and R^3 is methylphenyl, ethylphenyl, n-propylphenyl, n-butylphenyl, n-pentylphenyl, n-hexylphenyl, n-heptylphenyl, n-octylphenyl, n-nonylphenyl, n-decylphenyl, n-undecylphenyl, n-dodecylphenyl, n-tridecylphenyl, n-tetradecylphenyl, n-pentadecylphenyl, n-hexadecylphenyl, n-heptadecylphenyl, n-octadecylphenyl, n-nonadecylphenyl, or n-icosylphenyl.

A13. The compound of any of the above paragraphs A1 to A12 wherein E is nitrogen.

A14. The compound of any of the above paragraphs A1 to A13 wherein M is boron.

- A15. The compound of any of the above paragraphs A1 to A14 wherein Q is an optionally substituted aryl group, preferably a halogen substituted aryl group.
- A16. The compound of any of the above paragraphs A1 to A15 wherein Q is a perfluoroaryl group.
- 5 A17. The compound of any of the above paragraphs A1 to A16 wherein when Q is a fluorophenyl group, then R² is not an optionally substituted C₁-C₄₀ linear alkyl group.
- A18. The compound of any of the above paragraphs A1 to A17 wherein when Q is a substituted phenyl group, then R² is not a C₁-C₄₀ linear alkyl group, preferably R² is not a C₁-C₂₀ linear alkyl group.
- 10 A19. The compound of any of the above paragraphs A1 to A18 wherein each Q is perfluoronaphthyl.
- A20. The compound of paragraph A1, A14, A15, A16, A17, A18, or A19, wherein the cation represented by the formula [R¹R²R³EH]_d⁺ is selected from the group consisting of:

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4		5		6	
7		8		9	
10		11		12	

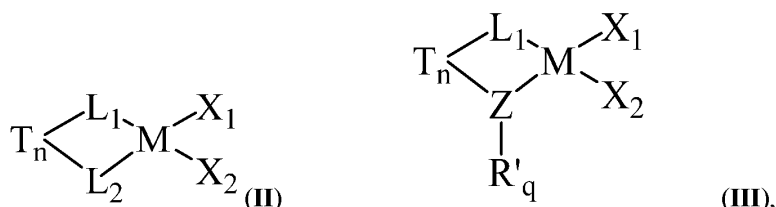
13		14		15	
16		17 A		18	
19		20 A		21	
22		23		24	
25		26		27	
28		29		30	
31	 , and	32		33	

A21. The compound of any of paragraphs A1 to A20, wherein the compound has a solubility of more than 10 mM at 25°C (stirred 2 hours) in methylcyclohexane and /or a solubility of more than 1 mM at 25°C (stirred 2 hours) in isohexane.

5 A22. A catalyst system comprising a catalyst and the activator compound of any of paragraphs A1 to A21.

A23. The catalyst system of paragraph A22, further comprising a support material, preferably selected from Al₂O₃, ZrO₂, SiO₂, SiO₂/Al₂O₃, SiO₂/TiO₂, silica clay, silicon oxide/clay, or mixtures thereof.

10 A24. The catalyst system of paragraph A22 or A23, wherein the catalyst is represented by formula (II) or formula (III):



wherein in formula (II) and formula (III): M is the metal center, and is a Group 4 metal; n is 0 or 1; T is an optional bridging group selected from dialkylsilyl, diarylsilyl, dialkylmethyl, ethylenyl or hydrocarbylethylenyl wherein one, two, three or four of the hydrogen atoms in ethylenyl are substituted by hydrocarbyl; Z is nitrogen, oxygen, sulfur, or phosphorus; R' is a cyclic, linear or branched C₁ to C₄₀ alkyl or substituted alkyl group, preferably R' is a linear C₁-C₄₀ alkyl or substituted alkyl group, preferably a linear C₁-C₄₀ alkyl or substituted alkyl group; q is 1 or 2; and X₁ and X₂ are, independently, hydrogen, halogen, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, silylcarbyl radicals, substituted silylcarbyl radicals, germylcarbyl radicals, or substituted germylcarbyl radicals; or both X₁ and X₂ are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.

A25. The catalyst system of paragraph A24, wherein the catalyst is C₂ symmetrical.

25 A26. The catalyst system of paragraph A22 or A23, wherein the catalyst is rac-dimethylsilyl-bis(indenyl)hafnium dimethyl.

A27. The catalyst system of paragraph A22 or A23, wherein the catalyst is one or more of:
dimethylsilylbis(tetrahydroindenyl)MX_n,
dimethylsilyl bis(2-methylindenyl)MX_n,

- dimethylsilyl bis(2-methylfluorenyl)MX_n,
 dimethylsilyl bis(2-methyl-5,7-propylindenyl)MX_n,
 dimethylsilyl bis(2-methyl-4-phenylindenyl)MX_n,
 dimethylsilyl bis(2-ethyl-5-phenylindenyl)MX_n,
 5 dimethylsilyl bis(2-methyl-4-biphenylindenyl)MX_n,
 dimethylsilylene bis(2-methyl-4-carbazolylindenyl)MX_n,
rac-dimethylsilyl-bis-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-methyl-1H-benz(f)indene)MX_n,
 diphenylmethylenecyclopentadienyl(fluorenyl)MX_n,
 10 bis(methylcyclopentadienyl)MX_n,
rac-dimethylsilylbis(2-methyl,3-propylindenyl)MX_n,
 dimethylsilylbis(indenyl)MX_n,
Rac-meso-diphenylsilyl-bis(n-propylcyclopentadienyl)MX_n,
 1,1'-bis(4-triethylsilylphenyl)methylene-(cyclopentadienyl)(3,8-di-tertiary-butyl-1-fluorenyl)MX_n (bridge is considered the 1 position),
 15 bis-trimethylsilylphenyl-methylene(cyclopentadienyl)(di-*t*-butylfluorenyl)MX_n,
 bis-trimethylsilylphenyl-methylene(cyclopentadienyl)(fluorenyl)MX_n,
 bisphenylmethylenecyclopentadienyl(dimethylfluorenyl)MX_n,
 bis(n-propylcyclopentadienyl)MX_n,
 20 bis(n-butylcyclopentadienyl)MX_n,
 bis(n-pentylcyclopentadienyl)MX_n,
 (n-propylcyclopentadienyl)(n-butylcyclopentadienyl)MX_n,
 bis[(2-trimethylsilyl)ethylcyclopentadienyl]MX_n,
 bis(trimethylsilylcyclopentadienyl)MX_n,
 25 dimethylsilylbis(n-propylcyclopentadienyl)MX_n,
 dimethylsilylbis(n-butylcyclopentadienyl)MX_n,
 bis(1-n-propyl-2-methylcyclopentadienyl)MX_n,
 (n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)MX_n,
 bis(1-methyl,3-n-butylcyclopentadienyl)MX_n,
 30 bis(indenyl)MX_n,
 dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)MX_n,
 dimethylsilyl(tetramethylcyclopentadienyl)(*t*-butylamido)MX_n,
 μ-(CH₃)₂Si(cyclopentadienyl)(1-adamantylamido)MX_n,

- $\mu\text{-(CH}_3)_2\text{Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)MX}_n$,
 $\mu\text{-(CH}_3)_2\text{(tetramethylcyclopentadienyl)(1-adamantylamido)MX}_n$,
 $\mu\text{-(CH}_3)_2\text{Si(tetramethylcyclopentadienyl)(1-adamantylamido)MX}_n$,
 $\mu\text{-(CH}_3)_2\text{C(tetramethylcyclopentadienyl)(1-adamantylamido)MX}_n$,
5 $\mu\text{-(CH}_3)_2\text{Si(tetramethylcyclopentadienyl)(1-tertbutylamido)MX}_n$,
 $\mu\text{-(CH}_3)_2\text{Si(fluorenyl)(1-tertbutylamido)MX}_n$,
 $\mu\text{-(CH}_3)_2\text{Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)MX}_n$,
 $\mu\text{-(C}_6\text{H}_5)_2\text{C(tetramethylcyclopentadienyl)(1-cyclododecylamido)MX}_n$,
 $\mu\text{-(CH}_3)_2\text{Si}(\eta^5\text{-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl})(\text{tertbutylamido)MX}_n$,
10 where M is selected from Ti, Zr, and Hf; X is selected from the group consisting of halogens, hydrides, C₁₋₁₂ alkyls, C₂₋₁₂ alkenyls, C₆₋₁₂ aryls, C₇₋₂₀ alkylaryls, C₁₋₁₂ alkoxys, C₆₋₁₆ aryloxys, C₇₋₁₈ alkylaryloxys, C₁₋₁₂ fluoroalkyls, C₆₋₁₂ fluoroaryls, and C₁₋₁₂ heteroatom-containing hydrocarbons, substituted derivatives thereof, and combinations thereof, and where n is zero or an integer from 1 to 4, preferably X is selected from halogens (such as bromide, fluoride, chloride), or C₁ to C₂₀ alkyls (such as methyl, ethyl, propyl, butyl, and pentyl) and n is 1 or 2, preferably 2.
15 A28. The catalyst system of paragraph A22 or A23, wherein the catalyst is one or more of:
bis(1-methyl, 3-n-butyl cyclopentadienyl) M(R)₂;
dimethylsilyl bis(indenyl)M(R)₂;
20 bis(indenyl)M(R)₂;
dimethylsilyl bis(tetrahydroindenyl)M(R)₂;
bis(n-propylcyclopentadienyl)M(R)₂;
dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)M(R)₂;
dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)M(R)₂;
25 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)M(R)₂;
dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)M(R)₂;
 $\mu\text{-(CH}_3)_2\text{Si(cyclopentadienyl)(1-adamantylamido)M(R)}_2$;
 $\mu\text{-(CH}_3)_2\text{Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)M(R)}_2$;
 $\mu\text{-(CH}_3)_2\text{(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)}_2$;
30 $\mu\text{-(CH}_3)_2\text{Si(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)}_2$;
 $\mu\text{-(CH}_3)_2\text{C(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)}_2$;
 $\mu\text{-(CH}_3)_2\text{Si(tetramethylcyclopentadienyl)(1-tertbutylamido)M(R)}_2$;
 $\mu\text{-(CH}_3)_2\text{Si(fluorenyl)(1-tertbutylamido)M(R)}_2$;

$\mu\text{-(CH}_3)_2\text{Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)}_2$;

$\mu\text{-(C}_6\text{H}_5)_2\text{C(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)}_2$;

$\mu\text{-(CH}_3)_2\text{Si}(\eta^5\text{-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl})(\text{tertbutylamido)M(R)}_2$;

where M is selected from Ti, Zr, and Hf; and R is selected from halogen or C₁ to C₅ alkyl.

- 5 A29. The catalyst system of paragraph A22 or 23, wherein the catalyst is represented by the catalyst is represented by the catalyst compound **(BI)**, **(BII)**, **(BIII)**, **(CI)**, **(CII)**, **(CIII)**, **(IV)**, **(VII)**, **(VIII)**, **(IX)**, **(X)**, **(XI)**, **(XII)**, **(XIII)**, **(XIV)**, or **(XV)**, as described herein.

A30. A method of polymerizing olefins to produce at least one polyolefin, the method comprising contacting at least one olefin with the catalyst system of any of paragraphs A22 to

- 10 A29, and obtaining a polyolefin.

A31. The method of paragraph A30, wherein the at least one olefin is propylene and the polyolefin is isotactic polypropylene.

A32. A method of polymerizing olefins to produce at least one polyolefin, the method comprising contacting two or more different olefins with the catalyst system of any of paragraphs A22 to A31; and obtaining a polyolefin.

- 15

A33. The method of paragraph A32, wherein the two or more olefins are ethylene and propylene.

A34. The method of paragraph A32 or A33, wherein the two or more olefins further comprise a diene.

- 20 A35. The method of any of paragraphs A30 to A34, wherein the polyolefin has an Mw of from about 50,000 to about 300,000 g/mol and a melt temperature of from about 120°C to about 140°C, alternately the polyolefin has an Mw of from about 100,000 to about 300,000 g/mol and a melt temperature of from about 125°C to about 135°C.

- A36. The method of any of paragraphs A30 to A35, wherein the method is performed in gas phase or slurry phase.

- 25 A37. The method of any of paragraphs A30 to A36, wherein the method is performed in solution phase.

A38. A composition comprising the compound of any of paragraphs A1 to A22 or the catalyst system of any of paragraphs A23 to A29 and an aliphatic solvent, where aromatic solvents are absent.

- 30

A39. The method of paragraphs A30 to A36, where the method is performed in the absence of aromatic solvents.

Experimental

[0337] Lithium tetrakis(pentafluorophenyl)borate etherate (Li-BF20) was purchased from Boulder Scientific. N,N-Dimethylanilinium tetrakis(pentafluorophenyl)borate (DMAH-BF20) was purchased from Albemarle Corporation, Baton Rouge, Louisiana. Sodium tetrakis(heptafluoronaphthalen-2-yl)borate (Na-BF28) and N,N-dimethylanilinium tetrakis(heptafluoronaphthalen-2-yl)borate (DMAH-BF28) were purchased from Grace Davison. Di(hydrogenated tallow)methylamine (M2HT) was purchased from Akzo Nobel. Didocecylmethylamine, tridodecylamine, p-toluidine, Celite, silica gel, ethereal HCl (2M) were purchased from Sigma-Aldrich. N-methyldioctadecylamine was provided by AkzoNobel.

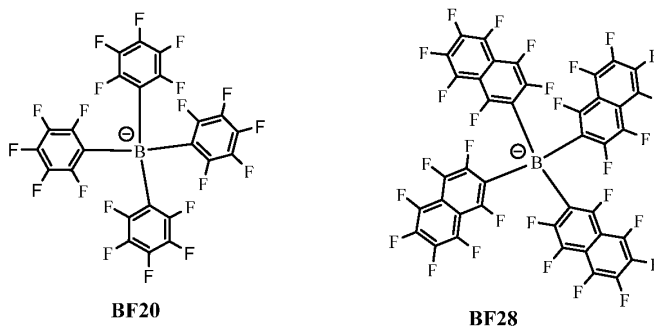
[0338] *¹H NMR for Compound Characterization:* Chemical structures are determined by ¹H NMR. ¹H NMR data are collected at room temperature (e.g., 23°C) in a 5 mm probe. The ¹H NMR measurements were recorded on a 400 MHz or 500 MHz Bruker spectrometer with chemical shifts referenced to residual solvent peaks (CDCl₃: 7.27 ppm for ¹H, 77.23 ppm for ¹³C).

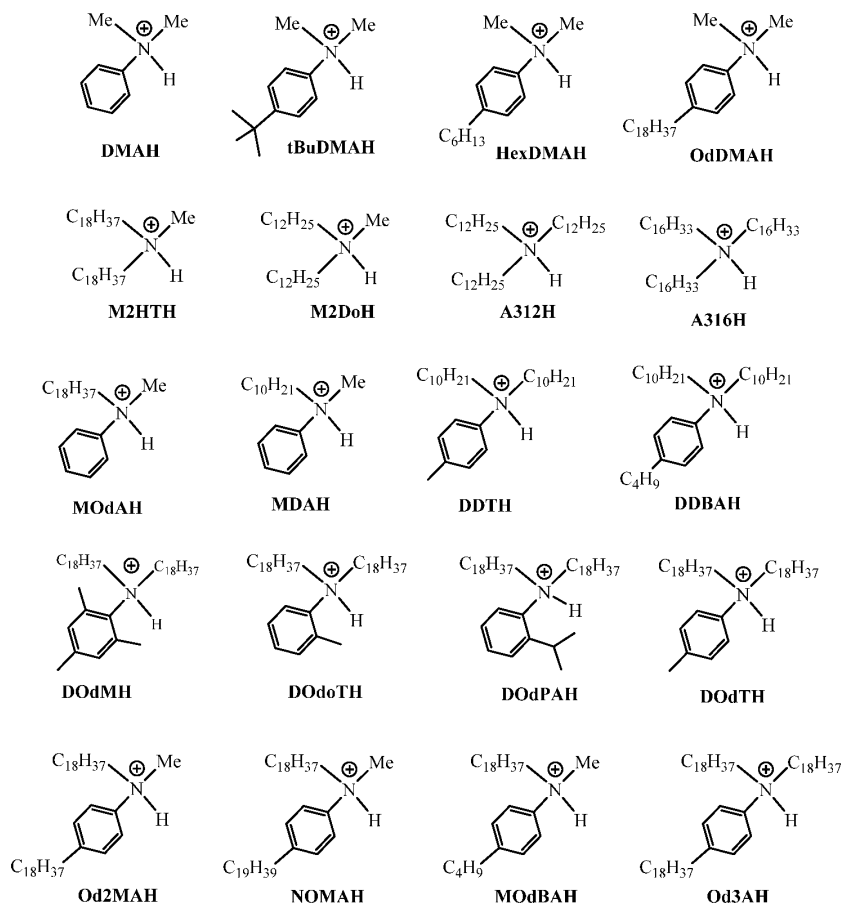
[0339] All anhydrous solvents were purchased from Sigma-Aldrich. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Examples

[0340] Borate anions and ammonium cations used as activator components are shown in Scheme 1.

Scheme 1: Borate Anions and Ammonium Cations used as Activator Components.





Synthesis of Activators

[0341] General Synthesis of Ammonium Borate Activators: Ammonium borate activators were prepared using a two-step process. In the first step, an amine was dissolved in a solvent (e.g. hexane, cyclohexane, methylcyclohexane, ether, dichloromethane, toluene) and an excess (ca. 1.2 molar equivalents) of hydrogen chloride was added to form an ammonium chloride salt. This salt was isolated by filtration from the reaction medium and dried under reduced pressure. The isolated ammonium chloride was then heated to reflux with one molar equivalent of an alkali metal borate in a solvent (e.g. cyclohexane, dichloromethane, methylcyclohexane) to form the ammonium borate along with byproduct alkali metal chloride, the latter which typically is removed by filtration. Examples describing the synthetic details for selected ammonium borates are given below.

[0342] 4-(*tert*-butyl)-*N,N*-dimethylanilium-BF₂₀ (tBuDMAH-BF₂₀): 4-(*tert*-butyl)-*N,N*-dimethylaniline (4.0 g, 23 mmol) was dissolved in hexane (100 mL). A 2 M ethereal solution of HCl (12.4 mL, 25 mmol) was added slowly, causing a white precipitate to form.

The reaction was allowed to stir for 3 hours, then the solid was collected by filtration, washed with hexane, and dried in vacuo. The salt was obtained in 88% yield and used without further purification. This salt (0.5 g, 20 mmol) was suspended in 500 mL of cyclohexane and mixed with a suspension of Li-BF₂O (1.6 g, 23 mmol) in 50 mL cyclohexane. The mixture was heated at reflux for 1.5 h, then cooled to ambient. A white solid precipitate was collected, giving the product in 60% yield: ¹H NMR (400 MHz, CDCl₃, δ): 1.34 (s, 9 H), 3.26 (d, *J* = 4.0 Hz, 6 H), 7.35 (m, 2H), 7.58 (m, 2H).

[0343] 4-(*tert*-butyl)-*N,N*-dimethylanilinium-BF₂O (tBuDMAH-BF₂O): The HCl salt of 4-(*tert*-butyl)-*N,N*-dimethylaniline prepared above (0.5 g, 23 mmol) was suspended in 500 mL of cyclohexane and mixed with a suspension of Li-BF₂O (2.4 g, 23 mmol) in 50 mL cyclohexane. The mixture was heated at reflux for 1.5 h, then cooled to ambient. A brown solid precipitate was collected, giving the product in 64% yield: ¹H NMR (400 MHz, CDCl₃, δ): 1.31 (s, 9 H), 3.24 (d, *J* = 4.0 Hz, 6 H), 7.34 (m, 2H), 7.52 m, 2H).

[0344] 4-hexyl-*N,N*-dimethylanilinium- BF₂O (Hex-DMAH-BF₂O): 4-Hexyl-*N,N*-dimethylaniline (4.0 g, 14.5 mmol) was dissolved in 100 mL of hexane. A 2 M ethereal solution of HCl (10.7 mL, 21.43 mmol) was added slowly, causing a white precipitate to form. After 2 hours, the solid was collected and dried under vacuum, to give the anilinium salt in 83% yield. The dimethylanilinium salt (0.5 g, 2.07 mmol) was suspended in 50 mL of cyclohexane and mixed with a suspension of Li-BF₂O in 50 mL cyclohexane. The mixture was heated at reflux for 1.5 hours, then cooled to ambient. The solvent was decanted and the remaining solid dissolved in methylene chloride, filtered and concentrated under vacuum to give the product as a tan solid.

[0345] 4-hexyl-*N,N*-dimethylanilinium-BF₂O (Hex-DMAH-BF₂O): The dimethylanilinium salt (0.5 g, 2.07 mmol) prepared above was suspended in 50 mL of cyclohexane and mixed with a suspension of Na-BF₂O in 50 mL cyclohexane. The mixture was heated at reflux for 1.5 hours, then cooled to ambient. The solution was filtered and the filtrate concentrated, then redissolved in methylene chloride, then filtered again. Upon concentration under vacuum, the product was obtained as a pale green solid.

[0346] *N,N*-dimethyl-4-octadecylbenzenaminium-BF₂O (OdDMAH-BF₂O): *N,N*-dimethyl-4-octadecylaniline (1.0 g, 2.67 mmol) was dissolved in 80 mL of hexane. A 2 M ethereal solution of HCl (1.6 mL, 3.2 mmol) was added slowly, causing a white precipitate to form. After stirring for 30 min, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the anilinium salt in 67% yield. The octadecylaniline HCl salt (400

mg, 0.97 mmol) was suspended in 50 mL of cyclohexane and combined with a suspension of Li-BF₂O (741 mg, 0.97 mmol) in 500 mL of cyclohexane. The mixture was heated at reflux for 2 hours, then cooled to ambient and filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered, and then concentrated to give the product as a white foam in 65% yield. ¹H NMR (500 MHz, CDCl₃, δ): 0.88 (t, *J* = 7.0 Hz, 3H), 1.26 (m, 30H), 1.61 (m, 2H), 2.68 (m, 2H), 3.29 (s, 6H), 7.24 (m, 2H), 7.36 (m, 2H).

[0347] ***N,N*-dimethyl-4-octadecylbenzenaminium-BF₂8 (OdDMAH-BF₂8):** The octadecylaniline HCl salt (360 mg, 0.87 mmol) described above was suspended in 50 mL of cyclohexane and combined with a suspension of Na-BF₂8 (918 mg, 0.87 mmol) in 500 mL of cyclohexane. The mixture was heated at reflux for 1.5 hours, then cooled to ambient and filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered, and then concentrated to give the product as a yellow oil in 23% yield. ¹H NMR (500 MHz, CDCl₃, δ): 0.88 (t, *J* = 7.0 Hz, 3H), 1.25 (m, 30H), 1.56 (m, 2H), 2.61 (m, 2H), 3.21 (s, 6H), 7.31 (m, 4H).

[0348] **Di(hydrogenated tallow)methylamine-BF₂8 (M2HTH-BF₂8):** Di(hydrogenated tallow)methylamine (M2HT) (10.0 g, 18.66 mmol) was dissolved in 600 mL of hexane. A 2 M ethereal solution of HCl (11.2 mL, 22.4 mmol) was added slowly, causing a white precipitate to form. After stirring for 1 hour, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the amine-HCl salt in 65% yield. The salt (500 mg, 0.873 mmol) was combined with Na-BF₂8 (914 mg, 873 mmol) and suspended in 100 mL of cyclohexane. The mixture was heated at reflux for 1.5 hours, then cooled to ambient temperature and filtered. The filtrate was concentrated under vacuum to give a viscous yellow oil in 61% yield. ¹H NMR (500 MHz, CDCl₃, δ): 0.88 (d, *J* = 6.6 Hz, 6H), 1.26 (m, 60H), 1.61 (m, 4H), 2.87 (d, *J* = 4.3 Hz, 3H), 3.03 (m, 2H), 3.16 (m, 2H), 5.44 (br s, 1H).

[0349] **Di(hydrogenated tallow)methylamine-BF₂0 (M2HTH-BF₂0):** The M2HT-HCl salt (1.1 g, 1.92 mmol) described above, was suspended in 100 mL of cyclohexane and combined with a suspension of Li-BF₂O (1.4 g, 1.92 mmol) in 100 mL of cyclohexane. The mixture was heated at reflux for 1.5 hours, then cooled to ambient and filtered. The filtrate was concentrated, redissolved in isohexane, filtered through Celite, and then concentrated to a viscous white oil to give the product in 67% yield. ¹H NMR (500 MHz, CDCl₃, δ): 0.85 (m, 6H), 1.22 (m, 60H), 1.61 (m, 4H), 2.85 (m, 3H), 3.01 (m, 2H), 3.13 (m, 2H).

[0350] ***N*-methyl-*N*-octadecylanilinium chloride (M_{Od}AH):** *N*-methylaniline (5.0 mL, 46.1 mmol), 1-bromooctadecane (17.2 g, 55 mmol), and potassium carbonate (19.1 g, 138 mmol) were dissolved in 200 mL of acetonitrile and heated at 80°C overnight. Once cooled,

the mixture was filtered and concentrated. The product was purified by silica gel column chromatography (10% acetone/isohexane). The alkylated aniline (2.0 g, 5.5 mmol) was dissolved in 300 mL of hexane and 2 M ethereal solution of HCl (3.3 mL, 6.6 mmol) was added slowly, causing a white precipitate to form. After stirring 1 hour, the white solid was collected,
5 washed with fresh hexane, and dried under vacuum to give the anilinium salt as a white powder in 80% yield.

[0351] *N*-methyl-*N*-octadecylanilinium-BF₂₀ (M_{Od}AH-BF₂₀): A slurry of the M_{Od}AH salt (500 mg, 1.3 mmol) and Li-BF₂₀ (959 mg, 1.3 mmol) was heated at reflux for 1.5 hr in 100 mL cyclohexane. Once cooled to ambient, the supernatant was decanted away
10 from the white, cloudy oil. The oil was dissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a clear, colorless oil in 49% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, *J* = 6.8 Hz, 3H), 1.24 (m, 30H), 1.42 (m, 1H), 1.57 (m, 1H), 3.28 (d, *J* = 5.2 Hz, 3H), 3.50 (m, 2H), 7.29 (m, 2H), 7.63 (m, 3H).

[0352] *N*-methyl-*N*-octadecylanilinium-BF₂₈ (M_{Od}AH-BF₂₈): A slurry of the above anilinium HCl salt (500 mg, 1.3 mmol) and Na-BF₂₈ (1.32 g, 1.3 mmol) in 100 mL cyclohexane was heated at reflux for 1.5 hours. Once cooled to ambient, the supernatant was decanted away from the resulting brown oily solid. The oily solid was dissolved in dichloromethane, filtered through Celite, and then dried under vacuum to give the product as a brown solid in 40% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, *J* = 6.9 Hz, 3H), 1.10-1.24
15 (m, 30H), 1.36 (m, 1H), 1.48 (m, 1H), 3.29 (d, *J* = 5.2 Hz, 3H), 3.51 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.55 (m, 3H).

[0353] *N*-decyl-*N*-methylanilinium chloride (M_DAH): *N*-methylaniline (5.0 mL, 46.1 mmol), 1-bromodecane (12.2 g, 55 mmol), and potassium carbonate (19.1 g, 138 mmol) were dissolved in 200 mL of acetonitrile and heated at 80°C overnight. Once cooled, the mixture
25 was filtered and concentrated. The product was purified by silica gel column chromatography (10% acetone/isohexane). The alkylated aniline (1.6 g, 6.4 mmol) was dissolved in 300 mL of hexane and 1 M ethereal solution of HCl (13.6 mL, 7.7 mmol) was added slowly, causing a white precipitate to form. After stirring for 30 min, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the anilinium salt as a white powder in 87%
30 yield.

[0354] *N*-decyl-*N*-methylanilinium-BF₂₀ (M_DAH-BF₂₀): The above M_DAH salt (0.5 g, 1.76 mmol) was suspended in 100 mL of cyclohexane and combined with a suspension of Li-BF₂₀ (741 mg, 0.97 mmol) in 100 mL of cyclohexane. The mixture was heated at reflux

for 1.5 hours, then cooled to ambient and the solvent decanted off. The remaining solid was dissolved in methylene chloride, filtered through Celite, and concentrated under vacuum to a tan solid.

5 **[0355] *N*-decyl-*N*-methylanilinium-BF28 (MDAH-BF28):** The above MDAH salt (0.5 g, 1.76 mmol) was suspended in 50 mL of cyclohexane and mixed with a suspension of Na-BF28 (1.84 g, 1.76 mmol) in 50 mL cyclohexane. The mixture was heated at reflux for 1.5 hours, then cooled to ambient and the solvent decanted off. The remaining solid was dissolved in methylene chloride, filtered through Celite, and concentrated under vacuum to a clear colorless oil.

10 **[0356] *N,N*-didecyl-4-methylanilinium chloride (DDTH):** Toluidine (5.0 g, 46.6 mmol), 1-bromodecane (103 mmol), and potassium carbonate (19.3 g, 140 mmol) were dissolved in 200 mL of acetonitrile and heated at 80°C overnight. Once cooled, the mixture was filtered and concentrated to a yellow oil. The product was purified by silica gel column chromatography (10% acetone/isohexane). The dialkylated toluidine (1.0 g, 2.5 mmol) was
15 dissolved in 100 mL of hexane and 2 M ethereal solution of HCl (1.5 mL, 3.1 mmol) was added slowly, causing a white precipitate to form. After stirring for 30 min, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the anilinium salt as a white powder in 91% yield.

20 **[0357] *N,N*-didecyl-4-methylanilinium-BF20 (DDTH-BF20):** The above DDTH salt (0.5 g, 1.17 mmol) was suspended in 100 mL of cyclohexane and combined with a suspension of Li-BF-20 (741 mg, 0.97 mmol) in 100 mL of cyclohexane. The mixture was heated at reflux for 2 h, then cooled to ambient and filtered. Concentration of the filtrate gave the product as a clear colorless oil.

25 **[0358] *N,N*-didecyl-4-methylanilinium-BF28 (DDTH-BF28):** The above DDTH salt (0.5 g, 1.17 mmol) was suspended in 100 mL of cyclohexane and mixed with a suspension of Na-BF28 (1.23g, 1.17 mmol) in 100 mL cyclohexane. The mixture was heated at reflux for 1.5 h, then cooled to ambient and the solvent decanted off. The remaining solid was dissolved in methylene chloride, filtered through Celite, and concentrated under vacuum to a tan solid.

30 **[0359] 4-butyl-*N,N*-didecylaniline (DDBA):** 4-Butylaniline (2.0 g, 13 mmol), 1-iododecane (7.9 g, 29 mmol), potassium carbonate (5.6 g, 40 mmol), and a catalytic amount of tetrabutylammonium iodide (approx. 100 mg) were combined in 150 mL of DMF and heated at 120°C for 16 hours. After cooling, the solution was diluted with water and extracted with three portions of diethyl ether. Combined organic fractions were washed twice with water and

once with brine, then dried with MgSO_4 , filtered and concentrated to an orange liquid. The dialkylated product was purified by silica gel chromatography using 2% ethyl acetate/isohexane as eluent. It was obtained as a yellow oil in 50% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 0.90 (m, 9H), 1.26 (m, 30H), 1.55 (m, 6H), 2.49 (m, 2H), 3.21 (m, 4H), 6.57 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H).

[0360] 4-butyl-*N,N*-didecylbenzenaminium-BF₂₀ (DDBAH-BF₂₀): The above 4-butyl-*N,N*-didecylaniline (2.94 g, 6.84 mmol) was dissolved in 150 mL of hexane. A 2 M ethereal solution of HCl (3.42 mL, 6.84 mmol) was added slowly, causing a white precipitate to form. After stirring for 3 hours, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the anilinium salt in 90% yield. A slurry of the aniline HCl salt (500 mg, 1.1 mmol) and Li-BF₂₀ (815 mg, 1.1 mmol) was heated at reflux for 1.5 hours in 150 mL cyclohexane. Once cooled to ambient, the mixture was filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a clear, colorless oil in 38% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 0.85 (t, J = 7.0 Hz, 6H), 0.95 (t, J = 7.3 Hz, 3H), 1.16 (m, 30H), 1.36 (m, 4H), 1.62 (m, 4H), 2.69 (m, 2H), 3.37 (m, 2H), 3.47 (m, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H).

[0361] 4-butyl-*N,N*-didecylbenzenaminium-BF₂₈ (DDBAH-BF₂₈): A slurry of the above aniline HCl salt (500 mg, 0.77 mmol) and Na-BF₂₈ (1.12 g, 0.77 mmol) in 100 mL cyclohexane was heated at reflux for 1.5 hours. Once cooled to ambient, the supernatant was decanted away from the resulting brown oil. The oil was concentrated, redissolved in dichloromethane, filtered through Celite, and then dried under vacuum to give the product as a brown solid in 55% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 0.83 (t, J = 7.1 Hz, 6H), 0.93 (t, J = 7.3 Hz, 3H), 1.11 (m, 30H), 1.34 (m, 4H), 1.57 (m, 2H), 1.67 (m, 2H), 2.63 (m, 2H), 3.31 (m, 2H), 3.45 (m, 2H), 7.29 (s, 4H).

[0362] 2,4,6-trimethyl-*N,N*-dioctadecylaniline (DOdM): 2,4,6-trimethylaniline (4.0 g, 30 mmol), 1-bromooctadecane (21.7 g, 65 mmol), potassium carbonate (8.18 g, 59 mmol), cesium carbonate (9.64 g, 30 mmol) and a catalytic amount of tetrabutylammonium iodide (approx. 100 mg) were combined in 250 mL of DMF and heated at 120°C for 48 hours. After cooling, the solution was diluted with water and extracted with three portions of diethyl ether. Combined organic fractions were washed twice with water and once with brine, then dried with MgSO_4 , filtered and concentrated to a white solid. The dialkylated product was purified by silica gel chromatography using 2% ethyl acetate/isohexane as eluent. It was obtained as a

white solid in 11% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, *J* = 6.8 Hz, 6H), 1.25 (m, 64H), 2.23 (s, 3H), 2.25 (s, 6H), 2.94 (m, 4H), 6.81 (s, 2H).

[0363] **2,4,6-trimethyl-*N,N*-dioctadecylbenzenaminium-BF₂8 (DOdMH-BF₂8):** The above 2,4,6-trimethyl-*N,N*-dioctadecylaniline (0.70 g, 1.1 mmol) was dissolved in 100 mL of
5 hexane and a 2 M ethereal solution of HCl (0.55 mL, 1.1 mmol) was added slowly. After stirring for 16 hours, a small amount of white solid was removed via filtration. The filtrate was dried under vacuum to give the anilinium salt in 88% yield. A slurry of the aniline HCl salt (400 mg, 0.59 mmol) and Na-BF₂8 (618 mg, 0.59 mmol) was heated at reflux for 1.5 hours in 100 mL cyclohexane. Once cooled to ambient, the mixture was filtered. The filtrate was
10 concentrated, redissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a viscous, orange oil in 85% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, *J* = 6.9 Hz, 6H), 1.24 (m, 62H), 1.60 (m, 2H), 2.30 (s, 3H), 2.43 (s, 3H), 2.46 (s, 3H), 3.60 (m, 2H), 3.68 (m, 2H), 6.98 (d, *J* = 10.7 Hz, 2H).

[0364] **2-methyl-*N,N*-dioctadecylaniline (DOdoT):** ortho-Toluidine (4.0 g, 37 mmol), 1-bromo-octadecane (27.4 g, 82 mmol), potassium carbonate (15.5 g, 112 mmol), and a catalytic amount of tetrabutylammonium iodide (approx. 100 mg) were combined in 250 mL of DMF and heated at 120°C for 24 hours. After cooling, the solution was diluted with water and extracted with three portions of diethyl ether. Combined organic fractions were washed twice with water and once with brine, then dried with MgSO₄, filtered and concentrated to a white
20 solid. The dialkylated product was purified by silica gel chromatography using 2% ethyl acetate/isohexane as eluent. It was obtained as a white solid in 10% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, *J* = 6.8 Hz, 6H), 1.24 (m, 60H), 1.39 (m, 4H), 2.28 (s, 3H), 2.88 (m, 4H), 6.95 (td, *J* = 1.3, 7.2 Hz, 1H), 7.06 (dd, *J* = 1.3, 7.9 Hz, 1H), 7.14 (m, 2H).

[0365] **2-methyl-*N,N*-dioctadecylbenzenaminium-BF₂8 (DOdoTH-BF₂8):** The above
25 2-methyl-*N,N*-dioctadecylaniline (2.0 g, 3.3 mmol) was dissolved in 100 mL of hexane. A 2 M ethereal solution of HCl (1.63 mL, 3.3 mmol) was added slowly, causing a white precipitate to form. After stirring for 1 hour, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the anilinium salt in 94% yield. A slurry of the aniline HCl salt (500 mg, 0.77 mmol) and Na-BF₂8 (807 mg, 0.77 mmol) was heated at reflux for 1.5 hours in
30 100 mL cyclohexane. Once cooled to ambient, the mixture was filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a viscous, brown oil in 82% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t,

$J = 6.9$ Hz, 6H), 1.24 (m, 64H), 2.48 (s, 3H), 3.40 (m, 2H), 3.60 (m, 2H), 7.25 (m, 1H), 7.25 (m, 1H), 7.46 (m, 2H).

[0366] **2-isopropyl-*N,N*-dioctadecylaniline (DODPA):** 2-isopropylaniline (4.0 g, 30 mmol), 1-bromooctadecane (21.7 g, 65 mmol), potassium carbonate (12.3 g, 89 mmol), and a catalytic amount of tetrabutylammonium iodide (approx. 100 mg) were combined in 250 mL of DMF and heated at 120°C for 48 hours. After cooling, the solution was diluted with water and extracted with three portions of diethyl ether. Combined organic fractions were washed twice with water and once with brine, then dried with MgSO_4 , filtered and concentrated to a white solid. The dialkylated product was purified by silica gel chromatography using 2% ethyl acetate/isohexane as eluent. It was obtained as a white solid in 7% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 0.89 (t, $J = 6.7$ Hz, 6H), 1.16 (d, $J = 6.9$ Hz, 6H), 1.25 (m, 64H), 2.84 (m, 4H), 3.69 (H, $J = 6.8$ Hz, 1H), 7.12 (m, 3H), 7.25 (m, 1H).

[0367] **2-isopropyl-*N,N*-dioctadecylbenzenaminium-BF₂₈ (DODPAH-BF₂₈):** The above 2-isopropyl-*N,N*-dioctadecylaniline (0.54 g, 0.85 mmol) was dissolved in 50 mL of hexane. A 2 M ethereal solution of HCl (0.43 mL, 0.85 mmol) was added slowly. After stirring for 30 minutes, a white precipitate formed. After stirring for an additional 16 hours, the white solid was collected, washed with fresh hexane, and dried under vacuum to give the anilinium salt in 89% yield. A slurry of the aniline HCl salt (510 mg, 0.75 mmol) and Na-BF₂₈ (790 mg, 0.75 mmol) was heated at reflux for 1.5 hours in 100 mL cyclohexane. Once cooled to ambient, the mixture was filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a viscous, brown oil in 80% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 0.87 (t, $J = 6.7$ Hz, 6H), 1.24 (m, 64H), 1.31 (d, $J = 6.5$ Hz, 6H), 3.24 (br s, 1H), 3.38 (m, 2H), 3.61 (m, 2H), 7.21 (d, $J = 8.3$ Hz, 1H), 7.42 (m, 1H), 7.52 (m, 2H).

[0368] ***N,N*-dioctadecyl-4-methylaniline (DODT):** *p*-Toluidine (1.5 g, 14.0 mmol), bromooctadecane (10.2 g, 31 mmol), potassium carbonate (5.8 g, 42 mmol), and a catalytic amount of tetrabutylammonium iodide (approx. 100 mg) were combined in 150 mL of *N,N*-dimethylformamide (DMF) and heated at 120°C for 3 days. After cooling, the solution was diluted with water and extracted with three portions of ethyl acetate. Combined organic fractions were washed twice with water and once with brine, then dried (MgSO_4), filtered, and concentrated to a yellow solid. The dialkylated product was purified by silica gel chromatography using isohexane as eluent. It was obtained as a white powder in 20% yield.

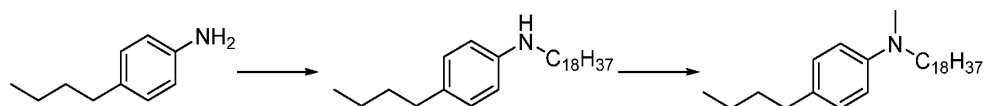
¹H NMR (400 MHz, CDCl₃, δ): 0.90 (t, *J* = 6.7 Hz, 6H), 1.25 (m, 64H), 2.23 (s, 3H), 3.20 (m, 4H), 6.56 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H).

[0369] 4-methyl-*N,N*-dioctadecylbenzenaminium-BF₂₀ (DOdTH-BF₂₀): The above dioctadecyl toluidine (1.68 g, 3 mmol) was dissolved in 150 mL of hexane. A 2 M ethereal solution of HCl (1.3 mL, 3 mmol) was added slowly, causing a white precipitate to form. After stirring for 30 min, the white solid was collected, washed with fresh hexane, and dried under vacuum. A slurry of dioctadecyl toluidine HCl salt (500 mg, 0.77 mmol) and Li-BF₂₀ (959 mg, 0.77 mmol) in 100 mL of cyclohexane was heated at reflux for 1.5 hours. Once cooled to ambient temperature, the mixture was filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a white powder in quantitative yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (d, *J* = 6.9 Hz, 6H), 1.20 (m, 64H), 2.48 (s, 3H), 3.49 (m, 4H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H).

[0370] 4-methyl-*N,N*-dioctadecylbenzenaminium-BF₂₈ (DOdTH-BF₂₈): A slurry of the above toluidine HCl salt (500 mg, 0.77 mmol) and Na-BF₂₈ (847 mg, 0.77 mmol) in 100 mL of cyclohexane was heated at reflux for 1.5 hours. Once cooled to ambient temperature, the mixture was filtered. The filtrate was concentrated, redissolved in dichloromethane, filtered through Celite, and then concentrated to give the product as a clear brownish oil. ¹H NMR (400 MHz, CDCl₃, δ): 0.86 (d, *J* = 7.0 Hz, 6H), 1.16 (m, 60H), 1.67 (m, 4H), 2.39 (s, 3H), 3.31 (m, 2H), 3.45 (m, 2H), 7.28 (s, 4H).

[0371] 4-Undecyl-*N*-methyl-*N*-octadecylanilinium-BF₂₈ (UOMAH-BF₂₈): The *N*-methyl-4-octadecyl-*N*-undecylaniline HCl salt (1.0 g, 1.8 mmol) described above was suspended in 75 mL of cyclohexane and combined with Na-BF₂₈ (1.9 g, 1.8 mmol). The mixture was heated at reflux for 1.5 hours, then cooled to ambient and filtered. The filtrate was concentrated to give the product as a sticky, tan oil in 73% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, *J* = 6.5 Hz, 6H), 1.25 (m, 46H), 1.53 (m, 4H), 2.61 (m, 2H), 3.19 (s, 3H), 3.42 (m, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H).

[0372] 4-butyl-*N*-octadecylaniline:

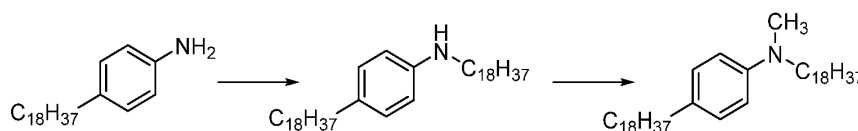


4-butylaniline (5.0 g, 33.5 mmol) was combined with octadecylbromide (11.1 g, 33.5 mmol), potassium carbonate (11.5 g, 83.7 mmol), and tetrabutylammonium iodide (approx. 100 mg) in 300 mL of acetonitrile was heated at 80°C overnight. The mixture was then filtered and concentrated, then purified by silica gel column chromatography (10% acetone/isohexane) to

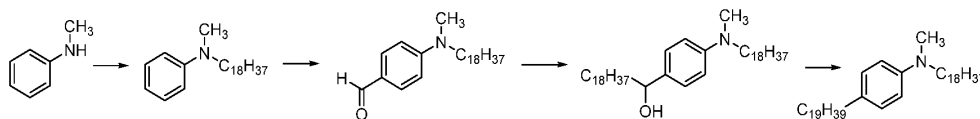
give the product in 57% yield as a white solid. $R_f = 0.79$ (10:90 acetone:isohexane); ^1H NMR (500 MHz, CDCl_3 , δ): 0.90 (m, 6H), 1.26 (m, 32H), 1.56 (m, 4H), 2.50 (t, $J = 7.7$ Hz, 2H), 3.08 (t, $J = 7.7$ Hz, 2H), 6.58 (d, $J = 8.5$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H).

- [0373] **4-butyl-*N*-methyl-*N*-octadecylaniline:** The above aniline (7.7 g, 19.1 mmol), methyl iodide (2.28 mL, 47.9 mmol), potassium carbonate (6.6 g, 47.9 mmol), and tetrabutylammonium iodide (approx. 100 mg) were combined in 200 mL of acetonitrile. The mixture was heated at 60°C overnight, then filtered and concentrated. The product was purified by silica gel chromatography (isohexane – 10% diethyl ether/isohexane) and obtained as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3 , δ): 0.91 (m, 6H), 1.26 (m, 32H), 1.55 (m, 4H), 2.51 (t, $J = 7.7$ Hz, 2H), 2.89 (s, 3H), 3.26 (t, $J = 7.5$ Hz, 2H), 6.65 (m, 2H), 7.05 (m, 2H).

[0374] ***N*,4-diocadecylaniline:**



- 4-octadecylaniline (7.5 g, 21.7 mmol), bromooctadecane (7.2 g, 21.7 mmol), and triethylamine (6.0 mL, 43.4 mmol) were dissolved in 200 mL of DMF. The reaction was heated at reflux overnight. A precipitate formed upon cooling which was collected and purified by column chromatography (isohexane to 5% acetone/isohexane). Product can alternatively be obtained by adding warm water and extracting with ethyl acetate: $R_f = 0.55$ (5:95 acetone:isohexane); ^1H NMR (500 MHz, CDCl_3 , δ): 0.88 (t, $J = 7.0$ Hz, 6H), 1.26 (m, 61H), 1.62 (m, 4H), 2.50 (t, $J = 7.5$ Hz, 2H), 2.10 (t, $J = 7.2$ Hz, 2H), 6.68 (m, 2H), 7.02 (d, $J = 8.5$ Hz, 2H).
- [0375] ***N*-methyl-*N*,4-diocadecylaniline:** The above aniline (5.0 g, 8.3 mmol) was dissolved in 200 mL of THF. Sodium hydride (95%, 253 mg, 10.0 mmol) was added slowly and the mixture stirred for over 1 hour. Methyl iodide (1.52 mL, 24.4 mmol) was added and the reaction allowed to stir at ambient overnight before quenching with ice. The mixture was extracted with three portions of ethyl acetate and the combined organic layers washed with brine, dried (MgSO_4), filtered, and concentrated. The solid residue was purified by silica gel column chromatography (5% acetone/isohexane) to give the product as a white solid in 41% yield: ^1H NMR (500 MHz, CDCl_3 , δ): 0.88 (m, 6H), 1.27 (m, 61H), 1.57 (m, 4H), 2.51 (m, 2H), 2.90 (s, 1H), 3.26 (t, $J = 7.5$ Hz, 2H), 6.65 (m, 2H), 7.05 (m, 2H).

[0376] N-methyl-4-nonadecyl-N-octadecylaniline:

[0377] N-methyl-N-octadecylaniline: N-methylaniline (10.2 g, 96 mmol), bromooctadecane (38.4 g, 115 mmol), and triethylamine (19.9 mL, 144 mmol) were dissolved in 400 mL of DMSO and heated overnight at 100°C. The solution was diluted with water and extracted three times with ethyl acetate. The organic fractions were combined, rinsed with brine, dried with MgSO₄ and concentrated to yield a yellow oily solid. The product was purified by silica gel chromatography (2% ethyl acetate/isohehexane) and isolated as a white solid. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, J = 8.0 Hz, 3H), 1.25 (m, 32H), 1.56 (m, 2H), 2.92 (s, 3H), 3.29 (m, 2H), 6.68 (m, 3H), 7.22 (m, 2H).

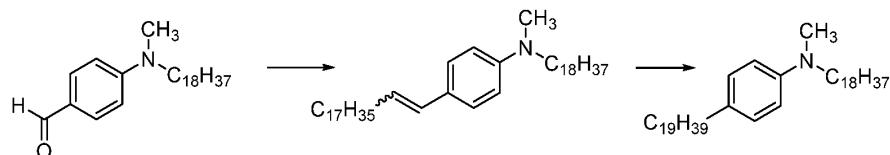
[0378] Large Scale: N-methylaniline (30.0 g, 280 mmol), bromooctadecane (130.6 g, 392 mmol), and triethylamine (58.2 mL, 420 mmol) were dissolved in 500 mL of DMF and heated for over 48 h at 100°C. The solution was diluted with hot water and extracted twice with ethyl acetate. Combined organic fractions were washed with 2 portions of hot brine, dried over MgSO₄, and concentrated to a pale yellow solid. NMR analysis revealed the presence of <10% N-methylaniline, which was removed by vacuum distillation with a Kugelrohr at 125°C. ¹³C NMR: 14.18, 22.76, 26.70, 27.26, 29.44 – 29.77 (12C), 32.00, 28.31, 52.90, 112.12 (2C), 115.83, 129.16 (2C), 149.39.

[0379] 4-(methyl(octadecyl)amino)benzaldehyde: To DMF (0.34 mL, 4.4 mmol) cooled to 0°C, was added phosphoryl chloride (0.49 mL, 5.3 mmol) dropwise. The reaction was warmed to room temperature over 30 min, turning bright red. It was cooled to 0°C and a solution of the above alkylated aniline (1.6 g, 4.4 mmol) in 20 mL of THF added. After stirring for 20 min, the reaction was heated at 80°C for 2 hours. The cooled solution was quenched by dropwise addition of 20 mL of 1M KOH. The mixture was extracted with 3x 15 mL EtOAc. The organic fractions were combined, rinsed with brine, dried with MgSO₄, and concentrated. The orange residue was purified by silica gel chromatography (2% ethyl acetate/isohehexane) and isolated as a pale pink crystalline solid in 70% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, J = 7.0 Hz, 3H), 1.25 (m, 30H), 1.61 (m, 2H), 3.04 (s, 3H), 3.39 (t, J = 8.0 Hz, 2H), 6.69 (d, J = 7.0 Hz, 2H), 7.72 (d, J = 7.0 Hz, 2H), 9.72 (s, 1H).

[0380] 1-(4-(methyl(octadecyl)amino)phenyl)nonadecan-1-ol: Bromooctadecylmagnesium chloride was prepared from bromooctadecane (1.03 g, 2.5 mmol)

and magnesium turnings (88 mg, 3.5 mmol) in THF. It was filtered into a solution of the above aminobenzaldehyde (1.0 g, 2.5 mmol) in THF and stirred at ambient temperature overnight. The reaction was quenched with water and extracted with ethyl acetate. Organic fractions were combined, rinsed with brine, dried with MgSO_4 , filtered and concentrated. The product was used without further purification. ^1H NMR (400 MHz, CDCl_3 , δ): 0.88 (m, 6H), 1.24 - 1.80 (m, 67H), 2.92 (s, 3H), 3.28 (t, $J = 8.0$ Hz, 2H), 4.55 (br s, 1H), 6.66 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H).

[0381] *N*-methyl-4-nonadecyl-*N*-octadecylaniline (NOMA): To the above alcohol (1.6 g, 2.5 mmol) dissolved in 50 mL of THF was added 27 mg of 10% Pd/C and 0.5 mL conc. HCl. The reaction was stirred under an atmosphere of hydrogen for over 48 hours. It was filtered through Celite, concentrated, and purified by silica gel chromatography (2% ethyl acetate/isohehexane). ^1H NMR (400 MHz, CDCl_3 , δ): 0.89 (m, 6H), 1.27 (m, 62H), 1.56 (m, 4H), 2.50 (m, 2H), 2.90 (s, 3H), 3.26 (m, 2H), 6.65 (m, 2H), 7.04 (m, 2H).



[0382] *N*-methyl-4-nonadecyl-*N*-octadecylanilinium tetrakis(perfluoronaphthalen-2-yl)borate (NOMAH-BF28): The above *N*-methylaniline (15 g, 24 mmol) was dissolved in 250 mL of hexane in a 500 mL round bottom flask. A 2 M solution of HCl in ether (12 mL, 24 mmol) was added slowly, causing a white precipitate to appear, and the mixture was allowed to stir overnight. The solid was collected by gravity filtration, washed with hexane, and dried under vacuum. The HCl salt (13.1 g, 20 mmol) and Na-BF28 (20.7 g, 20 mmol) was heated at reflux for 1.5 hours in 100 mL of cyclohexane. Once cooled to ambient, the mixture was filtered and concentrated to a brown oil. The oil was redissolved in hexane and filtered through Celite. The filtrate was concentrated to give the product as a thick oil in 57% yield.

[0383] *N*-methyl-4-nonadecyl-*N*-octadecylanilinium tetrakis(pentafluorophenyl)borate (NOMAH-BF20): Made from *N*-methyl-4-nonadecyl-*N*-octadecylanilinium chloride (1.50 g, 2.26 mmol) and Li-BF20 (1.72 g, 2.26 mmol) in a similar procedure as described above. The product was obtained as a colorless oil in 61% yield.

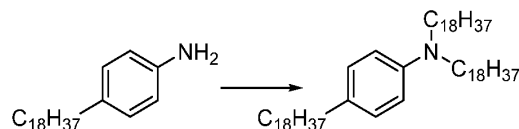
[0384] (*N*-methyl-4-(nonadecenyl)-*N*-octadecylaniline: 4-(methyl(octadecyl)amino)benzaldehyde (4.1 g) was refluxed with octadecyltriphenylphosphonium bromide (1.2 equiv. prepared from bromooctadecane and

triphenylphosphine) and potassium tert-butoxide (1.1 equiv.) in THF overnight. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, *J* = 6.6 Hz, 6H), 1.26 (m, 62H), 2.35 (m, 2H), 2.93 (s, 3H), 3.29 (m, 2H), 5.44 (m, 1H), 6.27 (d, *J* = 11.6 Hz, 1H), 6.63 (m, 2H), 7.19 (m, 2H).

- [0385] ***N,N*,4-trioctadecylbenzenaminium tetrakis(perfluoronaphthalen-2-yl)borate (Od3H-BF28):** The above aniline (900 mg, 1.0 mmol) was dissolved in hexanes in a 100 mL round bottom flask. A 2 M solution of HCl in ether (0.52 mL, 1.0 mmol) was added slowly, after which a white precipitate immediately appeared. The solution was stirred for 1 hour. The solid was isolated via filtration, rinsed twice with hexanes and dried in vacuo. The HCl salt (500 mg, 0.56 mmol) and Na-BF₂₈ (590 mg, 0.56 mmol) was heated at reflux for 1.5 hours in 10 75 mL cyclohexane. Once cooled to ambient, the mixture was filtered and concentrated to a brown oil. The oil was redissolved in methylene chloride and filtered through Celite. The filtrate was concentrated to give the product in 89% yield.

- [0386] ***N*-methyl-4-nonadecyl-*N*-octadecylaniline (NOMA):** The above aniline (4.4 g) and 10% palladium on carbon (880 mg) were combined in THF/methanol (17:1) and 15 hydrogenated at 40 psi hydrogen for 1 hour.

[0387] ***N,N*,4-trioctadecylaniline:**



- Obtained from the reaction of 4-octadecylaniline and bromooctadecane in the presence of base (triethylamine or potassium carbonate). ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (m, 9H), 1.26 20 (m, 94H), 1.58 (m, 2H), 2.62 (m, 2H), 3.41 (br s, 4H), 7.16 (m, 2H), 7.28 (m, 2H).

- [0388] **4-butyl-*N*-methyl-*N*-octadecylanilium tetrakis(perfluoronaphthalen-2-yl)borate (MObAH-BF28):** The above *N,N*-dialkylated aniline (1.0 g, 2.4 mmol) was dissolved in 50 mL of hexane. A 2 M solution of HCl in ether (1.4 mL, 2.8 mmol) was added slowly and the reaction stirred overnight. Upon concentrating to half volume, a white 25 precipitate formed. This solid was collected and dried under vacuum. The HCl salt (500 mg, 1.1 mmol) and Na-BF₂₈ (4.15 g, 1.1 mmol) was heated at reflux for 1.5 hours in 75 mL cyclohexane. Once cooled to ambient, the mixture was filtered. The filtrate was concentrated to give the product as a brown oil in 65% yield.

Solubility Studies of the Activators

- 30 [0389] **Procedure for solid activators.** A saturated solution of each of the solid ammonium borate activators was prepared by stirring an excess of the activator with either

isohexane or methylcyclohexane solvent for several hours at 25°C. The mixture was then filtered and a known volume of the filtrate was evaporated to dryness in a tared vial. The vial was then weighed to determine the mass of activator that was dissolved in the aliquot. The concentration of the saturated solution is presented in millimoles of activator per liter of solution (mM).

[0390] Procedure for activators that form emulsions. A saturated solution of the activator was prepared by slowly adding the solvent to a pre-weighed amount of the activator. The final volume was determined as the minimum amount of solvent required to convert the emulsion into a homogeneous solution. The concentration of the saturated solution is presented in millimoles of activator per liter of solution (mM). Alternatively, an emulsion of the activator was prepared by adding the solvent to an excess amount of activator. The resulting emulsion was separated from the undissolved solids by decanting the emulsion into a tared vial. Solvent was then added dropwise until the emulsion became homogeneous. The mass of the final solution was measured and then the solvent was evaporated to dryness to obtain the mass of the activator. The concentration of the saturated solution is presented in millimoles of activator per liter of solution (mM).

[0391] Solubility of Activators. The solubility of the activators is summarized in Table 1. The activators used for this study had a variety of ammonium groups (cations) and a BF20 borate or BF28 borate. In general, the effect of the borate selection on solubility of an activator was relatively minor compared to the effect of the ammonium group on solubility of an activator. In addition, the tetrakis(perfluoronaphthyl) borate (BF28) did not substantially hinder activator solubility in an aliphatic hydrocarbon solvent, as compared to BF20, even though BF28 has four more aryl rings and eight more fluorine atoms than BF20. The activators that had solubility of >10 mM at 25°C in either isohexane or methylcyclohexane (MeCy) were M2HTH-BF20, M2HTH-BF28, DOdTH-BF20, DOdTH-BF28, DDHxAH-BF20, and DDHxAH-BF28. Those with very high solubility in methylcyclohexane (>100 mM) were M2HTH-BF20, M2HTH-BF28, DOdTH-BF20, and DOdTH-BF28. In comparison, the following activators demonstrated solubility of <10 mM under identical conditions: DMAH-BF20, DMAH-BF28, DDTH-BF20, DDTH-BF28, MDAH-BF20, MDAH-BF28, OdDMAH-BF20, and OdDMAH-BF28. In general the solubility of the ammonium borate activators in aliphatic hydrocarbon solvents increases with the number of aliphatic carbons in the ammonium group.

Table 1. Solubility data of ammonium borate activators

Activator	Solubility limit in i-hexane (mM at 25°C)	Solubility limit in MeCy (mM at 25°C)	Solubility limit in i-hexane (wt% at 25°C)	Solubility limit in MeCy (wt% at 25°C)	Number of aliphatic carbons in ammonium group
DMAH-BF20	<0.1	<0.1	<0.1	<0.1	2
DMAH-BF28	<0.1	<0.1	<0.1	<0.1	2
MDAH-BF20	1.3	1.4	0.18	0.17	11
MDAH-BF28	0.9	1.7	0.12	0.21	11
OdDMAH-BF20	0.8	7.9	0.10	1.1	20
OdDMAH-BF28	<0.1	1.9	<0.1	0.3	20
DDTH-BF20	1.5	1.7	0.22	0.21	21
DDTH-BF28	1.8	3.7	0.35	0.63	21
DDBAH-BF20	2.0	21	0.32	3.0	24
DDBAH-BF28	2.2	17	0.47	3.3	24
DOdoTH-BF28	3.0	>1.9E+02	0.73	>40	37
DOdoTH-BF20	19	1.1E+02	3.7	19	37
DOdoTH-BF28	1.2E+02	1.6E+02	29	35	37
M2HTH-BF20	9.6	2.0E+02	1.7	31	37
M2HTH-BF28	6.5	1.2E+02	1.5	25	37
DOdMH-BF28	7.6	>1.8E+02	0.70	>42	39
DOdPAH-BF28	2.9	>2.0E+02	1.9	>40	39
NOMAH-BF28	>213	>227	>52	>49	37

Polymerization in Parallel Pressure Reactor

[0392] Solvents, polymerization-grade toluene, and isohexane were supplied by ExxonMobil Chemical Company and purified by passing through a series of columns: two 500 cc Oxyclear cylinders in series from Labclear (Oakland, Calif.), followed by two 500 cc columns in series packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and two 500 cc columns in series packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company). 1-octene (C8) and 1-hexene (C6) (98%, Aldrich Chemical Company) were dried by stirring over NaK overnight followed by filtration through basic alumina (Aldrich Chemical Company, Brockman Basic 1).

[0393] Polymerization-grade ethylene (C2) was used and further purified by passing the gas through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, CA) followed by a 500 cc column packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical

Company) and a 500 cc column packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company).

[0394] Polymerization grade propylene (C3) was used and further purified by passing it through a series of columns: 2250 cc Oxiclear cylinder from Labclear followed by a 2250 cc
5 column packed with 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then two 500 cc columns in series packed with 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then a 500 cc column packed with Selexsorb CD (BASF), and finally a 500 cc column packed with Selexsorb COS (BASF).

[0395] Solutions of the metal complexes and activators were prepared in a drybox using
10 toluene or methylcyclohexane. Concentrations were typically 0.2 mmol/L. Tri-n-octylaluminum (TNOAL, neat, AkzoNobel) was typically used as a scavenger. Concentration of the TNOAL solution in toluene ranged from 0.5 to 2.0 mmol/L.

[0396] Polymerizations were carried out in a parallel pressure reactor, as generally described in US Pat Nos. 6,306,658; 6,455,316; 6,489,168; WO 00/09255; and Murphy, V. et
15 al. (2003) "A Fully Integrated High-Throughput Screening Methodology for the Discovery of New Polyolefin Catalysts: Discovery of a New Class of High Temperature Single-Site Group (IV) Copolymerization Catalysts," *J. Am. Chem. Soc.*, v.125, pp. 4306-4317, each of which is fully incorporated herein by reference. The experiments were conducted in an inert atmosphere (N₂) drybox using autoclaves equipped with an external heater for temperature control, glass
20 inserts (internal volume of reactor = 23.5 mL for C2 and C2/C8; 22.5 mL for C3 runs), septum inlets, regulated supply of nitrogen, ethylene and propylene, and equipped with disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen at 110°C or 115°C for 5 hours and then at 25°C for 5 hours. Although the specific quantities, temperatures, solvents, reactants, reactant ratios, pressures, and other variables are
25 frequently changed from one polymerization run to the next, the following describes a typical polymerization performed in a parallel pressure reactor.

[0397] Catalyst systems dissolved in solution were used in the polymerization examples below, unless specified otherwise.

[0398] **Ethylene-Octene Copolymerization (EO).** A pre-weighed glass vial insert and
30 disposable stirring paddle were fitted to each reaction vessel of the reactor, which contains 48 individual reaction vessels. The reactor was then closed and purged with ethylene. Each vessel was charged with enough solvent (typically isohexane) to bring the total reaction volume, including the subsequent additions, to the desired volume, typically 5 mL. 1-octene, if required,

was injected into the reaction vessel and the reactor was heated to the set temperature and pressurized to the predetermined pressure of ethylene, while stirring at 800 rpm. The aluminum compound (such as tri-n-octylaluminum) in toluene was then injected as scavenger followed by addition of the activator solution (typically 1.0-1.2 molar equivalents).

- 5 **[0399]** The catalyst (and activator solutions for Run A) were all prepared in toluene. The catalyst solution (typically 0.020-0.080 μ mol of metal complex) was injected into the reaction vessel and the polymerization was allowed to proceed until a pre-determined amount of ethylene (quench value typically 20 psi) had been used up by the reaction. Alternatively, the reaction may be allowed to proceed for a set amount of time (maximum reaction time typically
- 10 30 minutes). Ethylene was added continuously (through the use of computer controlled solenoid valves) to the autoclaves during polymerization to maintain reactor gauge pressure (P setpt, $\pm$ 2 psig) and the reactor temperature (T) was monitored and typically maintained within $\pm$ 1°C. The reaction was quenched by pressurizing the vessel with compressed air. After the reactor was vented and cooled, the glass vial insert containing the polymer product and solvent
- 15 was removed from the pressure cell and the inert atmosphere glove box, and the volatile components were removed using a Genevac HT-12 centrifuge and Genevac VC3000D vacuum evaporator operating at elevated temperature and reduced pressure. The vial was then weighed to determine the yield of the polymer product. The resultant polymer was analyzed by Rapid GPC (see below) to determine the molecular weight, by FT-IR (see below) to determine percent
- 20 octene incorporation, and by DSC (see below) to determine melting point (T_m).

[0400] Equivalence is determined based on the mole equivalents relative to the moles of the transition metal in the catalyst complex.

- [0401] RUN A: Propylene Homopolymerization (PP).** The reactor was prepared as described above and purged with propylene. For the examples in Table 2, the catalyst and
- 25 activator solutions were prepared in toluene. For the examples in Table 3, the solutions of MCN-1, DOdTH-BF28 and M2HTH-BF28 were prepared in methylcyclohexane while DMAH-BF28 was prepared in toluene. Isohexane was then injected into each vessel at room temperature followed by a predetermined amount of propylene gas. The reactor was heated to the set temperature while stirring at 800 rpm, and the scavenger, activator and catalyst solutions
- 30 were injected sequentially to each vessel. The polymerization was allowed to proceed as described previously.

[0402] Polymer Characterization. Polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich)

containing 2,6-di-tert-butyl-4-methylphenol (BHT, 99% from Aldrich) at 165°C in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was between 0.1 to 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB.

[0403] To determine various molecular weight related values by GPC, high temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as generally described in US Pat. Nos. 6,491,816; 6,491,823; 6,475,391; 6,461,515; 6,436,292; 6,406,632; 6,175,409; 6,454,947; 6,260,407; and 6,294,388; each of which is fully incorporated herein by reference. This apparatus has a series of three 30 cm x 7.5 mm linear columns, each containing PLgel 10 μ m, Mix B. The GPC system was calibrated using polystyrene standards ranging from 580 to 3,390,000 g/mol. The system was operated at an eluent flow rate of 2.0 mL/minutes and an oven temperature of 165°C. 1,2,4-trichlorobenzene was used as the eluent. The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 0.28 mg/mL and 400 μ L of a polymer solution was injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. The molecular weights presented are relative to linear polystyrene standards and are uncorrected, unless indicated otherwise.

[0404] Differential Scanning Calorimetry (DSC-Procedure 1) measurements were performed on a TA-Q100 instrument to determine the melting point (T_m) of the polymers. Samples were pre-annealed at 220°C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/min and then cooled at a rate of 50°C/min. Melting points were collected during the heating period.

[0405] The weight percent of ethylene incorporated in polymers was determined by rapid FT-IR spectroscopy on a Bruker Equinox 55+ IR in reflection mode. Samples were prepared in a thin film format by evaporative deposition techniques. FT-IR methods were calibrated using a set of samples with a range of known wt% ethylene content. For ethylene-1-octene copolymers, the wt% octene in the copolymer was determined via measurement of the methyl deformation band at ~ 1375 cm^{-1} . The peak height of this band was normalized by the combination and overtone band at ~ 4321 cm^{-1} , which corrects for path length differences.

[0406] A series of propylene polymerizations were performed in parallel pressure reactors (PPRs) developed by Symyx Technologies, Inc. In these polymerizations, the metallocene rac-dimethylsilyl-bis(indenyl)hafnium dimethyl (**MCN-1**) was used along with several different ammonium borate activators. Polymerizations were performed at 85°C and 100°C. The data and run conditions are shown in Table 2.

Table 2. Data for the polymerization of propylene at different temperatures.

<i>General conditions:</i> MCN-1 = 20 nmol; activator = 20 nmol; solvent = isohexane; total volume = 5 mL; tri(n-octyl)aluminum = 500 nmol.										
run	catalyst	activator	T (°C)	time (s)	yield (mg)	P (psi)	activity (kg/mmol /h)	Mw (g/mol)	Mn (g/mol)	T _m (°C)
1	MCN-1	DMAH-BF28	85	121	92	135	138	217,267	127,899	132
2	MCN-1	Hex-DMAH-BF20	85	96	102	135	192	95,168	58,293	129
3	MCN-1	Hex-DMAH-BF20	85	100	83	135	150	89,028	56,814	128
4	MCN-1	Hex-DMAH-BF20	85	103	94	135	163	96,937	55,573	129
5	MCN-1	M2HTH-BF20	85	420	43	135	18	106,312	66,842	129
6	MCN-1	M2HTH-BF20	85	263	56	135	39	120,173	81,599	130
7	MCN-1	M2HTH-BF20	85	330	52	135	28	109,915	69,782	128
8	MCN-1	M2HTH-BF28	85	167	69	135	75	234,285	141,653	133
9	MCN-1	M2HTH-BF28	85	200	83	135	75	227,845	140,560	132
10	MCN-1	M2HTH-BF28	85	213	66	135	55	241,256	155,512	133
11	MCN-1	DMAH-BF28	100	350	59	150	30	110,008	68,702	125
12	MCN-1	DMAH-BF28	100	212	73	150	61	101,407	54,859	124
13	MCN-1	DMAH-BF28	100	103	101	150	176	86,882	52,491	121
14	MCN-1	Hex-DMAH-BF20	100	283	74	150	47	46,035	27,303	114
15	MCN-1	Hex-DMAH-BF20	100	181	82	150	81	46,835	25,582	115
16	MCN-1	Hex-DMAH-BF20	100	188	79	150	75	43,318	26,095	114
17	MCN-1	M2HTH-BF20	100	275	71	150	46	45,705	29,527	119
18	MCN-1	M2HTH-BF20	100	367	61	150	30	46,509	24,838	119
19	MCN-1	M2HTH-BF20	100	375	75	150	36	44,129	24,377	119
20	MCN-1	M2HTH-BF28	100	280	77	150	49	102,926	62,391	125
21	MCN-1	M2HTH-BF28	100	247	82	150	60	99,387	57,774	124
22	MCN-1	M2HTH-BF28	100	188	101	150	96	95,788	58,463	124

[0407] *Polymerization at 85°C (Table 2, Entries 1-10)* Runs 2-7 show the results obtained for the activators BuDMAH-BF20 and M2HTH-BF20. The data from these runs may be compared to those of runs 1, 8, 9, and 10 which used activators DMAH-BF28 and M2HTH-BF28. The data show that runs 2-7 produced polymer that has Mw in the range of 95-120 kg/mol and a melting point in the range of 128-130°C. In comparison, runs 1, 8, 9, and 10 produced polymer that has Mw in the range of 217-241 kg/mol and a melting point in the range of 132-133°C. These data show that the catalyst(s) formed from **MCN-1** and activators having the BF28 anion have improved ability to produce polymer of high molecular weight and high

melting point, as compared to polymer produced from **MCN-1** and activators having the BF20 anion.

[0408] *Polymerization at 100°C (Table 2, Entries 11-22)* Runs 14-19 show the results obtained for the activators BuDMAH-BF20 and M2HTH-BF20. The data from these runs may be compared to those of runs 11-13 and 20-22 which used activators DMAH-BF28 and M2HTH-BF28. The data show that runs 14-19 produced polymer that has Mw in the range of 43-47 kg/mol and a melting point in the range of 114-119°C. In comparison, runs 11-13 and 20-22 produced polymer that has Mw in the range of 86-110 kg/mol and a melting point in the range of 121-125°C. These data show that the catalyst(s) formed from **MCN-1** and activators that feature the BF28 anion have improved ability to produce polymer of high molecular weight and high melting point, as compared to polymer produced from **MCN-1** and activators having the BF20 anion.

[0409] In addition, as shown in Table 2, the polypropylene polymers formed by the catalyst systems having catalyst **MCN-1** and the different activators of formula (I) produce high molecular weight polymers. The propylene polymer formed at 85°C or 100°C by the catalyst system having catalyst **MCN-1** and M2HTH-BF28 as the activator has a higher Mw value as compared to M2HTH-BF20 (Entries 5 to 7 versus 8 to 10; Entries 17 to 19 versus 20 to 22). The catalyst system having catalyst **MCN-1** with M2HTH-BF28 as the activator has the highest Mw of greater than 200,000, an Mw/Mn value of about 1.55, and a T_m of 132°C-133°C. Furthermore, activators containing BF28 have a higher productivity than activators containing-BF20, with yields of the polymerizations being greater for activators containing-BF28. Furthermore, at 85°C, activators containing-BF28 generally had a higher productivity than activators containing-BF20, with average yields of the polymerizations being 73 g versus 50.3 g, respectively. Furthermore, at 100°C, activators containing-BF28 generally had a higher productivity than activators containing-BF20, with average yields of the polymerizations being 87 g versus 69 g, respectively.

[0410] Figure 1 is a graph illustrating polymer Mn versus activator equivalent and umol of TNOAL (data from Table 3), according to one aspect of the present disclosure. As shown in Figure 1 and Table 3, increased polymer molecular weight can be obtained with DODTH-BF28 and M2HTH-BF28 versus DMAH-BF28.

Table 3. Data for the polymerization of propylene with different activator equivalents and scavenger concentration.

General conditions: MCN-1 = 30 nmol; solvent = isohexane; total volume = 5 mL; temperature = 85°C; propylene pressure = 135 psi							
Run	Replicate	Catalyst	Activator	Activator Equiv	TNOAL (μ mol)	Time* (s)	Yield (g)
1	1	MCN-1	DMAH-BF28	1.0	0.25	48.5	0.244
2	2	MCN-1	DMAH-BF28	1.0	0.25	48.5	0.203
3	1	MCN-1	DMAH-BF28	1.2	0.25	36.2	0.212
4	2	MCN-1	DMAH-BF28	1.2	0.25	46.2	0.259
5	1	MCN-1	DMAH-BF28	1.4	0.25	40.3	0.238
6	2	MCN-1	DMAH-BF28	1.4	0.25	43.1	0.243
7	1	MCN-1	DMAH-BF28	1.6	0.25	37.8	0.253
8	1	MCN-1	DOdTH-BF28	1.0	0.25	77.8	0.176
9	2	MCN-1	DOdTH-BF28	1.0	0.25	87.7	0.189
10	3	MCN-1	DOdTH-BF28	1.0	0.25	87.2	0.179
11	1	MCN-1	DOdTH-BF28	1.2	0.25	82.7	0.244
12	2	MCN-1	DOdTH-BF28	1.2	0.25	83.0	0.204
13	3	MCN-1	DOdTH-BF28	1.2	0.25	82.3	0.193
14	1	MCN-1	DOdTH-BF28	1.4	0.25	78.5	0.206
15	2	MCN-1	DOdTH-BF28	1.4	0.25	76.8	0.182
16	3	MCN-1	DOdTH-BF28	1.4	0.25	81.5	0.177
17	1	MCN-1	DOdTH-BF28	1.6	0.25	79.3	0.187
18	2	MCN-1	DOdTH-BF28	1.6	0.25	85.1	0.189
19	1	MCN-1	M2HTH-BF28	1.0	0.25	89.2	0.139
20	2	MCN-1	M2HTH-BF28	1.0	0.25	109.9	0.153
21	3	MCN-1	M2HTH-BF28	1.0	0.25	92.9	0.124
22	1	MCN-1	M2HTH-BF28	1.2	0.25	99.7	0.169
23	2	MCN-1	M2HTH-BF28	1.2	0.25	104.6	0.170
24	3	MCN-1	M2HTH-BF28	1.2	0.25	99.5	0.138
25	1	MCN-1	M2HTH-BF28	1.4	0.25	103.6	0.176
26	2	MCN-1	M2HTH-BF28	1.4	0.25	102.1	0.167
27	3	MCN-1	M2HTH-BF28	1.4	0.25	95.3	0.141
28	1	MCN-1	M2HTH-BF28	1.6	0.25	95.5	0.182
29	2	MCN-1	M2HTH-BF28	1.6	0.25	102.5	0.173
30	3	MCN-1	M2HTH-BF28	1.6	0.25	77.2	0.116
31	1	MCN-1	DMAH-BF28	1.0	0.50	49.0	0.161
32	2	MCN-1	DMAH-BF28	1.0	0.50	60.7	0.178
33	1	MCN-1	DMAH-BF28	1.2	0.50	44.6	0.188

34	2	MCN-1	DMAH-BF28	1.2	0.50	52.8	0.202
35	1	MCN-1	DMAH-BF28	1.4	0.50	43.1	0.199
36	2	MCN-1	DMAH-BF28	1.4	0.50	50.7	0.182
37	1	MCN-1	DMAH-BF28	1.6	0.50	41.1	0.175
38	2	MCN-1	DMAH-BF28	1.6	0.50	48.6	0.189
39	1	MCN-1	DOdTH-BF28	1.0	0.50	92.1	0.163
40	2	MCN-1	DOdTH-BF28	1.0	0.50	91.0	0.147
41	3	MCN-1	DOdTH-BF28	1.0	0.50	100.3	0.146
42	1	MCN-1	DOdTH-BF28	1.2	0.50	83.3	0.168
43	2	MCN-1	DOdTH-BF28	1.2	0.50	88.6	0.156
44	3	MCN-1	DOdTH-BF28	1.2	0.50	92.9	0.148
45	1	MCN-1	DOdTH-BF28	1.4	0.50	75.7	0.142
46	2	MCN-1	DOdTH-BF28	1.4	0.50	88.9	0.138
47	3	MCN-1	DOdTH-BF28	1.4	0.50	91.2	0.137
48	1	MCN-1	DOdTH-BF28	1.6	0.50	82.5	0.182
49	2	MCN-1	DOdTH-BF28	1.6	0.50	92.6	0.151
50	3	MCN-1	DOdTH-BF28	1.6	0.50	86.9	0.136
51	1	MCN-1	M2HTH-BF28	1.0	0.50	116.7	0.147
52	2	MCN-1	M2HTH-BF28	1.0	0.50	131.5	0.124
53	3	MCN-1	M2HTH-BF28	1.0	0.50	103.0	0.101
54	1	MCN-1	M2HTH-BF28	1.2	0.50	103.6	0.146
55	2	MCN-1	M2HTH-BF28	1.2	0.50	109.7	0.140
56	1	MCN-1	M2HTH-BF28	1.4	0.50	91.9	0.120
57	2	MCN-1	M2HTH-BF28	1.4	0.50	111.2	0.132
58	1	MCN-1	M2HTH-BF28	1.6	0.50	104.4	0.146
59	2	MCN-1	M2HTH-BF28	1.6	0.50	110.8	0.133
60	1	MCN-1	DMAH-BF28	1.0	0.75	61.3	0.119
61	2	MCN-1	DMAH-BF28	1.0	0.75	69.5	0.123
62	1	MCN-1	DMAH-BF28	1.2	0.75	49.9	0.138
63	2	MCN-1	DMAH-BF28	1.2	0.75	67.9	0.145
64	1	MCN-1	DMAH-BF28	1.4	0.75	48.0	0.148
65	2	MCN-1	DMAH-BF28	1.4	0.75	62.2	0.173
66	1	MCN-1	DMAH-BF28	1.6	0.75	44.5	0.150
67	2	MCN-1	DMAH-BF28	1.6	0.75	58.3	0.173
68	1	MCN-1	DOdTH-BF28	1.0	0.75	104.2	0.120
69	2	MCN-1	DOdTH-BF28	1.0	0.75	98.9	0.109
70	3	MCN-1	DOdTH-BF28	1.0	0.75	107.7	0.108
71	1	MCN-1	DOdTH-BF28	1.2	0.75	97.3	0.136
72	2	MCN-1	DOdTH-BF28	1.2	0.75	97.1	0.115
73	3	MCN-1	DOdTH-BF28	1.2	0.75	108.6	0.121

74	1	MCN-1	DOdTH-BF28	1.4	0.75	95.3	0.137
75	2	MCN-1	DOdTH-BF28	1.4	0.75	97.3	0.124
76	3	MCN-1	DOdTH-BF28	1.4	0.75	89.3	0.107
77	1	MCN-1	DOdTH-BF28	1.6	0.75	91.7	0.133
78	2	MCN-1	DOdTH-BF28	1.6	0.75	94.7	0.118
79	3	MCN-1	DOdTH-BF28	1.6	0.75	94.9	0.106
80	1	MCN-1	M2HTH-BF28	1.0	0.75	130.4	0.111
81	2	MCN-1	M2HTH-BF28	1.0	0.75	130.0	0.103
82	1	MCN-1	M2HTH-BF28	1.2	0.75	116.1	0.115
83	2	MCN-1	M2HTH-BF28	1.2	0.75	129.8	0.112
84	1	MCN-1	M2HTH-BF28	1.4	0.75	115.1	0.122
85	2	MCN-1	M2HTH-BF28	1.4	0.75	132.1	0.113
86	1	MCN-1	M2HTH-BF28	1.6	0.75	108.6	0.117
87	2	MCN-1	M2HTH-BF28	1.6	0.75	117.1	0.114

*time not corrected for induction period

Table 3: Continued

Run	Replicate	Catalyst	Activator	activity (kg/mmol- hr)	Mw (g/mol)	Mn (g/mol)	PDI Mw/Mn	Tm (°C)
1	1	MCN-1	DMAH-BF28	604	139,625	68,378	2.0	127
2	2	MCN-1	DMAH-BF28	502	152,003	80,712	1.9	128
3	1	MCN-1	DMAH-BF28	703	134,516	67,691	2.0	128
4	2	MCN-1	DMAH-BF28	673	158,859	65,705	2.4	128
5	1	MCN-1	DMAH-BF28	709	139,249	70,008	2.0	128
6	2	MCN-1	DMAH-BF28	677	145,757	66,816	2.2	128
7	1	MCN-1	DMAH-BF28	803	125,607	59,107	2.1	127
8	1	MCN-1	DOdTH-BF28	271	188,839	83,444	2.3	131
9	2	MCN-1	DOdTH-BF28	259	154,334	87,492	1.8	129
10	3	MCN-1	DOdTH-BF28	246	173,588	103,537	1.7	129
11	1	MCN-1	DOdTH-BF28	354	176,664	95,218	1.9	130
12	2	MCN-1	DOdTH-BF28	295	187,424	104,639	1.8	130
13	3	MCN-1	DOdTH-BF28	281	174,900	109,235	1.6	130
14	1	MCN-1	DOdTH-BF28	315	167,636	98,035	1.7	130
15	2	MCN-1	DOdTH-BF28	284	174,709	94,337	1.9	130
16	3	MCN-1	DOdTH-BF28	261	191,143	107,426	1.8	130
17	1	MCN-1	DOdTH-BF28	283	168,522	101,216	1.7	130
18	2	MCN-1	DOdTH-BF28	267	169,691	89,708	1.9	130
19	1	MCN-1	M2HTH-BF28	187	193,950	102,453	1.9	131
20	2	MCN-1	M2HTH-BF28	167	184,445	101,802	1.8	130
21	3	MCN-1	M2HTH-BF28	160	187,338	110,532	1.7	130
22	1	MCN-1	M2HTH-BF28	203	192,468	106,997	1.8	131
23	2	MCN-1	M2HTH-BF28	195	179,423	101,731	1.8	131
24	3	MCN-1	M2HTH-BF28	166	207,768	128,236	1.6	131
25	1	MCN-1	M2HTH-BF28	204	191,675	102,634	1.9	130
26	2	MCN-1	M2HTH-BF28	196	188,506	107,568	1.8	130
27	3	MCN-1	M2HTH-BF28	178	203,849	110,193	1.9	131

28	1	MCN-1	M2HTH-BF28	229	182,348	85,354	2.1	130
29	2	MCN-1	M2HTH-BF28	203	185,187	98,827	1.9	130
30	3	MCN-1	M2HTH-BF28	180	208,319	113,940	1.8	130
31	1	MCN-1	DMAH-BF28	394	176,336	100,295	1.8	130
32	2	MCN-1	DMAH-BF28	352	192,634	102,408	1.9	131
33	1	MCN-1	DMAH-BF28	506	148,426	84,581	1.8	129
34	2	MCN-1	DMAH-BF28	459	155,759	84,798	1.8	130
35	1	MCN-1	DMAH-BF28	554	136,225	71,584	1.9	129
36	2	MCN-1	DMAH-BF28	431	152,797	80,613	1.9	129
37	1	MCN-1	DMAH-BF28	511	157,116	88,755	1.8	130
38	2	MCN-1	DMAH-BF28	467	166,442	83,513	2.0	129
39	1	MCN-1	DOdTH-BF28	212	190,969	110,353	1.7	131
40	2	MCN-1	DOdTH-BF28	194	196,386	114,822	1.7	132
41	3	MCN-1	DOdTH-BF28	175	208,080	119,524	1.7	132
42	1	MCN-1	DOdTH-BF28	242	173,395	94,722	1.8	130
43	2	MCN-1	DOdTH-BF28	211	195,598	108,882	1.8	132
44	3	MCN-1	DOdTH-BF28	191	200,253	107,193	1.9	132
45	1	MCN-1	DOdTH-BF28	225	196,454	123,022	1.6	131
46	2	MCN-1	DOdTH-BF28	186	174,763	95,683	1.8	130
47	3	MCN-1	DOdTH-BF28	180	205,013	125,870	1.6	130
48	1	MCN-1	DOdTH-BF28	265	183,663	108,279	1.7	131
49	2	MCN-1	DOdTH-BF28	196	206,818	118,888	1.7	131
50	3	MCN-1	DOdTH-BF28	188	205,178	131,023	1.6	131
51	1	MCN-1	M2HTH-BF28	151	224,111	116,587	1.9	132
52	2	MCN-1	M2HTH-BF28	113	236,852	128,624	1.8	132
53	3	MCN-1	M2HTH-BF28	118	240,482	138,212	1.7	133
54	1	MCN-1	M2HTH-BF28	169	196,525	107,470	1.8	131
55	2	MCN-1	M2HTH-BF28	153	213,438	110,004	1.9	132
56	1	MCN-1	M2HTH-BF28	157	220,073	134,846	1.6	132
57	2	MCN-1	M2HTH-BF28	142	199,039	110,055	1.8	131
58	1	MCN-1	M2HTH-BF28	168	206,461	120,532	1.7	131
59	2	MCN-1	M2HTH-BF28	144	199,398	123,503	1.6	132
60	1	MCN-1	DMAH-BF28	233	197,124	124,675	1.6	132
61	2	MCN-1	DMAH-BF28	212	222,459	125,425	1.8	132
62	1	MCN-1	DMAH-BF28	332	185,475	110,164	1.7	131
63	2	MCN-1	DMAH-BF28	256	181,659	100,660	1.8	132
64	1	MCN-1	DMAH-BF28	370	157,862	92,645	1.7	130
65	2	MCN-1	DMAH-BF28	334	192,254	113,934	1.7	131
66	1	MCN-1	DMAH-BF28	404	161,904	90,031	1.8	130
67	2	MCN-1	DMAH-BF28	356	167,856	106,799	1.6	131
68	1	MCN-1	DOdTH-BF28	138	226,642	143,333	1.6	132
69	2	MCN-1	DOdTH-BF28	132	211,247	121,586	1.7	132
70	3	MCN-1	DOdTH-BF28	120	230,616	126,136	1.8	132
71	1	MCN-1	DOdTH-BF28	168	203,343	118,996	1.7	132
72	2	MCN-1	DOdTH-BF28	142	210,208	112,323	1.9	132
73	3	MCN-1	DOdTH-BF28	134	206,059	114,309	1.8	132
74	1	MCN-1	DOdTH-BF28	173	214,283	127,814	1.7	132
75	2	MCN-1	DOdTH-BF28	153	224,513	117,540	1.9	132
76	3	MCN-1	DOdTH-BF28	144	206,568	122,219	1.7	132
77	1	MCN-1	DOdTH-BF28	174	188,187	107,663	1.7	131
78	2	MCN-1	DOdTH-BF28	150	213,453	126,310	1.7	132
79	3	MCN-1	DOdTH-BF28	134	213,401	126,062	1.7	132

80	1	MCN-1	M2HTH-BF28	102	222,895	140,227	1.6	132
81	2	MCN-1	M2HTH-BF28	95	233,586	141,269	1.7	133
82	1	MCN-1	M2HTH-BF28	119	204,146	115,937	1.8	132
83	2	MCN-1	M2HTH-BF28	104	234,098	131,539	1.8	132
84	1	MCN-1	M2HTH-BF28	127	229,002	131,941	1.7	132
85	2	MCN-1	M2HTH-BF28	103	211,035	130,568	1.6	132
86	1	MCN-1	M2HTH-BF28	129	195,068	112,305	1.7	131
87	2	MCN-1	M2HTH-BF28	117	219,212	131,318	1.7	132

[0411] Activators of the present disclosure can also be used for activating non-metallocene catalysts for polymerization of olefins. Table 4 illustrates copolymerization of ethylene and octene using activators of the present disclosure and non-metallocene catalysts (CAT-1, CAT-2, CAT-3, and CAT-4).

Structures of CAT-1, CAT-2, CAT-3 and CAT-4

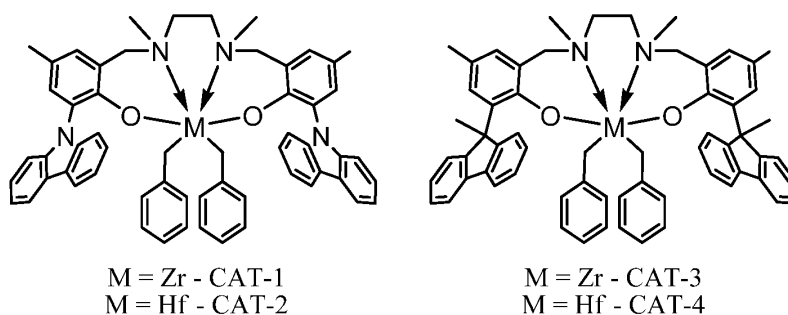


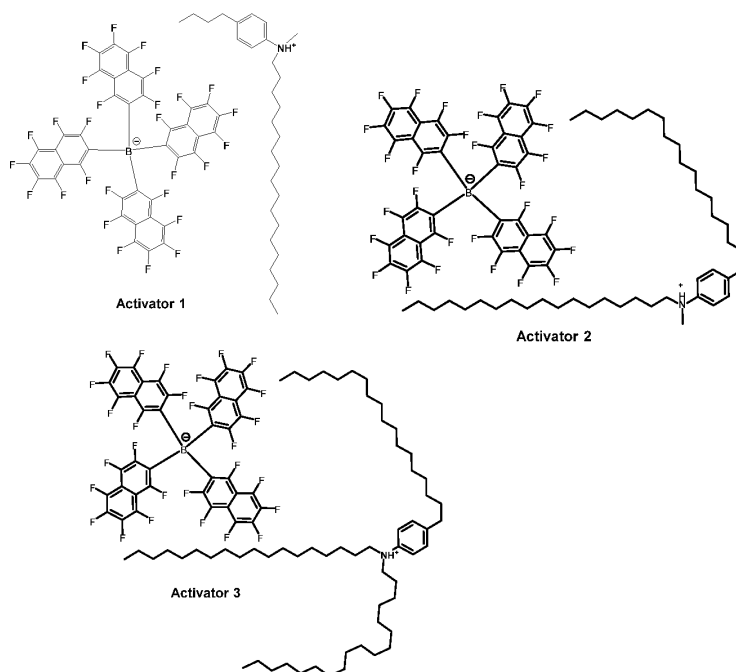
Table 4. Data for the copolymerization of ethylene and octene.

General conditions: catalyst = 20 nmol; activator = 1.1 equiv; solvent = isohexane; total volume = 5 mL; temperature = 100°C; pressure = 135 psi; 1-octene = 100 μ L; TNOAL = 0.5 μ mol									
Run	Replicate	Catalyst	Activator	Time (s)	Yield (g)	Activity (kg/mmol-hr)	Mw (g/mol)	Mn (g/mol)	Tm (°C)
1	1	CAT-1	DMAH-BF20	7.8	0.129	2977	16,389	8,031	117
2	2	CAT-1	DMAH-BF20	7.8	0.107	2469	14,089	6,843	118
3	1	CAT-1	DOdTH-BF20	6.2	0.128	3716	15,440	6,242	117
4	2	CAT-1	DOdTH-BF20	6.6	0.137	3736	16,487	8,134	117
5	1	CAT-1	M2HTH-BF20	9.4	0.106	2030	15,162	8,451	118
6	2	CAT-1	M2HTH-BF20	8.7	0.107	2214	14,939	6,863	118
7	1	CAT-1	DMAH-BF28	6.8	0.132	3494	13,175	6,302	115
8	2	CAT-1	DMAH-BF28	7.5	0.131	3144	13,760	5,531	117
9	1	CAT-1	DOdTH-BF28	6.6	0.142	3873	13,798	5,649	116
10	2	CAT-1	DOdTH-BF28	7.0	0.136	3497	13,982	6,867	116
11	1	CAT-1	M2HTH-BF28	7.0	0.097	2494	12,250	5,849	118

12	2	CAT-1	M2HTH-BF28	9.9	0.094	1709	12,541	6,117	118
13	1	CAT-2	DMAH-BF20	13.9	0.088	1140	84,264	48,353	120
14	2	CAT-2	DMAH-BF20	16.5	0.084	916	80,977	47,345	120
15	1	CAT-2	DOdTH-BF20	13.5	0.095	1267	84,273	49,098	120
16	2	CAT-2	DOdTH-BF20	13.1	0.084	1154	80,413	47,417	120
17	1	CAT-2	M2HTH-BF20	16.3	0.073	806	83,399	47,702	120
18	2	CAT-2	M2HTH-BF20	17.4	0.073	755	79,914	49,390	120
19	1	CAT-2	DMAH-BF28	13.8	0.089	1161	69,582	42,103	120
20	2	CAT-2	DMAH-BF28	19.4	0.078	724	71,962	44,081	120
21	1	CAT-2	DOdTH-BF28	14.1	0.081	1034	72,001	43,234	120
22	2	CAT-2	DOdTH-BF28	22.3	0.066	533	67,921	36,035	121
23	1	CAT-2	M2HTH-BF28	18.3	0.063	620	67,134	37,602	121
24	2	CAT-2	M2HTH-BF28	27.6	0.054	352	67,412	38,790	121
25	1	CAT-3	DMAH-BF20	20.0	0.091	819	368,047	210,891	122
26	2	CAT-3	DMAH-BF20	24.5	0.095	698	351,231	202,330	121
27	1	CAT-3	DOdTH-BF20	26.7	0.096	647	346,889	174,220	122
28	2	CAT-3	DOdTH-BF20	23.1	0.094	732	346,294	168,514	122
29	1	CAT-3	M2HTH-BF20	23.3	0.092	711	345,950	177,901	121
30	2	CAT-3	M2HTH-BF20	22.2	0.097	786	341,718	179,920	122
31	1	CAT-3	DMAH-BF28	21.6	0.097	808	332,302	174,424	122
32	2	CAT-3	DMAH-BF28	24.5	0.094	691	358,214	203,699	121
33	1	CAT-3	DOdTH-BF28	20.4	0.095	838	337,735	161,918	122
34	2	CAT-3	DOdTH-BF28	20.2	0.093	829	361,824	210,673	121
35	1	CAT-3	M2HTH-BF28	20.5	0.094	825	336,890	190,946	121
36	2	CAT-3	M2HTH-BF28	19.2	0.092	863	353,656	187,354	121
37	1	CAT-4	DMAH-BF20	195.0	0.082	76	1,141,114	532,201	117
38	2	CAT-4	DMAH-BF20	357.8	0.090	45	1,092,808	435,554	116
39	1	CAT-4	DOdTH-BF20	371.6	0.094	46	1,113,634	439,941	116
40	2	CAT-4	DOdTH-BF20	369.1	0.098	48	1,150,410	488,334	117
41	1	CAT-4	M2HTH-BF20	346.8	0.099	51	1,036,693	392,232	118
42	2	CAT-4	M2HTH-BF20	269.1	0.094	63	1,145,550	468,289	117
43	1	CAT-4	DMAH-BF28	298.2	0.098	59	1,075,381	411,908	116
44	2	CAT-4	DMAH-BF28	298.6	0.089	54	1,125,319	452,817	116
45	1	CAT-4	DOdTH-BF28	377.2	0.100	48	1,128,392	453,273	117
46	2	CAT-4	DOdTH-BF28	384.0	0.099	46	1,024,204	435,304	116
47	1	CAT-4	M2HTH-BF28	377.0	0.101	48	1,113,640	444,300	116
48	2	CAT-4	M2HTH-BF28	248.1	0.090	65	1,065,070	469,685	116

[0412] **RUN B: Polymerization in Parallel Pressure Reactor.** A series of ethylene-octene polymerizations were performed in the parallel pressure reactor according to the

procedure described above. In these studies rac-dimethylsilyl-bis(indenyl)hafnium dimethyl (MCN-1) was used along with ammonium borate activators 1, 2 and 3 (shown below, also referred to as LCSA 1, 2 and 3). In a typical experiment an automated syringe was used to introduce into the reactor the following reagents, if utilized, in the following order: isohexane (0.35 mL), an isohexane solution of TNOAL scavenger (0.005 M, 60 μ L), additional isohexane (0.35 mL), a toluene solution of the respective polymerization catalyst (150 μ L, 0.4 mM, 20 nm [cat]/100 μ L [toluene]), additional isohexane (0.35 mL), a toluene or methylcyclohexane solution of the respective activator (150 μ L, 0.4 mM, (20 nm[act]/100 μ L[diluent])), then additional isohexane so that the total solvent volume for each run was 5 mL. Catalyst and activator were used in a 1:1 ratio. Each reaction was performed at a specified temperature range between 50 and 120°C, typically 95°C, while applying about 100 psig of ethylene (monomer) gas. Each reaction was allowed to run for about 1 hour (~3600 seconds) or until approximately 20 psig of ethylene gas uptake was observed, at which point the reactions were quenched with air (~300 psig). When sufficient polymer yield was attained (*e.g.*, at least ~10 mg), the polyethylene product was analyzed by Rapid GPC, described below. Run conditions and data are reported in Table 5.



To demonstrate the enhanced solubility and performance of borate activators bearing long chain soluble anilinium moieties, the copolymerization of ethylene and 1-octene was conducted

utilizing Cat 1 as the pre-catalyst in conjunction with various anilinium containing borate activators. In a typical experiment, the anilinium borate activators were combined with toluene or methylcyclohexane as diluent and introduced to the parallel, pressure reactor via syringe. By this mechanism of activator introduction, only well dissolved activators could be delivered to the reactor providing a means to discriminate between the polymerization performance of long chain soluble anilinium borates vs. conventional anilinium borates. Following addition of activator, the catalyst Cat 1 was introduced, via syringe as well-dissolved toluene solution and the polymerization was conducted per the methodology described above.

[0413] Six anilinium borate activators, three long chain soluble anilinium borates (LCSA 1, 2 and 3) and three dimethyl anilinium borates (comparatives 1, 2, and 3), were screened for their ability activate Cat 1 for ethylene-octene copolymerization when toluene or methylcyclohexane was used as the activator diluent. Comparative 1 (C1) is DMAH-BF20, Comparative 2 (C2) is DMAH-BF28, Comparative 3 (C3) is N,N-dimethyl anilinium tetrakis(perfluorobiphenyl). The polymerization data show that activity (Figure 2), molecular weight (Figure 3), and co-monomer incorporation (Figure 4) for LCSAs 1, 2 and 3 remain approximately the same when either methyl cyclohexane or toluene are used as the activator diluent. Further, the data illustrate that the polymerization performance of LCSAs 1, 2 and 3 in either toluene or methyl cyclohexane are comparable to the performance of dimethylanilinium tetrakis perfluoronaphthylborate (Comparative 2) when it is in toluene diluent. These data demonstrate that long chain soluble anilinium activators retain their polymerization performance when methyl cyclohexane is used as a diluent while conventional dimethylanilinium borates, independent of borate identity (e.g., C₆F₅, C₁₀F₇ and C₁₂H₉) do not. (Note, for Figures 3 and 4 the data are uncorrected average Mn for ethylene-octene copolymers produced by Cat 1 in combination with activators C1, C2, C3, LCSA1, LCSA2, LCSA3 using methyl cyclohexane (MeCy) or toluene as the activator diluent. Utilization of LCSA1, LCSA2, or LCSA3 in methylcyclohexane or toluene resulted in ethylene-octene copolymers of similar molecular weights (M_n) as those obtained when activator C2 was used in conjunction with toluene as diluent. When C1, C2 and C3 were used with methylcyclohexane as diluent the quantity of polymer obtained was insufficient for analysis.)

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Table 5

Column	Row	Activator Diluent	Activator	Weights (g)	Quench Time (s)	Average Mn (g/mol)	Average Mw (g/mol)	Average Mz (g/mol)	Average Mw/Mn	wt % 1-octene	mol % 1-octene	Tm (°C)	Activity (kg/mmol _L)
1	A	Toluene	C1	0.093	25.4	101561	220280	708241	2.2	28	8.8	58.3	659.1
1	B	MeCy	C1	0.001	2159.1	-	-	-	-	-	0.0	-	0.1
1	C	Toluene	C1	0.093	24.6	98530	224056	641515	2.3	29	9.1	50.1	680.5
1	D	MeCy	C1	0	3600.62	-	-	-	-	-	0.0	-	0.0
1	E	Toluene	LCSA 3	0.077	47.7	262066	472959	1118519	1.8	33	10.8	53.7	290.6
1	F	MeCy	LCSA 3	0.077	49.4	268267	480296	1201763	1.8	30	9.8	51.5	280.6
1	G	Toluene	LCSA 3	0.078	50.5	257358	492586	1230830	1.9	29	9.2	62.7	278.0
1	H	MeCy	LCSA 3	0.076	53.1	240403	464198	1148933	1.9	27	8.4	51.9	257.6
2	A	Toluene	C2	0.076	31	249183	461835	1140095	1.9	24	7.4	70.0	441.3
2	B	MeCy	C2	0	3600.7	-	-	-	-	-	0.0	-	0.0
2	C	Toluene	C2	0.08	36.7	207640	433633	1123865	2.1	28	8.7	52.3	392.4
2	D	MeCy	C2	0	3600.82	-	-	-	-	-	0.0	-	0.0
2	E	Toluene	LCSA 2	0.082	30.9	230389	425784	1007444	1.8	34	11.2	49.9	477.7
2	F	MeCy	LCSA 2	0.082	32.7	247443	467956	1216060	1.9	31	9.9	43.6	451.4
2	G	Toluene	LCSA 2	0.082	34.3	211253	440430	1206377	2.1	27	8.7	47.4	430.3
2	H	MeCy	LCSA 2	0.079	36.6	208306	398860	882745	1.9	30	9.8	46.5	388.5
3	A	Toluene	C3	0.095	24.7	84182	190696	592290	2.3	33	10.8	49.4	692.3
3	B	MeCy	C3	0.006	3601.01	-	-	-	-	-	0.0	-	0.3
3	C	Toluene	C3	0.096	24.3	104093	243341	918401	2.3	31	10.2	51.4	711.1
3	D	MeCy	C3	0.002	3600.14	-	-	-	-	-	0.0	-	0.1
3	E	Toluene	LCSA 1	0.082	35.7	220088	408324	934291	1.9	29	9.4	51.6	413.4
3	F	MeCy	LCSA 1	0.073	39.5	267167	485923	1224625	1.8	28	8.9	47.4	332.7
3	G	Toluene	LCSA 1	0.08	28.2	238769	451334	1130031	1.9	30	9.5	43.8	510.6
3	H	MeCy	LCSA 1	0.077	36.7	291752	504620	1186843	1.7	32	10.7	49.9	377.7
4	A	Toluene	LCSA 1	0.086	36.3	203964	418810	1083002	2.1	29	9.1	48.5	426.4
4	B	MeCy	LCSA 1	0.082	37.5	242549	439679	998830	1.8	30	9.8	50.0	393.6
4	C	Toluene	LCSA 1	0.085	33.8	219099	449565	1343681	2.1	31	10.3	51.7	452.7
4	D	MeCy	LCSA 1	0.082	40.2	233302	438416	1032339	1.9	31	9.9	50.4	367.2
4	E	Toluene	C3	0.094	20.1	103739	218103	693469	2.1	32	10.4	48.6	841.8
4	F	MeCy	C3	0	3600.71	-	-	-	-	-	0.0	-	0.0
4	G	Toluene	C3	0.096	21.5	84619	192152	531649	2.3	30	9.5	42.1	803.7
4	H	MeCy	C3	0.001	3600.52	-	-	-	-	-	0.0	-	0.0
5	A	Toluene	LCSA 2	0.08	35.5	194469	392292	948798	2.0	32	10.6	51.7	405.6
5	B	MeCy	LCSA 2	0.085	37.1	228204	432196	1015931	1.9	31	10.0	50.0	412.4
5	C	Toluene	LCSA 2	0.083	35.3	215969	444320	1166464	2.1	29	9.4	51.8	423.2
5	D	MeCy	LCSA 2	0.083	32.8	220570	416185	967860	1.9	30	9.6	50.1	455.5
5	E	Toluene	C2	0.083	38.3	225367	449360	1096197	2.0	29	9.1	45.4	390.1
5	F	MeCy	C2	0	3600.42	-	-	-	-	-	0.0	-	0.0
5	G	Toluene	C2	0.078	34.4	252497	456293	996515	1.8	30	9.5	48.7	408.1
5	H	MeCy	C2	0	3600.61	-	-	-	-	-	0.0	-	0.0
6	A	Toluene	LCSA 3	0.075	46.6	239953	458672	1105198	1.9	31	10.2	52.7	289.7

6	B	MeCy	LCSA 3	0.08	43	250558	476571	1140387	1.9	29	9.4	52.4	334.9
6	C	Toluene	LCSA 3	0.077	49.8	273074	503018	1214488	1.8	29	9.1	54.2	278.3
6	D	MeCy	LCSA 3	0.077	38.4	275944	503106	1151742	1.8	28	9.0	52.2	360.9
6	E	Toluene	C1	0.09	21.2	101493	227087	676006	2.2	31	10.0	41.5	764.2
6	F	MeCy	C1	0	3601	-	-	-	-	-	0.0	-	0.0
6	G	Toluene	C1	0.087	23.2	104035	226021	634408	2.2	30	9.5	41.3	675.0
6	H	MeCy	C1	0	3600.41	-	-	-	-	-	0.0	-	0.0

- [0414] **Ethylene-Octene Copolymerization (EO).** A series of ethylene-octene polymerizations were performed in the parallel pressure reactor according to a similar procedure as described above. In these studies rac-dimethylsilyl-bis(indenyl)hafnium dimethyl
- 5 (MCN-1) was used along with ammonium borate activators.

Table 6. Data for the ethylene-octene copolymerization.

<i>General conditions:</i> MCN-1 = 20 nmol; activator = 22 nmol; 1-octene = 100 μ L; solvent = isohexane; total volume = 5 mL; tri(n-octyl)aluminum = 500 nmol; T = 80 $^{\circ}$ C; P=75 PSI.									
run	activator	yield (mg)	time (s)	activity (kg/mmol /h)	Mw (g/mol)	Mn (g/mol)	PDI Mw/Mn	% octene	T _m ($^{\circ}$ C)
1	DMAH-BF20	92	25.7	644.4	362,472	189,698	1.91	37.5	58.6
2	DMAH-BF20	75	26.5	509.4	371,373	213,514	1.74	35.4	42.3
3	NOMAH-BF20	90	37.6	430.9	413,270	207,838	1.99	33.9	46.7
4	NOMAH-BF20	75	32.6	414.1	420,680	245,773	1.71	37.4	44.9
5	NOMAH-BF20	71	26.7	478.7	411,768	223,321	1.84	32.6	45.6
6	NOMAH-BF20	71	31.2	409.6	393,303	209,625	1.88	36.1	43.7
7	NOMAH-BF28	71	42.3	302.1	591,099	359,399	1.65	35.5	47.7
8	NOMAH-BF28	71	39.8	321.1	583,582	341,973	1.71	32.9	49.1
9	NOMAH-BF28	65	39	300.0	582,671	331,198	1.76	34.5	48.8
10	NOMAH-BF28	62	32.3	345.5	571,103	342,670	1.67	29.9	50.3
11	UOMAH-BF20	84	30.1	502.3	371,052	193,095	1.92	35.7	44.4
12	UOMAH-BF20	77	30.4	455.9	383,249	209,834	1.83	37.9	44.4
13	UOMAH-BF20	84	29	521.4	385,925	175,125	2.20	34.9	43.6
14	UOMAH-BF20	69	29.5	421.0	398,237	198,141	2.01	38.2	44.0

15	UOMAH-BF28	72	35.4	366.1	563,133	308,209	1.83	31.3	48.9
16	UOMAH-BF28	66	33.1	358.9	560,328	299,937	1.87	34.3	47.8

- [0415] Ethylene homopolymerization (PE).** A series of ethylene polymerizations were performed in the parallel pressure reactor similar to the procedure described above. In these studies rac-dimethylsilyl-bis(indenyl)hafnium dimethyl (MCN-1) was used along with ammonium borate activators.

Table 2. Data for the ethylene homopolymerization.

General conditions: MCN-1 = 20 nmol; activator = 22 nmol; solvent = isohexane; total volume = 5 mL; tri(n-octyl)aluminum = 500 nmol; T = 80 °C; P=75 PSI.								
run	activator	yield (mg)	time (s)	activity (kg/mmol /h)	Mw (g/mol)	Mn (g/mol)	PDI Mw/Mn	T _m (°C)
1	DMAH-BF20	68	42.4	288.7	875,463	431,174	2.03	135.2
2	DMAH-BF20	57	25.2	407.1	663,329	336,644	1.97	135.1
3	NOMAH-BF20	70	58.5	215.4	847,700	412,612	2.05	135.6
4	NOMAH-BF20	64	48.5	237.5	740,474	365,330	2.03	135.6
5	NOMAH-BF20	59	26.6	399.2	759,613	467,750	1.62	135.3
6	NOMAH-BF20	58	30.7	340.1	728,453	418,731	1.74	135.6
7	NOMAH-BF28	65	54.9	213.1	1,036,055	459,313	2.26	135.6
8	NOMAH-BF28	68	60.5	202.3	1,005,982	536,968	1.87	136.1
9	NOMAH-BF28	57	59.1	173.6	885,931	451,497	1.96	135.5
10	NOMAH-BF28	57	37.7	272.1	815,148	421,742	1.93	136.5
11	UOMAH-BF20	70	37.9	332.5	848,026	404,702	2.10	135.3
12	UOMAH-BF20	66	37.4	317.6	760,501	411,335	1.85	135.5
13	UOMAH-BF20	65	37.7	310.3	745,301	387,497	1.92	135.5
14	UOMAH-BF20	58	26.1	400.0	694,140	383,259	1.81	135.6
15	UOMAH-BF28	81	58.1	250.9	1,033,427	553,947	1.87	135.7
16	UOMAH-BF28	60	57.9	186.5	946,713	446,910	2.12	135.4

Overall, activators, catalyst systems, and methods of the present disclosure can provide improved solubility in aliphatic solvents, as compared to conventional activator compounds and catalyst systems. Activators, catalyst systems, and methods of the present disclosure can provide polyolefins having a weight average molecular weight (Mw) of about 100,000 or greater and a melt temperature (T_m) of about 110°C or greater.

[0416] **Propylene homopolymerization (PP).** A series of propylene polymerizations were performed in the parallel pressure reactor similar to the procedure described above. In these studies rac-dimethylsilyl-bis(indenyl)hafnium dimethyl (MCN-1) was used along with ammonium borate activators.

Table 7. Propylene polymerization data

General conditions: MCN-1 = 30 nmol; activator = 33 nmol; temp = 100 °C, propylene = 150 psi, solvent = isohexane; total volume = 5 mL; tri(n-octyl)aluminum = 500 nmol.

run	activator	time (s)	yield (mg)	activity (kg/mmol /h)	Mw (g/mol)	Mn (g/mol)	T _m (°C)
1	M2HTH-BF28	155	106	82	90,810	58,164	123.3
2	M2HTH-BF28	175	101	69	93,833	59,058	124.1
3	M2HTH-BF28	309	60	23	103,129	68,948	124.1
4	DOdTH-BF28	116	133	138	86,642	53,700	123.4
5	DOdTH-BF28	115	146	153	79,224	43,938	122.1
6	DOdTH-BF28	139	117	101	87,468	56,895	117.0
7	DOdTH-BF28	80	92	138	93,833	62,979	122.9
8	NOMAH-BF28	93	109	141	92,648	55,422	117.3
9	NOMAH-BF28	73	127	208	80,126	43,955	115.2
10	NOMAH-BF28	73	118	193	90,669	54,991	117.1
11	NOMAH-BF28	71	125	210	93,117	59,292	117.4
12	NOMAH-BF28	79	119	181	94,033	56,845	118.3
13	NOMAH-BF28	79	116	178	92,581	54,568	116.9
14	NOMAH-BF28	67	124	223	90,452	55,255	122.9
15	NOMAH-BF28	58	101	207	91,222	52,091	122.7
16	DMAH-BF28	75	110	175	96,672	55,549	123.7

17	DMAH-BF28	69	134	231	94,031	53,670	117.1
18	DMAH-BF28	71	137	231	96,982	51,626	116.8
19	DMAH-BF28	73	98	160	87,808	53,950	116.6
20	DMAH-BF28	93	94	121	102,819	62,989	123.9
21	DMAH-BF28	73	128	211	90,136	54,933	116.3
22	DMAH-BF28	74	115	188	88,747	49,867	122.1
23	DMAH-BF28	70	110	190	97,132	60,185	124.1

Data in Table 7 illustrate the effect of using different activators with MCN-1 to produce polypropylene at 100°C in a high-throughput polymerization. Four different activators were used. A significant difference in catalyst activity was observed for the four activators. The data is presented in Figure 6. DMAH-BF28 and NOMAH-BF28 yielded catalysts with the highest average activities. DODTH-BF28 was of somewhat lower activity, and M2HTH-BF28 was of much lower activity.

[0417] Overall, activators, catalyst systems, and methods of the present disclosure can provide improved solubility in aliphatic solvents, as compared to conventional activator compounds and catalyst systems. Activators, catalyst systems, and methods of the present disclosure can provide polyolefins having a weight average molecular weight (Mw) of about 100,000 g/mol or greater and a melt temperature (Tm) of about 110°C or greater.

[0418] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term “comprising” is considered synonymous with the term “including.” Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

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