

Support-Bound Activators, Supported Catalyst Systems, and Processes for Use Thereof

Inventors: Nikola S. Lambic, An Michael Nguyen, Jo Ann M. Canich, Lubin Luo

5 **CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of and priority to US Provisional Application No. 63/604960 filed December 1, 2023, the disclosure of which is incorporated herein by reference.

FIELD

10 [0002] The present disclosure relates to support-bound activators, supported catalyst systems, and processes for use thereof.

BACKGROUND

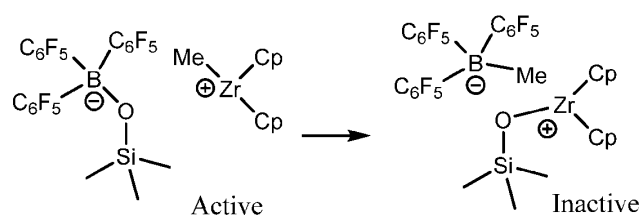
 [0003] Olefin polymerization catalysts are of great use in industry. Hence there is interest in finding new catalyst systems that increase the commercial usefulness of the catalyst and
15 allow the production of polymers having improved properties.

 [0004] For example, post-metallocene catalysts for olefin polymerization can be based on bis(phenolate) complexes as catalyst precursors, which are activated typically by an alumoxane or an activator containing a non-coordinating anion. One class of bis(phenolate) complexes known as 8-8 catalysts are described as transition metal complexes of a dianionic, tridentate
20 ligand that features a central neutral heterocyclic Lewis base and two phenolate donors, where the tridentate ligand coordinates to the metal center to form two eight-membered rings.

 [0005] The recent discovery of 8-8 catalysts allowed for a significant improvement in solution polymerizations, as such catalysts provide improved polymer molecular weights, comonomer incorporation ability, stereoregularity, and temperature stability relative to most
25 metallocenes.

 [0006] Nonetheless, post-metallocene catalysts including the 8-8 catalysts can have low catalyst productivity and remain a challenge to activate on a support, especially when a methyl alumoxane (MAO) activator is used, where the coexisted free AlMe₃ is believed to be capable of partially or completely destroying the catalyst structure due to the AlMe₃-reactive hetero-
30 atoms, *e.g.*, N or O or both in the catalyst ligand framework. In general, MAO is an active component in most supported catalysts used for metallocene-based propylene and ethylene polymerizations. While MAO activation is efficient and reliable for metallocene catalyst activation, MAO is often inefficient for activation of post-metallocene catalysts (such as 8-8 catalysts), requires cold storage, is pyrophoric, and is prone to gelation, which can further
35 reduce catalyst productivity.

- [0007] Active alkyl aluminum free silica supported perfluoroarylborate activators (J. Basset, et al., *Chem. Eur. J.*, 8 (2002) 1438; Walzer, US 5,643,847) were found to efficiently activate alkylated metallocene pre-catalysts to yield highly active catalyst systems. However, the system displays an undesired short catalyst life making for difficult use of this activator for practical use largely due to the weak O-B bond that is readily replaced with a stronger O-M bond, where M is a transition metal, such as Ti, Zr, or Hf that serves as the metallocene metal center. The decomposition pathway is reported by Basset, *et al.* (*J. Am. Chem. Soc.*, 128 (2006) 9361):



- [0008] There is a need for new supported post-metallocene catalysts having high productivity, methods of activating supported post-metallocene catalysts, and polymerizations thereof, while maintaining or improving other beneficial properties provided by post-metallocene catalysts provided by solution polymerizations.
- [0009] References for citing in an Information Disclosure Statement (37 C.F.R. 1.97(h)):
- US 5,643,847; US 5,939,347; US 6,388,017; US 6,395,666; US 6,524,988; US 7,034,173; US 8,088,952; US 11,370,860; US 2005/0159299; EP 1559730.

SUMMARY

- [0010] The present disclosure relates to support-bound aluminate activators, supported catalyst systems, and processes for use thereof.
- [0011] In some embodiments, a support-bound activator composition includes haloarylaluminates and a support material having surface oxygen atoms, wherein at least a portion of the surface oxygen atoms are bound (*e.g.*, covalent) to the haloarylaluminates, wherein each of the haloarylaluminates has at least one haloaryl substituent with a cationic group as the counter ion, wherein the haloarylaluminates are formed *in-situ* through bringing into contact an alkylaluminum compound and a haloarylborane compound.
- [0012] In some embodiments, a catalyst system includes a support-bound activator composition and a catalyst compound.
- [0013] In some embodiments, a method to polymerize olefins includes introducing a catalyst system comprising a support-bound activator composition and a catalyst compound, with one or more monomers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 illustrates density functional theory calculation results for support-bound activators, according to an embodiment.

5 [0015] FIG. 2 is images illustrating particle morphology under magnification of supported catalysts, according to an embodiment.

[0016] FIG. 3A is a graph illustrating catalyst productivities for gas phase polyethylene production relative to commercial metallocenes, according to an embodiment.

[0017] FIG. 3B is a graph illustrating catalyst productivities for slurry phase high density polyethylene production relative to commercial metallocenes, according to an embodiment.

10 [0018] FIG. 4 is a graph illustrating productivities of various catalyst systems, according to an embodiment.

Definitions

[0019] The new numbering scheme for the Periodic Table Groups is used as described in *Chemical and Engineering News*, v.63(5), pg. 27 (1985). Therefore, a “group 4 metal” is an
15 element from group 4 of the Periodic Table, *e.g.*, Hf, Ti, or Zr.

[0020] An “olefin,” alternatively referred to as “alkene,” is a linear, branched, or cyclic compound of 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
20 of the olefin. For example, when a copolymer is said to have an “ethylene” content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A “polymer” has two or more of the same or different mer units. A “homopolymer” is a polymer having mer units that are the same. A “copolymer” is a
25 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. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. “Different” as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. An “ethylene polymer” or “ethylene copolymer” is a polymer or copolymer
30 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.

[0021] Ethylene shall be considered an α -olefin.

[0022] Unless otherwise specified, the term “C_n” means hydrocarbon(s) having n carbon

atom(s) per molecule, wherein n is a positive integer.

[0023] The term "hydrocarbon" means a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon compounds, (ii) unsaturated hydrocarbon compounds, and (iii) mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different values of n. Likewise, a "C_m-C_y" group or compound refers to a group or compound comprising carbon atoms at a total number thereof in the range from m to y. Thus, a C₁-C₅₀ alkyl group refers to an alkyl group comprising carbon atoms at a total number thereof in the range from 1 to 50.

[0024] The terms "group," "radical," and "substituent" may be used interchangeably.

10 [0025] The terms "hydrocarbyl radical," "hydrocarbyl group," or "hydrocarbyl" may be used interchangeably and are defined to mean a group consisting of hydrogen and carbon atoms only. Hydrocarbyls may be C₁-C₁₀₀ radicals that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include, but are not limited to, alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 15 pentyl, iso-amyl, hexyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like, aryl groups, such as phenyl, benzyl, naphthalenyl, and the like.

[0026] Unless otherwise indicated, (*e.g.*, the definition of "substituted hydrocarbyl", "substituted aromatic", etc.), the term "substituted" means that at least one hydrogen atom has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a heteroatom, 20 or a heteroatom containing group, such as halide (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*₃, -GeR*₃, -SnR*₃, -PbR*₃, where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at 25 least one heteroatom has been inserted within a hydrocarbyl ring.

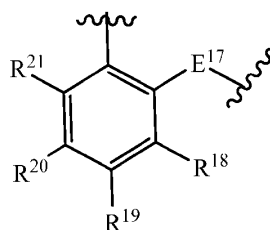
[0027] The term "substituted hydrocarbyl" means a hydrocarbyl radical in which at least one hydrogen atom of the hydrocarbyl radical has been substituted with at least one heteroatom (such as halide, *e.g.*, Br, Cl, F or I) or heteroatom-containing group (such as a functional group, *e.g.*, -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, 30 -SnR*₃, -PbR*₃, where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0028] The term "aryl" or "aryl group" means an aromatic ring and the substituted variants

thereof, such as phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. 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; likewise, the term aromatic also refers to substituted aromatics.

[0029] The term "substituted aromatic," means an aromatic group having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group.

[0030] A "substituted phenolate" is a phenolate group where at least one, two, three, four or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a 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*₃, -GeR*₃, -SnR*₃, -PbR*₃, and the like, where each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), where the 1 position is the phenolate group (Ph-O-, Ph-S-, and Ph-N(R[^])- groups, where R[^] is hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group). For example, a "substituted phenolate" group in the catalyst compounds described herein is represented by the formula:



where R¹⁸ is hydrogen, C₁-C₄₀ hydrocarbyl (such as C₁-C₄₀ alkyl) or C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, E¹⁷ is oxygen, sulfur, or NR¹⁷, and each of R¹⁷, R¹⁹, R²⁰, and R²¹ is independently selected from hydrogen, C₁-C₄₀ hydrocarbyl (such as C₁-C₄₀ alkyl) or C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or two or more of R¹⁸, R¹⁹, R²⁰, and R²¹ are joined together to form a C₄-C₆₂ cyclic or polycyclic ring structure, or a combination thereof, and the wavy line shows where the substituted phenolate group forms bonds to the rest of the catalyst compound.

[0031] An "alkyl substituted phenolate" is a phenolate group where at least one, two, three, four or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one alkyl group, such as a C₁ to C₄₀, alternately C₂ to C₂₀, alternately C₃ to C₁₂ alkyl, such as methyl, ethyl, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, 5 iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, adamantyl and the like including their substituted analogues.

[0032] An "aryl substituted phenolate" is a phenolate group where at least one, two, three, four or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one aryl group, such as a C₁ to C₄₀, alternately C₂ to C₂₀, alternately C₃ to C₁₂ aryl group, such as 10 phenyl, 4-fluorophenyl, 2-methylphenyl, 2-propylphenyl, 2,6-dimethylphenyl, mesityl, 2-ethylphenyl, naphthalenyl, and the like including their substituted analogues.

[0033] The term "ring atom" means an atom that is part of a cyclic ring structure. By this definition, a benzyl group has six ring atoms and tetrahydrofuran has 5 ring atoms.

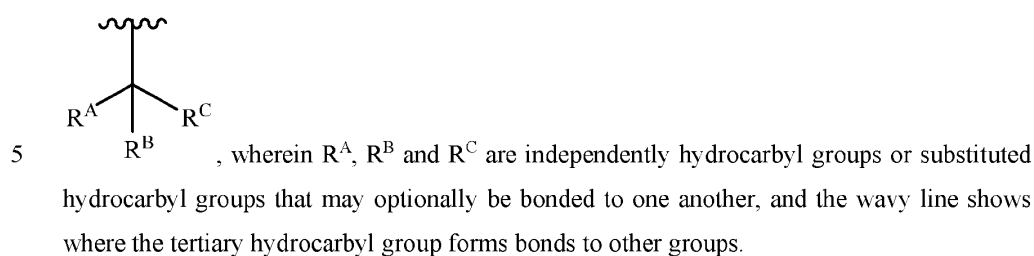
[0034] A heterocyclic ring, also referred to as a heterocyclic, is a ring having a heteroatom 15 in the ring structure as opposed to a "heteroatom-substituted ring" where a hydrogen on a ring atom is replaced with a heteroatom. For example, tetrahydrofuran is a heterocyclic ring and 4-N,N-dimethylamino-phenyl is a heteroatom substituted ring. A substituted heterocyclic ring means a heterocyclic ring having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group.

20 [0035] A substituted hydrocarbyl ring means a ring comprised of carbon and hydrogen atoms having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group.

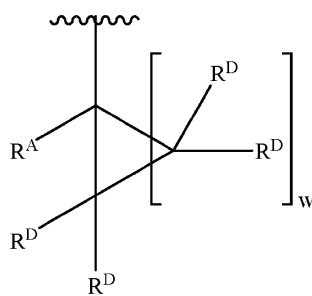
[0036] For purposes of the present disclosure, in relation to catalyst compounds (*e.g.*, substituted bis(phenolate) catalyst compounds), the term "substituted" means that a hydrogen 25 group has been replaced with a hydrocarbyl group, a heteroatom or heteroatom-containing group, such as halogen (such 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*₃, -GeR*₃, -SnR*₃, -PbR*₃, and the like, where each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely 30 saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0037] A tertiary hydrocarbyl group possesses a carbon atom bonded to three other carbon atoms. When the hydrocarbyl group is an alkyl group, tertiary hydrocarbyl groups are also

referred to as tertiary alkyl groups. Examples of tertiary hydrocarbyl groups include tert-butyl, 2-methylbutan-2-yl, 2-methylhexan-2-yl, 2-phenylpropan-2-yl, 2-cyclohexylpropan-2-yl, 1-methylcyclohexyl, 1-adamantyl, bicyclo[2.2.1]heptan-1-yl and the like. Tertiary hydrocarbyl groups can be illustrated by the formula:



[0038] A cyclic tertiary hydrocarbyl group is defined as a tertiary hydrocarbyl group that forms at least one alicyclic (non-aromatic) ring. Cyclic tertiary hydrocarbyl groups are also referred to as alicyclic tertiary hydrocarbyl groups. When the hydrocarbyl group is an alkyl group, cyclic tertiary hydrocarbyl groups are also referred to as cyclic tertiary alkyl groups or alicyclic tertiary alkyl groups. Examples of cyclic tertiary hydrocarbyl groups include 1-adamantyl, 1-methylcyclohexyl, 1-methylcyclopentyl, 1-methylcyclooctyl, 1-methylcyclodecyl, 1-methylcyclododecyl, bicyclo[3.3.1]nonan-1-yl, bicyclo[2.2.1]heptan-1-yl, bicyclo[2.3.3]hexan-1-yl, bicyclo[1.1.1]pentan-1-yl, bicyclo[2.2.2]octan-1-yl, and the like. Cyclic tertiary hydrocarbyl groups can be illustrated by formula B:



wherein R^A is a hydrocarbyl group or substituted hydrocarbyl group, each R^D is independently hydrogen or a hydrocarbyl group or substituted hydrocarbyl group, w is an integer from 1 to about 30, and R^A , and one or more R^D , and or two or more R^D may optionally be bonded to one another to form additional rings.

[0039] When a cyclic tertiary hydrocarbyl group contains more than one alicyclic ring, it can be referred to as polycyclic tertiary hydrocarbyl group or if the hydrocarbyl group is an alkyl group, it may be referred to as a polycyclic tertiary alkyl group.

25 [0040] The terms “alkyl radical,” and “alkyl” are used interchangeably throughout this

disclosure. For purposes of this disclosure, "alkyl radical" is 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 including their substituted analogues. 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 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*₃, -GeR*₃, -SnR*₃, -PbR*₃, and the like, where each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0041] Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (*e.g.*, n-butyl, iso-butyl, sec-butyl, and tert-butyl), 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).

[0042] The term halo appended to any group, for example haloalkyl, means the group is substituted with one or more halogen atoms.

[0043] 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. Unless otherwise noted, all molecular weight units (*e.g.*, Mw, Mn, Mz) are g/mol (g mol⁻¹).

[0044] The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, cPr is cyclopropyl, nPr is n-propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, Oct is octyl, Ph is phenyl, MAO is methylalumoxane, dme is 1,2-dimethoxyethane, p-tBu is para-tertiary butyl, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TMA is trimethylaluminum, TEAL is triethylaluminum, MAO is methylaluminoxane, BHT is butylated hydroxytoluene, also known as 2,6-bis(1,1-dimethylethyl)-4-methylphenol, p-Me is para-methyl, 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, and Cy is cyclohexyl.

[0045] A “catalyst system” is a combination of at least one catalyst compound, a support-bound activator, an optional coactivator. When “catalyst system” is used to describe such a pair before activation, it means the unactivated catalyst complex (precatalyst) together with an activator and, optionally, a coactivator. When it is used to describe such a pair after activation, it means the activated complex and the activator or other charge-balancing moiety. The catalyst compound may be neutral as in a precatalyst, or a charged species with a counter ion as in an activated catalyst system. For the purposes of the present disclosure and the claims thereto, when catalyst systems are described as including 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. A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer. Furthermore, catalyst compounds and activators (including support-bound activators) represented by formulae herein embrace both neutral and ionic forms of the catalyst compounds and activators.

[0046] In the description herein, the catalyst may be described as a catalyst, a catalyst precursor, a pre-catalyst compound, catalyst compound or a transition metal compound, and these terms are used interchangeably.

[0047] An “anionic ligand” is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. The term “anionic donor” is used interchangeably with “anionic ligand”. Examples of anionic donors may include, but are not limited to, methyl, chloride, fluoride, alkoxide, aryloxy, alkyl, alkenyl, thiolate, carboxylate, amido, methyl, benzyl, hydrido, amidinate, amidate, and phenyl. Two anionic donors may be joined to form a dianionic group.

[0048] A “neutral Lewis base or “neutral donor group” is an uncharged (*i.e.* neutral) group which donates one or more pairs of electrons to a metal ion. Non-limiting examples of neutral Lewis bases include ethers, thioethers, amines, phosphines, ethyl ether, tetrahydrofuran, dimethylsulfide, triethylamine, pyridine, alkenes, alkynes, alenes, and carbenes. Lewis bases may be joined together to form bidentate or tridentate Lewis bases.

[0049] For purposes of the present disclosure and the claims thereto, phenolate donors can include Ph-O-, Ph-S-, and Ph-N(R[^])- groups, where R[^] is hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, and Ph is optionally substituted phenyl.

DETAILED DESCRIPTION

[0050] The present disclosure relates to support-bound activators (also referred to as “modified support materials”), supported catalyst systems, and processes for use thereof.

[0051] For example, the present disclosure relates to catalyst systems including a transition metal compound and a support-bound activator, to the use of such support-bound activators for activating a transition metal compound in a catalyst system for polymerizing olefins. The present disclosure also relates to processes for polymerizing olefins, the process including
5 introducing under polymerization conditions one or more olefins with a catalyst system including a transition metal compound and a support-bound activator.

[0052] Support-bound activators of the present disclosure can have aluminum bound to a support and the aluminum is substituted with haloaryl groups. Support-bound activators of the present disclosure provide improved activation of post-metallocene catalysts, such as 8-8
10 catalysts.

[0053] Support-bound activators are a modified support material, including 1) a support material particle having surface oxygen atoms; 2) a capping agent coupled with the surface oxygen atoms of the support, wherein the capping agent comprises an aluminum based Lewis acid having one or more haloaryl substituents where the aluminum atom is coupled with the
15 surface oxygen atoms of the support; and 3) a cationic group, and 4) an optional second aluminum based Lewis acid capping agent having one or more alkyl, aryl, haloaryl, alkoxy, phenoxy or halophenoxy groups, where aluminum atom is bound to surface oxygen.

[0054] Support-bound activators of the present disclosure further improve upon cold storage, pyrophoricity, and gelation, as compared to MAO based activators. Without being
20 bound by theory, aluminum atoms can be strongly bonded to hydroxyl groups on a surface of a support. By comparison, boron atoms (such as from a borane activator) are weakly interacted with hydroxyl groups of a support which promotes reversible bonding of the boron atoms and hydroxyl groups which, during use, promotes solution-type polymerization conditions which lead to reactor fouling and reduced catalyst productivity. However, support-bound activators
25 of the present disclosure featuring aluminum-oxygen bonds provide reduced or eliminated reactor fouling due to strong aluminum-oxygen bond formation which maintains slurry phase or gas phase polymerization conditions in the reactor. The strong aluminum-oxygen bonds of a support-bound activator of the present disclosure provides better anchoring stability, while the highly electrophilic nature of aluminum metal leads to enhanced acidity of the neighboring
30 surface hydroxyl protons. This leads to more facile proton abstraction by an external Lewis base (such as aniline), which results in formation of anilinium cations capable of transition metal complex activation.

[0055] Supported post-metallocene catalysts utilizing a support-bound activator of the present disclosure can have high productivity for olefin polymerizations while maintaining or

improving upon other beneficial properties provided by post-metallocene catalysts such as improved polymer molecular weight, comonomer incorporation, stereoregularity, and temperature stability, as compared to conventional supported metallocene catalysts.

Support Materials

5 [0056] Support materials of the present disclosure can be any suitable support material having hydroxyl groups that can be treated with an aluminum capping agent to form a support-bound activator of the present disclosure.

[0057] The support material can be a porous support material, for example, talc, and inorganic oxides. Other support materials include zeolites, clays, organoclays, or any other
10 organic or inorganic support material and the like, or mixtures thereof.

[0058] In some embodiments, the support material is an inorganic oxide in a finely divided form. Suitable inorganic oxide materials for use in catalyst systems herein include Groups 2, 4, 13, and 14 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
15 magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided polyethylene. In some embodiments, a support material can be magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania, and
20 the like. Support materials can include Al_2O_3 , ZrO_2 , SiO_2 , and combinations thereof, such as SiO_2 , Al_2O_3 , or $\text{SiO}_2/\text{Al}_2\text{O}_3$. The support can be treated with a reactant that provides hydroxyl groups on the surface of the support material. For example, the solid oxide may be selected from silica, alumina, silica-alumina, silica-zirconia, alumina-zirconia, aluminum phosphate, heteropolytungstates, titania, magnesia, zinc oxide, mixed oxides thereof, and mixture(s)
25 thereof; and the reactant is a mineral acid, such as hydrochloric, nitric, phosphoric, sulfuric, boric acid.

[0059] In some embodiments, a support material that is an inorganic oxide has a surface area of about 10 to about 700 m^2/g , pore volume of about 0.1 to about 4.0 cc/g , and average particle size in the range of from about 5 to about 500 μm . In some embodiments, the surface
30 area of the support material is about 50 to about 500 m^2/g , pore volume of about 0.5 to about 3.5 cc/g , and average particle size of about 10 to about 200 μm . In some embodiments, the surface area of the support material is about 100 to about 400 m^2/g , pore volume of about 0.8 to about 3.0 cc/g , and average particle size is about 5 to about 100 μm . The average pore size

of the support material in some embodiments is about 10 to 1000 Å, such as about 50 to about 500 Å, such as about 75 to about 350 Å. In some embodiments, the support material is a high surface area, amorphous silica (surface area > 300 m²/gm; pore volume of 1.65 cm³/gm). Some silicas are available under the tradenames of DAVISON™ 952 or DAVISON™ 955 by the Davison Chemical Division of W.R. Grace and Company, such as SYLOPOL™ 952. In other embodiments, DAVISON™ 948 is used. Other silicas may be obtained from PQ Corporation, for example ES757, ES70, and ES70X, PD14024, PD17062, from Fuji (P10) or Asahi Glass Chemical (AGC) such as DM-L403 and DM-L303.

[0060] Before treating the support material with a capping agent of the present disclosure, the support material should be dry, that is, free of absorbed water. Drying of the support material can be effected by heating or calcining at about 100°C to about 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 about 200°C to about 850°C, such as about 600°C; and for a time of about 1 minute to about 100 hours, such as about 12 hours to about 72 hours, or about 24 hours to about 60 hours. The calcined support material may have reactive hydroxyl (OH) groups used to produce support-bound activators (and ultimately supported catalyst systems of the present disclosure). In other words, the calcined support material is contacted with a capping agent to form a support-bound activator that is then contacted with at least one catalyst compound.

Alkylaluminum Compound

[0061] The alkylaluminum compound serves as the supported haloarylaluminate precursor. The alkylaluminum compound is capable of exchanging the alkyl groups with the haloaryl groups on a haloaryl-borane compound to form haloarylalane before the formation of the supported haloarylaluminate through contacting the support surface hydroxyl groups; the compound may also exchange its alkyl groups with a haloarylborate pre-formed through contacting a haloarylborane compound with the support surface hydroxyl groups, with or without the optional Lewis base that serves as the active proton stabilizer; and the compound may form a supported alkylaluminate compound first through contacting the support surface hydroxyl, with or without the optional Lewis base as the active proton stabilizer, following by the exchange of its alkyl groups with a haloarylborane compound to form the supported haloarylaluminate under certain conditions, *e.g.*, at a low temperature.

[0062] Suitable alkylaluminum compounds to serve as the supported haloarylaluminate precursor have the formula (A):



wherein: each R is a C₁ to C₁₀ hydrocarbyl group, and can be the same or different; each X is

a halo atom or a bulky alkoxy group; $m = 1, 2, 3$.

- [0063] Some examples of R groups are methyl, ethyl, propyl and isopropyl, n-Butyl, sec-Butyl, and tert-Bu, n-pentyl group and its isomers, n-hexyl group and its isomers, n-heptyl group and its isomers, n-octyl group and its isomers; unlimited example of X groups are F, Cl, 2,6-di-Me-phenoxy, 2,6-di-iPr-phenoxy, 2,6-di-t-Bu-4-Me-phenoxy (BHT), and the like. Examples of $AlR_mX_{(3-m)}$ can include $AlMe_3$, $AlEt_3$, Al^iBu_3 , $Al(n-Oct)_3$, $AlMe_2F$, $AlMeF_2$, $AlEt_2F$, $AlEtF_2$, Al^iBu_2F , $AlMe_2Cl$, $AlMeCl_2$, $AlEt_2Cl$, $AlEtCl_2$, Al^iBu_2Cl , $AlMe_2BHT$, $AlMeBHT_2$, $AlEt_2BHT$, $AlEtBHT_2$, Al^iBu_2BHT , and the like.

Haloarylborane Compound

- 10 [0064] The haloarylborane compound serves as the haloaryl group provider to form the supported haloarylaluminate activator through the exchange of the alkyl groups on the alkylaluminum compound served as the aluminate precursor with the haloaryl groups on the haloarylborane compound. Haloarylborane compounds for use herein can include tri-substituted haloarylborane compound having the Formula (B):



wherein: each of R^1 , R^2 , and R^3 is independently C_1 - C_{40} hydrocarbyl group, such as a C_1 - C_{40} -alkyl, C_1 - C_{40} -haloalkyl, C_6 - C_{40} -aryl, C_6 - C_{40} -haloaryl, C_2 - C_{40} -alkynyl, C_2 - C_{40} -haloalkynyl, C_2 - C_{40} -alkenyl, C_2 - C_{40} -haloalkenyl, C_1 - C_{40} alkoxy C_6 - C_{40} -aryloxy, C_8 - C_{40} -alkylaryloxy, or C_8 - C_{40} -arylalkyleneoxy group; and at least one of R^1 , R^2 , or R^3 is C_6 - C_{40} haloaryl.

- 20 [0065] In some embodiments, aryl of the C_6 - C_{40} haloaryl group is a phenyl, naphthalenyl, or anthracenyl group that is substituted with at least one halogen atom. In some embodiments, aryl of the C_6 - C_{40} haloaryl group is a partially aromatic group, such as tetrahydronaphthalenyl, acenaphthalenyl, indenyl, or fluorenyl that is substituted with at least one halogen atom, such as a halogen atom on a phenyl portion of the partially aromatic group.

- 25 [0066] In some embodiments, a halogen atom is fluorine. In some embodiments, C_6 - C_{40} -haloaryl is a perhaloaryl group, such as a perfluoroaryl group, such as perfluorophenyl (*i.e.*, C_6F_5).

[0067] In some embodiments, R^1 , R^2 , and R^3 is independently haloaryl such as a perfluoroaryl group, such as perfluorophenyl (*i.e.*, C_6F_5).

- 30 [0068] In some embodiments, an aluminum-containing capping agent is selected from: tris(perfluorophenyl)borane, tris(nonafluoroanthracenyl) borane, (nonafluoroanthracenyl)bis(pentafluorophenyl)borane, tris(undecafluorotetrahydronaphthalenyl)borane,

- (undecafluorotetrahydronaphthalenyl)bis(pentafluorophenyl) borane,
(undecafluorotetrahydronaphthalenyl)bis(nonafluoroanthracenyl)borane,
tris(nonafluorofluorenyl)borane,
bis(nonafluorofluorenyl)(pentafluorophenyl)borane,
5 bis(nonafluorofluorenyl)(nonafluoroanthracenyl)borane,
bis(nonafluorofluorenyl)(undecafluorotetrahydronaphthalenyl)borane,
tris(2,3,4,6-tetrafluorophenyl)borane,
tris(2,3,5,6-tetrafluorophenyl)borane,
tris(2,3,5-trifluorophenyl)borane,
10 tris(2,4,6-trifluorophenyl)borane,
tris(1,3-difluorophenyl)borane,
tris(2,3,5,6-tetrafluoro-4-methylphenyl)borane,
tris(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
tris(2,4,5-trifluoro-6-methylphenyl)borane,
15 tris(2,3,6-trifluoro-4-methylphenyl)borane,
tris(2,4,6-trifluoro-3-methylphenyl)borane,
tris(2,6-difluoro-3-methylphenyl)borane,
tris(2,4-difluoro-5-methylphenyl)borane,
tris(3,5-difluoro-2-methylphenyl)borane,
20 tris(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
tris(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
tris(2-methoxy-3,5,6-trifluorophenyl)borane,
tris(3-methoxy-2,5,6-trifluorophenyl)borane,
tris(3-methoxy-2,4,6-trifluorophenyl)borane,
25 tris(2-methoxy-3,5-difluorophenyl)borane,
tris(3-methoxy-2,6-difluorophenyl)borane,
tris(3-methoxy-4,6-difluorophenyl)borane,
tris(2-methoxy-4,6-difluorophenyl)borane,
tris(4-methoxy-2,6-difluorophenyl)borane,
30 bis(2,3,4,6-tetrafluorophenyl)(2,3,5,6-tetrafluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,3,5-trifluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,4,6-trifluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(1,3-difluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)borane,

- bis(2,3,4,6-tetrafluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
5 bis(2,3,4,6-tetrafluorophenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
10 bis(2,3,4,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl) borane,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
15 bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,3,4,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,3,5-trifluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,4,6-trifluorophenyl)borane,
20 bis(2,3,5,6-tetrafluorophenyl)(1,3-difluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
25 bis(2,3,5,6-tetrafluorophenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
30 bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,

- bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
5 bis(2,3,5-trifluorophenyl)(2,4,6-trifluorophenyl)borane
bis(2,3,5-trifluorophenyl)(1,3-difluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)borane,
bis(2,3,5-trifluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
bis(2,3,5-trifluorophenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
10 bis(2,3,5-trifluorophenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
bis(2,3,5-trifluorophenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,3,5-trifluorophenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(2,3,5-trifluorophenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,3,5-trifluorophenyl)(3,5-difluoro-2-methylphenyl)borane,
15 bis(2,3,5-trifluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
20 bis(2,3,5-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,3,5-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
25 bis(2,4,6-trifluorophenyl)(1,3-difluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
30 bis(2,4,6-trifluorophenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,4,6-trifluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,

- bis(2,4,6-trifluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
5 bis(2,4,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,4,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
10 bis(1,3-difluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)borane,
bis(1,3-difluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
bis(1,3-difluorophenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
bis(1,3-difluorophenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
bis(1,3-difluorophenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
15 bis(1,3-difluorophenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(1,3-difluorophenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(1,3-difluorophenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(1,3-difluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(1,3-difluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
20 bis(1,3-difluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(1,3-difluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(1,3-difluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(1,3-difluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(1,3-difluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
25 bis(1,3-difluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(1,3-difluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(1,3-difluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
30 bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,

- bis(2,3,5,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
5 bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
10 bis(2,3,5,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,4,5-trifluoro-6-methylphenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,6-difluoro-3-methylphenyl)borane,
15 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
20 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5-(difluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
25 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(2,3,6-trifluoro-4-methylphenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(2,6-difluoro-3-methylphenyl)borane,
30 bis(2,4,5-trifluoro-6-methylphenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,

- bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
5 bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,4,5-trifluoro-6-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(2,6-difluoro-3-methylphenyl)borane,
10 bis(2,3,6-trifluoro-4-methylphenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
15 bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
20 bis(2,3,6-trifluoro-4-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,3,6-trifluoro-4-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(2,6-difluoro-3-methylphenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(2,4-difluoro-5-methylphenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,
25 bis(2,4,6-trifluoro-3-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
30 bis(2,4,6-trifluoro-3-methylphenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,4,6-trifluoro-3-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,

- bis(2,6-difluoro-3-methylphenyl) (2,4-difluoro-5-methylphenyl)borane,
bis(2,6-difluoro-3-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,6-difluoro-3-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
5 bis(2,6-difluoro-3-methylphenyl) (2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl) (3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl) (3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl) (2-methoxy-3,5-difluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl) (3-methoxy-2,6-difluorophenyl)borane,
10 bis(2,6-difluoro-3-methylphenyl) (3-methoxy-4,6-difluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl) (2-methoxy-4,6-difluorophenyl)borane,
bis(2,6-difluoro-3-methylphenyl) (4-methoxy-2,6-difluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(3,5-difluoro-2-methylphenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
15 bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(2-methoxy-3,5-difluorophenyl)borane,
20 bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2,4-difluoro-5-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)borane,
25 bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(2-methoxy-3,5-difluorophenyl)borane,
30 bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(3,5-difluoro-2-methylphenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)borane,

- bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
5 bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)borane,
10 bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
15 bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)borane,
bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
bis(2-methoxy-3,5,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
20 bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(2-methoxy-3,5,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(2-methoxy-3,5,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
bis(3-methoxy-2,5,6-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)borane,
25 bis(3-methoxy-2,5,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl) borane,
bis(3-methoxy-2,5,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(3-methoxy-2,5,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(3-methoxy-2,5,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(3-methoxy-2,5,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
30 bis(3-methoxy-2,4,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)borane,
bis(3-methoxy-2,4,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
bis(3-methoxy-2,4,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
bis(3-methoxy-2,4,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
bis(3-methoxy-2,4,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,

- bis(2-methoxy-3,5-difluorophenyl)(3-methoxy-2,6-difluorophenyl)borane,
 bis(2-methoxy-3,5-difluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
 bis(2-methoxy-3,5-difluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
 bis(2-methoxy-3,5-difluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
 5 bis(3-methoxy-4,6-difluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
 bis(3-methoxy-4,6-difluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
 bis(3-methoxy-2,6-difluorophenyl)(3-methoxy-4,6-difluorophenyl)borane,
 bis(3-methoxy-2,6-difluorophenyl)(2-methoxy-4,6-difluorophenyl)borane,
 bis(3-methoxy-2,6-difluorophenyl)(4-methoxy-2,6-difluorophenyl)borane,
 10 bis(2-methoxy-4,6-difluorophenyl)(4-methoxy-2,6-difluorophenyl) borane,
 and combinations thereof.

Haloarylaluminum Compound

- [0069] Although multiple methods can be used to prepare the supported haloarylaluminate activator, the preferred method is the *in-situ* formation of the haloarylaluminum compound through bringing into contact of the alkylaluminum compound and the haloarylborane compound before contacting the support material to form the supported activator.

[0070] Examples of haloarylaluminum compounds for use herein can include tri-substituted aluminum compound having the Formula (1a):



- 20 wherein: each of R^1 , R^2 , and R^3 is independently C_1 - C_{40} hydrocarbyl group, such as a C_1 - C_{40} -alkyl, C_1 - C_{40} -haloalkyl, C_6 - C_{40} -aryl, C_6 - C_{40} -haloaryl, C_2 - C_{40} -alkynyl, C_2 - C_{40} -haloalkynyl, C_2 - C_{40} -alkenyl, C_2 - C_{40} -haloalkenyl, C_1 - C_{40} alkoxy C_6 - C_{40} -aryloxy, C_8 - C_{40} -alkylaryloxy, or C_8 - C_{40} -arylalkyleneoxy group; and at least one of R^1 , R^2 , or R^3 is C_6 - C_{40} haloaryl.

- [0071] In some embodiments, aryl of the C_6 - C_{40} haloaryl group is a phenyl, naphthalenyl, 25 or anthracenyl group that is substituted with at least one halogen atom. In some embodiments, aryl of the C_6 - C_{40} haloaryl group is a partially aromatic group, such as tetrahydronaphthalenyl, acenaphthalenyl, indenyl, or fluorenyl that is substituted with at least one halogen atom, such as a halogen atom on a phenyl portion of the partially aromatic group.

- [0072] In some embodiments, a halogen atom is fluorine. In some embodiments, 30 C_6 - C_{40} -haloaryl is a perhaloaryl group, such as a perfluoroaryl group, such as perfluorophenyl (*i.e.*, C_6F_5).

[0073] In some embodiments, R^1 , R^2 , and R^3 is independently haloaryl such as a perfluoroaryl group, such as perfluorophenyl (*i.e.*, C_6F_5).

[0074] In some embodiments, an aluminum-containing capping agent is selected from:

- tris(perfluorophenyl)aluminum,
tris(nonafluoroanthracenyl) aluminum,
(nonafluoroanthracenyl)bis(pentafluorophenyl)aluminum,
tris(undecafluorotetrahydronaphthalenyl)aluminum,
5 (undecafluorotetrahydronaphthalenyl)bis(pentafluorophenyl) aluminum,
(undecafluorotetrahydronaphthalenyl)bis(nonafluoroanthracenyl)aluminum,
tris(nonafluorofluorenyl)aluminum,
bis(nonafluorofluorenyl)(pentafluorophenyl)aluminum,
bis(nonafluorofluorenyl)(nonafluoroanthracenyl)aluminum,
10 bis(nonafluorofluorenyl)(undecafluorotetrahydronaphthalenyl)aluminum,
tris(2,3,4,6-tetrafluorophenyl)aluminum,
tris(2,3,5,6-tetrafluorophenyl)aluminum,
tris(2,3,5-trifluorophenyl)aluminum,
tris(2,4,6-trifluorophenyl)aluminum,
15 tris(1,3-difluorophenyl)aluminum,
tris(2,3,5,6-tetrafluoro-4-methylphenyl)aluminum,
tris(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
tris(2,4,5-trifluoro-6-methylphenyl)aluminum,
tris(2,3,6-trifluoro-4-methylphenyl)aluminum,
20 tris(2,4,6-trifluoro-3-methylphenyl)aluminum,
tris(2,6-difluoro-3-methylphenyl)aluminum,
tris(2,4-difluoro-5-methylphenyl)aluminum,
tris(3,5-difluoro-2-methylphenyl)aluminum,
tris(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
25 tris(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
tris(2-methoxy-3,5,6-trifluorophenyl)aluminum,
tris(3-methoxy-2,5,6-trifluorophenyl)aluminum,
tris(3-methoxy-2,4,6-trifluorophenyl)aluminum,
tris(2-methoxy-3,5-difluorophenyl)aluminum,
30 tris(3-methoxy-2,6-difluorophenyl)aluminum,
tris(3-methoxy-4,6-difluorophenyl)aluminum,
tris(2-methoxy-4,6-difluorophenyl)aluminum,
tris(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,3,5,6-tetrafluorophenyl)aluminum,

- bis(2,3,4,6-tetrafluorophenyl)(2,3,5-trifluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,4,6-trifluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(1,3-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)aluminum,
5 bis(2,3,4,6-tetrafluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2,6-difluoro-3-methylphenyl)aluminum,
10 bis(2,3,4,6-tetrafluorophenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
15 bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
20 bis(2,3,4,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,3,5-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,4,6-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(1,3-difluorophenyl)aluminum,
25 bis(2,3,5,6-tetrafluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
30 bis(2,3,5,6-tetrafluorophenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,

- bis(2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
5 bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,4,6-trifluorophenyl)aluminum,
10 bis(2,3,5-trifluorophenyl)(1,3-difluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
15 bis(2,3,5-trifluorophenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,3,5-trifluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
20 bis(2,3,5-trifluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
25 bis(2,3,5-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,5-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(1,3-difluorophenyl)aluminum,
30 bis(2,4,6-trifluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,

- bis(2,4,6-trifluorophenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,4,6-trifluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
5 bis(2,4,6-trifluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
10 bis(2,4,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(1,3-difluorophenyl)(2,3,5,6-tetrafluoro-4-methylphenyl)aluminum,
15 bis(1,3-difluorophenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
bis(1,3-difluorophenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(1,3-difluorophenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
bis(1,3-difluorophenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(1,3-difluorophenyl)(2,6-difluoro-3-methylphenyl)aluminum,
20 bis(1,3-difluorophenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(1,3-difluorophenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(1,3-difluorophenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(1,3-difluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(1,3-difluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
25 bis(1,3-difluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(1,3-difluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(1,3-difluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(1,3-difluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(1,3-difluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
30 bis(1,3-difluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(1,3-difluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,3,4,6-tetrafluoro-5-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,

- bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
5 bis(2,3,5,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
10 bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,5,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
15 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,4,5-trifluoro-6-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2,4-difluoro-5-methylphenyl)aluminum,
20 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
25 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2-methoxy-3,5-(difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,4,6-tetrafluoro-4-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
30 bis(2,3,4,6-tetrafluoro-4-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(2,3,6-trifluoro-4-methylphenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(2,4-difluoro-5-methylphenyl)aluminum,

- bis(2,4,5-trifluoro-6-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
5 bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
10 bis(2,4,5-trifluoro-6-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4,5-trifluoro-6-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(2,4,6-trifluoro-3-methylphenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(2,4-difluoro-5-methylphenyl)aluminum,
15 bis(2,3,6-trifluoro-4-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
20 bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,3,6-trifluoro-4-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
25 bis(2,3,6-trifluoro-4-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(2,6-difluoro-3-methylphenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
30 bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,

- bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4,6-trifluoro-3-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
5 bis(2,6-difluoro-3-methylphenyl)(2,4-difluoro-5-methylphenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
10 bis(2,6-difluoro-3-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
15 bis(2,6-difluoro-3-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,6-difluoro-3-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(3,5-difluoro-2-methylphenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
20 bis(2,4-difluoro-5-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
25 bis(2,4-difluoro-5-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2,4-difluoro-5-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(4-methoxy-2,3,5,6-tetrafluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
30 bis(3,5-difluoro-2-methylphenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(3-methoxy-2,6-difluorophenyl)aluminum.

- bis(3,5-difluoro-2-methylphenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(3,5-difluoro-2-methylphenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,5,6-tetrafluorophenyl)aluminum,
5 bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
10 bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(4-methoxy-2,3,5,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(2-methoxy-3,5,6-trifluorophenyl)aluminum,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
15 bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
20 bis(3-methoxy-2,4,5,6-tetrafluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-2,5,6-trifluorophenyl)aluminum,
bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(2-methoxy-3,5,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
25 bis(2-methoxy-3,5,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(2-methoxy-3,5,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(2-methoxy-3,5,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(3-methoxy-2,5,6-trifluorophenyl)(3-methoxy-2,4,6-trifluorophenyl)aluminum,
bis(3-methoxy-2,5,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,
30 bis(3-methoxy-2,5,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
bis(3-methoxy-2,5,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
bis(3-methoxy-2,5,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
bis(3-methoxy-2,5,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
bis(3-methoxy-2,4,6-trifluorophenyl)(2-methoxy-3,5-difluorophenyl)aluminum,

- bis(3-methoxy-2,4,6-trifluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
 bis(3-methoxy-2,4,6-trifluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
 bis(3-methoxy-2,4,6-trifluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
 bis(3-methoxy-2,4,6-trifluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
 5 bis(2-methoxy-3,5-difluorophenyl)(3-methoxy-2,6-difluorophenyl)aluminum,
 bis(2-methoxy-3,5-difluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
 bis(2-methoxy-3,5-difluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
 bis(2-methoxy-3,5-difluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
 bis(3-methoxy-4,6-difluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
 10 bis(3-methoxy-4,6-difluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
 bis(3-methoxy-2,6-difluorophenyl)(3-methoxy-4,6-difluorophenyl)aluminum,
 bis(3-methoxy-2,6-difluorophenyl)(2-methoxy-4,6-difluorophenyl)aluminum,
 bis(3-methoxy-2,6-difluorophenyl)(4-methoxy-2,6-difluorophenyl)aluminum,
 bis(2-methoxy-4,6-difluorophenyl)(4-methoxy-2,6-difluorophenyl) aluminum,
 15 and combinations thereof.

In-Situ Formation of Supported Haloarylaluminate Activator

[0075] Supported haloarylaluminate activators of the present disclosure have an aluminum atom that is substituted with one or more haloaryl groups formed *in-situ* through the ligand exchange between an alkylaluminum compound and a haloarylborane compound. Some pure
 20 form of haloarylalane compounds such as pure $\text{Al}(\text{C}_6\text{F}_5)_3$ may be unsafe to prepare and store. The *in-situ* formation of supported haloarylaluminate activator bypasses the isolation and storage of the pure $\text{Al}(\text{C}_6\text{F}_5)_3$ compound to make this reaction practical for scaling up as well as to reduce the processing cost.

[0076] Methods to form the supported haloarylaluminate activators *in-situ* can include;
 25 1) bringing into contact of a haloarylborane and aluminumalkyl compound to form a mixture in a diluent before it is added to support containing hydroxyl groups such that the Al:OH ratio <1 to allow excess OH to serve as the active proton source as the actual activator, with an optional Lewis base as the active proton stabilizer; 2) adding a haloarylborane to the support with or without the optional Lewis base active proton stabilizer, followed by an aluminumalkyl
 30 treatment, preferably at a low temperature, to form the supported activator composition; and 3) treating the support surface with at least one aluminumalkyl compound, preferably at a low temperature, by controlling the Al:OH ratio <1, with or without the Lewis base active proton stabilizer, followed by adding a haloarylborane compound, to form the supported haloarylaluminate activator. The above methods allow the formation of a supported

haloarylaluminate activator featuring the aluminate directly bound to an oxygen atom of the support material. The supported haloarylaluminate is further associated with a cationic group (further described below) to provide a counterion to the negatively charged aluminum. The negatively charged aluminum and cationic group act as an activator for activating a catalyst compound. The aluminum atom with one or more substituted haloaryl groups, the support material, and the cationic group collectively provide a support-bound activator of the present disclosure.

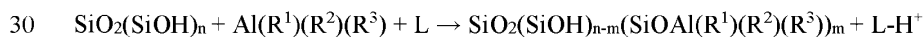
[0077] In addition, it is within the scope of the present disclosure to, in addition to using a support-bound activator, further using an additional activator as part of a catalyst system of the present disclosure. Additional activators can include any suitable ionizing activator, neutral or ionic, alumoxane, or modified alumoxane.

[0078] A haloaryl aluminate compound (a capping agent used to form the support-bound activators) can be prepared/synthesized according to any suitable method. For example, a trialkyl aluminum compound can be treated with a tris(haloaryl)boron compound to form a trialkyl boron and an aluminum having three haloaryl groups. The aluminum having three haloaryl groups can then be introduced with the support material and cationic group to form a support-bound activator of the present disclosure.

[0079] Conveniently, trimethylaluminum can be treated with a tris(haloaryl)boron compound to form trimethylboron (*e.g.*, a gas) and an aluminum having three haloaryl groups. For example, trimethylaluminum can be reacted with tris(pentafluorophenyl)boron to form trimethylboron and tris(pentafluorophenyl)aluminum.

[0080] The trialkyl aluminum starting material (such as trimethylaluminum) can be obtained commercially. Tris(haloaryl)boron compounds can likewise be obtained commercially or may be prepared using any suitable method, such as those described in US Pat. Nos. 6,118,026 and 6,410,810, incorporated by reference herein.

[0081] A haloaryl aluminate compound may act as capping agent, combining with free hydroxyl groups located on and/or within the support material. For example, the aluminum-containing capping agent can combine with a silica-based support material according to the following equation:



wherein:

R^1 , R^2 , and R^3 are defined as above;

each of n and m are independently positive integers; and

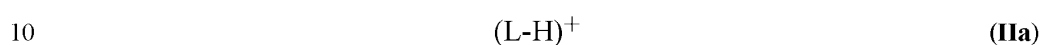
L is a neutral form of a cationic group that abstracts a hydrogen atom from a hydroxyl

group of SiOH to form $L-H^+$ which is the cationic group.

Lewis Base and Cationic Groups

[0082] Cationic groups can be ammonium groups. Ammonium groups can be formed by treating the support material with the aluminum-containing capping agent and an amine which is the neutral form of the ammonium group. The neutral form of the ammonium group (the amine) can abstract a hydrogen atom from a hydroxyl group of the support material to form the ammonium group. Without being bound by theory, it is believed that the ammonium group coordinates with a negatively charged aluminum atom bonded to the support material.

[0083] In some embodiments, the cationic group is represented by Formula (IIa):



wherein L is a neutral Lewis base; and H is hydrogen. $(L-H)^+$ is a Bronsted acid. Without being bound by theory, for activation of a catalyst compound, $(L-H)^+$ as a Bronsted acid is capable of donating a proton to the transition metal catalyst precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, sulfoniums, and mixtures thereof. Examples of ammoniums are those derived from methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, N-methyl-4-nonadecyl-N-octadecylaniline, N-methyl-4-octadecyl-N-octadecylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, dioctadecylmethylamine, and the like. Examples of phosphoniums are those derived from triethylphosphine, triphenylphosphine, and diphenylphosphine, and the like. Examples of oxoniums are those derived from ethers such as dimethyl ether, diethyl ether, tetrahydrofuran, dioxane, and the like. Examples of sulfoniums are those derived from thioethers, such as diethyl thioethers, tetrahydrothiophene, and the like.

[0084] In some embodiments, a cationic group is represented by Formula (IIIa):



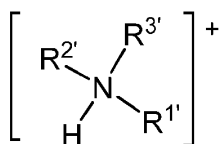
wherein:

E is nitrogen or phosphorous; and

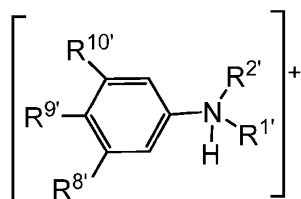
each of R^1 , R^2 , and R^3 are independently a C_1 to C_{50} hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, halogen atoms, or halogen containing groups.

[0085] In some embodiments, R^1 is a methyl or ethyl group; R^2 and R^3 are independently C_4 - C_{50} hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, halogen atoms, or halogen containing groups.

[0086] In some embodiments, a cationic group is represented by one or both of the following formulae:



and



5

wherein:

N is nitrogen;

each of $R^{1'}$, $R^{2'}$ and $R^{3'}$ is independently C_1 - C_{40} hydrocarbyl groups optionally substituted with one or more alkoxy groups, silyl groups, halogen atoms, or halogen containing groups; and

each of $R^{8'}$, $R^{9'}$, and $R^{10'}$ is independently a hydrogen, a C_1 - C_{30} hydrocarbyl or substituted C_1 - C_{30} hydrocarbyl group.

[0087] In some embodiments, each of $R^{8'}$ and $R^{10'}$ is hydrogen, and $R^{9'}$ is a C_1 - C_{30} hydrocarbyl group, preferably a C_4 - C_{30} hydrocarbyl group, which is optionally substituted with one or more alkoxy groups, silyl groups, halogen atoms, or halogen containing groups. In some

embodiments, $R^{9'}$ is a C_8 - C_{22} hydrocarbyl group which is optionally substituted with one or more alkoxy groups, silyl groups, halogen atoms, or halogen containing groups.

[0088] In some embodiments, each of $R^{2'}$ and $R^{3'}$ is independently a C_{12} - C_{22} hydrocarbyl group and $R^{1'}$ is methyl.

[0089] In some embodiments, $R^{2'}$ and $R^{3'}$ 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).

[0090] In some embodiments, $R^{8'}$, $R^{9'}$, and $R^{10'}$ 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

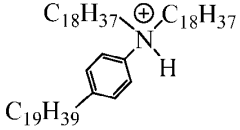
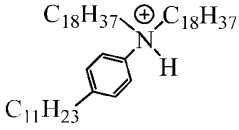
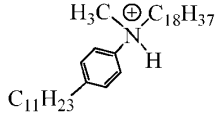
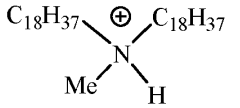
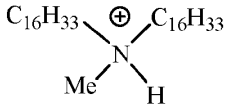
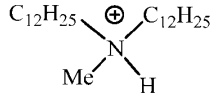
carbon atoms, such as 38 or more carbon atoms, such as 40 or more carbon atoms, such as 15 to 100 carbon atoms, such as 25 to 75 carbon atoms).

[0091] In some embodiments, $R^{1'}$ is a methyl group; $R^{2'}$ is C_6 - C_{50} aryl group; and $R^{3'}$ is independently C_1 - C_{40} linear alkyl or C_5 - C_{50} -aryl group.

- 5 [0092] In some embodiments, each of $R^{2'}$ and $R^{3'}$ is independently unsubstituted or substituted with at least one of halide, C_1 - C_{35} alkyl, or C_5 - C_{15} aryl.

[0093] In some embodiments, a cationic group is selected from:

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	

[0094] In some embodiments, a cationic group is selected from:

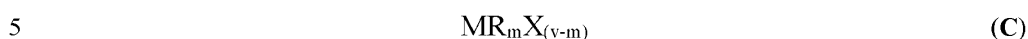
- N,N*-di(methyl)anilinium,
- N,N*-di(ethyl)anilinium,
- 5 *N,N*-di(propyl)anilinium,
- N,N*-di(butyl)anilinium,
- N,N*-di(pentyl)anilinium,
- N,N*-di(hexyl)anilinium,
- N,N*-di(heptyl)anilinium,
- 10 *N,N*-di(octyl)anilinium,
- N,N*-di(nonyl)anilinium,
- N,N*-di(decyl)anilinium,
- or combinations thereof.

[0095] In some embodiments, a cationic group is selected from:

- 15 *N,N*-di(hydrogenated tallow)methylammonium,
- N*-methyl-4-nonadecyl-*N*-octadecylanilinium,
- N*-methyl-4-hexadecyl-*N*-octadecylanilinium,
- N*-methyl-4-tetradecyl-*N*-octadecylanilinium,
- N*-methyl-4-dodecyl-*N*-octadecylanilinium,
- 20 *N*-methyl-4-decyl-*N*-octadecylanilinium,
- N*-methyl-4-octyl-*N*-octadecylanilinium,
- N*-methyl-4-hexyl-*N*-octadecylanilinium,
- N*-methyl-4-butyl-*N*-octadecylanilinium,
- N*-methyl-4-octadecyl-*N*-decylanilinium,
- 25 *N*-methyl-4-nonadecyl-*N*-dodecylanilinium,
- N*-methyl-4-nonadecyl-*N*-tetradecylanilinium,
- N*-methyl-4-nonadecyl-*N*-hexadecylanilinium,
- N*-ethyl-4-nonadecyl-*N*-octadecylanilinium,

- N*-methyl-*N,N*-dioctadecylammonium,
N-methyl-*N,N*-dihexadecylammonium,
N-methyl-*N,N*-ditetradecylammonium,
N-methyl-*N,N*-didodecylammonium,
5 *N*-methyl-*N,N*-didecylammonium,
N-methyl-*N,N*-dioctylammonium,
N-ethyl-*N,N*-dioctadecylammonium,
N,N-di(octadecyl)tolylammonium,
N,N-di(hexadecyl)tolylammonium,
10 *N,N*-di(tetradecyl)tolylammonium,
N,N-di(dodecyl)tolylammonium,
N-octadecyl-*N*-hexadecyl-tolylammonium,
N-octadecyl-*N*-tetradecyl-tolylammonium,
N-octadecyl-*N*-dodecyl-tolylammonium,
15 *N*-octadecyl-*N*-decyl-tolylammonium,
N-hexadecyl-*N*-tetradecyl-tolylammonium,
N-hexadecyl-*N*-dodecyl-tolylammonium,
N-hexadecyl-*N*-decyl-tolylammonium,
N-tetradecyl-*N*-dodecyl-tolylammonium,
20 *N*-tetradecyl-*N*-decyl-tolylammonium,
N-dodecyl-*N*-decyl-tolylammonium,
N-methyl-*N*-octadecylanilinium,
N-methyl-*N*-hexadecylanilinium,
N-methyl-*N*-tetradecylanilinium,
25 *N*-methyl-*N*-dodecylanilinium,
N-methyl-*N*-decylanilinium, or
N-methyl-*N*-octylanilinium, or
combinations thereof. Combinations of any of the cationic groups listed or illustrated above
may be used.
- 30 Optional Support Surface Hydroxyl Group Capping Agent
[0096] The optional main group compound capping agent is used to convert the uncovered
support surface hydroxyl groups left when a sub-stoichiometric charge of the haloarylaluminate
based on total reactive surface hydroxyl groups is desired for the purpose of preventing
hydroxyl group poisoning of the activated catalyst molecules. Depending on the support

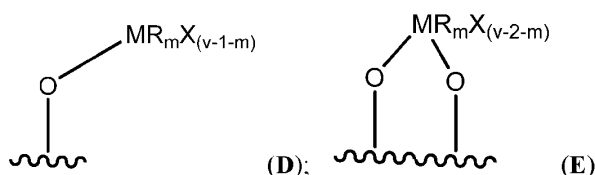
calcination conditions, isolated or hydrogen bonded hydroxyl groups may be dominant, *e.g.*, at <300°C calcination, hydrogenated hydroxyl is dominant whereas at >600°C calcination, the isolated hydroxyl is dominant. The suitable optional main group compound capping agents are represented by formula (C):



wherein:

M is a group 2 or 13 metal; each of R is independently C₁-C₁₀-alkyl; X is F or OR¹ where R¹ is substituted or unsubstituted C₁-C₄₀-alkyl, C₁-C₄₀-alkoxy, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl; v is the valence state of the metal M 2 or 3; m = 1, 2, or 3 but not larger than v. Some examples are AlMe₃, AlEt₃, AlⁱBu₃, Al(n-Oct)₃, AlMe₂F, AlMeF₂, AlEt₂F, AlEtF₂, AlⁱBu₂F, AlMe₂Cl, AlMeCl₂, AlEt₂Cl, AlEtCl₂, AlⁱBu₂Cl, AlMe₂BHT, AlMeBHT₂, AlEt₂BHT, AlEtBHT₂, AlⁱBu₂BHT, MgMe₂, MgEt₂, MgPr₂, MgBu₂, MgⁱBu₂, Mg(n-Oct)₂, MgMeF, MgEtF, MgⁱBuF, MgMeCl, MgEtCl, MgPrCl, MgⁱBuCl, MgMeBHT, MgEtBHT, and the like.

[0097] Depending on the calcination temperature of the supported material, a portion of the hydroxyl groups on the support surface can be capped with the main group capping agent with represented formulas (D and E):



wherein:

M is a group 2 or 13 metal; each of R is independently C₁-C₁₀₄₀-alkyl; X is F or OR¹ where R¹ is substituted or unsubstituted C₁-C₄₀-alkyl, C₁-C₄₀-alkoxy, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl; v is the valence state of the metal M 2 or 3; m = 1, 2, or 3 but not larger than v.

25 Conditions for Forming Support-Bound Activators

[0098] In some embodiments, prior to contacting the support material with one or more capping agents of the present disclosure, the support material can have a hydroxyl concentration from about 100 millimoles per gram (mmol/g) to about 1,000 mmol/g. After contacting the support material with one or more capping agents (haloarylaluminates) to reduce the number of available hydroxyl groups on the support material, the support material can have

a hydroxyl concentration from about 0.001 millimoles per gram of support-bound activator (mmol/g) to about 10 mmol/g.

5 [0099] Independently, the aluminum-containing capping agent having haloaryl groups and the cationic group (in neutral form) may be introduced with the support at a molar ratio of about 0.01:1 to about 1:1, based on the molar concentration of, respectively, the aluminum-containing capping agent having haloaryl groups or the cationic group (in neutral form) relative to the molar concentration of hydroxyl groups of the support. Within this range, a molar ratio of less than or equal to about 1:1 can be employed, such as less than or equal to about 0.5:1, such as less than or equal to about 0.25:1.

10 [0100] In some embodiments, the aluminum-containing capping agent (once bound to the support material) is substantially dispersed over substantially all of the total surface area of the support material, where substantially all refers to at least about 75%, such as greater than 90% of the aluminum-containing capping agent present with the support material.

15 [0101] As discussed with respect to hydroxyl concentration above, the presence of aluminum-containing capping agent can be determined from Attenuated Total Reflectance Infrared Spectroscopy (ATRIR), X-ray Photoelectron Spectroscopy (XPS), NMR, as well as being directly measured by Secondary Ion Mass Spectroscopy (SIMS), all of which are well known to those skilled in the respective arts.

20 [0102] After an aluminum-containing capping agent is introduced with the support material, there may be remaining hydroxyl groups on the support material. The residual uncapped hydroxyls can be detrimental to overall catalyst activity. To prevent catalyst deactivation, the remaining hydroxyl groups can be treated with additional equivalents of aluminum compound (referred to as second aluminum compound, such as the optional main group compound capping agent) having the following formula: $\text{Al}(\text{R}^1)(\text{R}^2)(\text{R}^3)$; where Al is aluminum, R^1 is C_1 - C_{40} alkyl, a substituted or unsubstituted C_6 - C_{40} aryl, or hydride; R^2 and R^3 are independently, C_1 - C_{40} alkyl, alkoxy, heteroalkyl, a substituted or unsubstituted C_6 - C_{40} aryloxy or heteroaryl group.

30 [0103] The second aluminum compound typically contains simple components such as an alkyl aluminum and phenolic derivatives, such as BHT). The protonolysis reaction of either aluminum alkyl or aluminum hydride groups by surface hydroxyls results in deactivation of hydroxyl groups via release of hydrocarbon or hydrogen, and leads to anchoring of second aluminum compound on support. This effectively reduces or eliminates the possibility of active protons interfering with catalyst activity.

[0104] The second aluminum compound (optional main group compound capping agent)

may be introduced with the activator-bound support at a molar ratio of independently about 0.1:1 to about 10:1, based on the molar concentration of, respectively, the second aluminum compound relative to the molar concentration of hydroxyl groups of the support (before treatment with aluminum-containing capping agent). Within this range, a molar ratio of less than or equal to about 5:1 can be employed, such as less than or equal to about 2:1, and most preferably less than or equal to about 1:1. In some embodiments within these ranges is molar ratio of second aluminum compound relative to hydroxyl groups can be less than or equal to about 0.9:1, such as less than or equal to about 0.8:1, such as less than or equal to 0.5:1, such as less than or equal to 0.25:1.

10 Supportation of Catalyst Compound(s) onto Support-Bound Activators

[0105] The support-bound activator is slurried in a non-polar solvent and the resulting slurry is contacted with a solution of a catalyst compound (and optional additional activator). In some embodiments, the slurry of the support-bound activator is first contacted with the catalyst compound for a period of time of about 0.5 hours to about 24 hours, about 2 hours to about 16 hours, or about 4 hours to about 8 hours. The mixture of the catalyst compound and support-bound activator is heated to about 0°C to about 70°C, such as about 23°C to about 60°C, such as at room temperature.

[0106] Suitable non-polar solvents are materials in which all of the reactants used herein, *e.g.*, the support-bound activator and the catalyst compound, are at least partially miscible or soluble and which are liquid at reaction temperatures. In some embodiments, non-polar solvents are alkanes, such as isopentane, hexane, isohexane, *n*-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as methylcyclohexane, aromatics, such as benzene, toluene, and ethylbenzene, may also be employed. Mixed hydrocarbon solvents including Isopar™ and Nappar™ may also be used.

25 [0107] In some embodiments, a molar ratio of Aluminum atoms to Metal atoms (of the catalyst compound) is a 1:1 molar ratio. Alternatively, ranges include about 1:1 to about 250:1, such as about 250:1 to about 100:1, such as about 100:1 to about 50:1, such as about 50:1 to about 20:1, such as about 20:1 to about 10:1, such as about 10:1 to about 5:1, such as about 5:1 to about 2:1.

30 Catalyst Compounds

[0108] The terms “catalyst”, “catalyst compound”, “catalyst complex”, “transition metal complex”, “transition metal compound”, “precatalyst compound”, and “precatalyst complex” are used interchangeably to describe a transition metal or lanthanide metal complex that forms an olefin polymerization catalyst when combined with a suitable activator.

[0109] In an embodiment of the present disclosure, the catalyst complexes of the present disclosure include a metal selected from groups 3, 4, 5 or 6 or lanthanide metals of the Periodic Table of the Elements, a tridentate dianionic ligand containing two anionic donor groups and a neutral heterocyclic Lewis base donor, wherein the heterocyclic donor is covalently bonded between the two anionic donors. In some embodiments, the dianionic, tridentate ligand features a central heterocyclic donor group and two phenolate donors and the tridentate ligand coordinates to the metal center to form two eight-membered rings.

[0110] The metal can be selected from group 3, 4, 5, or 6 elements. In some embodiments, the metal, M, is a group 4 metal, such as zirconium or hafnium.

[0111] A catalyst of the present disclosure can be a metal complex having: a metal selected from groups 3-6 or lanthanide metals, and a tridentate, dianionic ligand containing two anionic donor groups and a neutral Lewis base donor, where the neutral Lewis base donor is covalently bonded between the two anionic donors, and where the metal-ligand complex features a pair of 8-membered metallocycle rings.

[0112] In some embodiments, the heterocyclic Lewis base donor of the catalyst compound features a nitrogen or oxygen donor atom. For example, heterocyclic groups include derivatives of pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, and substituted variants of thereof. In some embodiments, the heterocyclic Lewis base lacks hydrogen(s) in the position alpha to the donor atom. In some embodiments, a heterocyclic Lewis base donor includes pyridine, 3-substituted pyridines, and 4-substituted pyridines.

[0113] The anionic donors of the tridentate dianionic ligand may be arylthiolates, phenolates, or anilides. In some embodiments, anionic donors are phenolates. The tridentate dianionic ligand coordinates to the metal center to form a complex that may lack a mirror plane of symmetry. In some embodiments, the tridentate dianionic ligand coordinates to the metal center to form a complex that has a two-fold rotation axis of symmetry; when determining the symmetry of the bis(phenolate) complexes only the metal and dianionic tridentate ligand are considered (*i.e.*, ignore remaining ligands).

[0114] Catalyst compounds of the present disclosure can be bis(aryl phenolate)pyridine complexes. Bis(aryl phenolate)pyridine complexes may have a tridentate bis(aryl phenolate)pyridine ligand that is coordinated to a group 4 transition metal with the formation of two eight-membered rings. In some embodiments, a bis(aryl phenolate)pyridine complexes includes transition metal complexes of a dianionic, tridentate ligand that features a central neutral donor group and two phenolate donors, where the tridentate ligands coordinate to the

metal center to form two eight-membered rings, for example, the post-metallocene catalyst can be an 8-8 catalyst. In complexes of this type, it is advantageous for the central neutral donor to be a heterocyclic group. It is advantageous for the heterocyclic group to lack hydrogens in the position alpha to the heteroatom. In complexes of this type it may also be advantageous for the phenolates to be substituted with one or more cyclic tertiary alkyl substituents. The use of cyclic tertiary alkyl substituted phenolates can improve the ability of these catalysts to produce high molecular weight polymer.

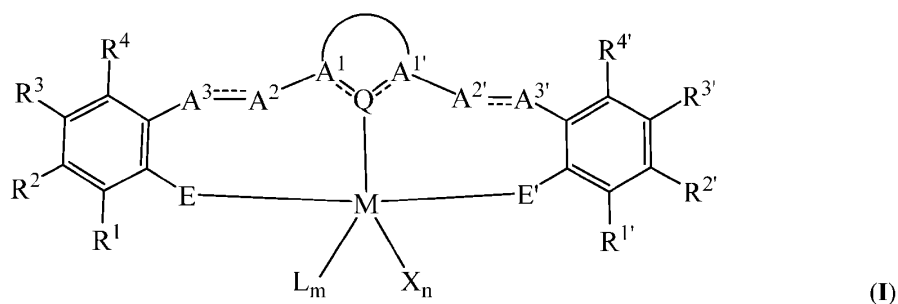
[0115] In some embodiments, bis(phenolate) ligands can be tridentate dianionic ligands that coordinate to the metal M in such a fashion that a pair of 8-membered metallocycle rings are formed. The bis(phenolate) ligands wrap around the metal to form a complex with a 2-fold rotation axis, thus giving the complexes C_2 symmetry. The C_2 geometry and the 8-membered metallocycle rings are features of these complexes that make them effective catalyst components for the production of polyolefins, particularly isotactic poly(alpha olefins). If the ligands were coordinated to the metal in such a manner that the complex had mirror-plane (C_s) symmetry, then the catalyst would be expected to produce only atactic poly(alpha olefins); these symmetry-reactivity concepts are summarized by Bercaw, J. E. (2009) in *Macromolecules*, v.42, pp. 8751-8762. The pair of 8-membered metallocycle rings of the catalyst compounds is also a notable feature that is advantageous for temperature stability, and isoselectivity of monomer enchainment. Related group 4 complexes featuring smaller 6-membered metallocycle rings are known (*Macromolecules* 2009, v.42, pp. 8751-8762) to form mixtures of C_2 and C_s symmetric complexes when used in olefin polymerizations and are thus not well suited to the production of highly isotactic poly(alpha olefins).

[0116] Bis(phenolate) ligands that contain oxygen donor groups (*i.e.*, E = E' = oxygen of Formula (I)) can be substituted with alkyl, substituted alkyl, aryl, or other groups. It can be advantageous that each phenolate group be substituted in the ring position that is adjacent to the oxygen donor atom. For example, that substitution at the position adjacent to the oxygen donor atom can be an alkyl group containing 1-20 carbon atoms. The substitution at the position next to the oxygen donor atom can be a non-aromatic cyclic alkyl group with one or more five- or six-membered rings. Substitution at the position next to the oxygen donor atom can be a cyclic tertiary alkyl group. In some embodiments, substitution at the position next to the oxygen donor atom is adamantan-1-yl or substituted adamantan-1-yl.

[0117] The neutral heterocyclic Lewis base donor is covalently bonded between the two anionic donors (*e.g.*, between two phenolate groups) via "linker groups" that join the heterocyclic Lewis base to the anionic donors. The "linker groups" are indicated by (A³A²)

and (A^{2'}A^{3'}) in Formula (I). The choice of each linker group may affect the catalyst performance, such as the tacticity of the poly(alpha olefin) produced. Each linker group can be a C₂-C₄₀ divalent group that is two-atoms in length. One or both linker groups may independently be phenylene, substituted phenylene, heteroaryl, vinylene, or a non-cyclic two-carbon long linker group. When one or both linker groups are phenylene, the alkyl substituents on the phenylene group may be chosen to optimize catalyst performance. Typically, one or both phenylenes may be unsubstituted or may be independently substituted with C₁ to C₂₀ alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or an isomer thereof, such as isopropyl, etc.

[0118] In some embodiments, a catalyst compound is represented by Formula (I):



wherein:

- M is a group 3, 4, 5, or 6 transition metal or a lanthanide (such as Hf, Zr or Ti);
- E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group, such as O, such as both E and E' are O;
- Q is group 14, 15, or 16 atom that forms a dative bond to metal M, such as Q is C, O, S or N, such as Q is C, N, or O, such as Q is N;
- A¹QA^{1'} are part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A² to A^{2'} via a 3-atom bridge with Q being the central atom of the 3-atom bridge (A¹QA^{1'} combined with the curved line joining A¹ and A^{1'} represents the heterocyclic Lewis base);
- each of A¹ and A^{1'} are independently C, N, or C(R²²), where R²² is selected from hydrogen, C₁-C₂₀ hydrocarbyl, and C₁-C₂₀ substituted hydrocarbyl (for example, each of A¹ and A^{1'} are C);

A³---A² is a divalent group containing 2 to 40 non-hydrogen atoms that links A¹ to the E-bonded aryl group via a 2-atom bridge, such as ortho-phenylene, substituted ortho-

phenylene, ortho-arene, substituted ortho-arene, indolene, substituted indolene, benzothiophene, substituted benzothiophene, pyrroline, substituted pyrroline, thiophene, substituted thiophene, 1,2-ethylene (-CH₂CH₂-), substituted 1,2-ethylene, 1,2-vinylene (-HC=CH-), or substituted 1,2-vinylene, such as $A^3 \equiv A^2$ is a divalent hydrocarbyl group;

- 5 $A^{2'} \equiv A^{3'}$ is a divalent group containing 2 to 40 non-hydrogen atoms that links A^{1'} to the E'-bonded aryl group via a 2-atom bridge such as ortho-phenylene, substituted ortho-phenylene, ortho-arene, substituted ortho-arene, indolene, substituted indolene, benzothiophene, substituted benzothiophene, pyrroline, substituted pyrroline, thiophene, substituted thiophene, 1,2-ethylene (-CH₂CH₂-), substituted 1,2-ethylene, 1,2-vinylene
- 10 (-HC=CH-), or substituted 1,2-vinylene, such as $A^{2'} \equiv A^{3'}$ is a divalent hydrocarbyl group;
- each L is independently a Lewis base;
- each X is independently an anionic ligand;
- n is 1, 2 or 3;
- m is 0, 1, or 2;
- 15 n+m is not greater than 4;
- each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group (such as R^{1'} and R¹ are independently a cyclic group, such as a cyclic tertiary alkyl group), or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be
- 20 joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings;
- any 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; and
- 25 any two X groups may be joined together to form a dianionic ligand group.

[0119] The metal, M, is selected from group 3, 4, 5, or 6 elements, such as group 4. For example, the metal, M, is zirconium or hafnium.

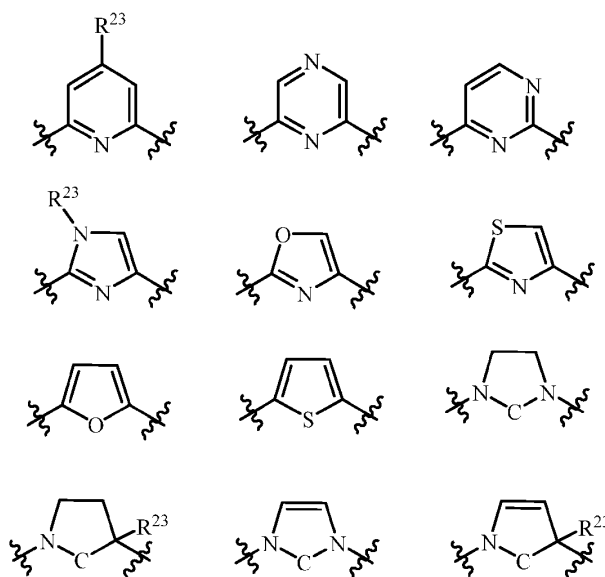
[0120] The donor atom Q of the neutral heterocyclic Lewis base (in Formula (I)) can be nitrogen, carbon, or oxygen. In some embodiments, Q is nitrogen.

- 30 [0121] Non-limiting examples of neutral heterocyclic Lewis base groups include derivatives of pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, and substituted variants of thereof. Heterocyclic Lewis base groups can include

derivatives of pyridine, pyrazine, thiazole, and imidazole.

[0122] Each of A^1 and $A^{1'}$ of the heterocyclic Lewis base (of Formula (I)) is independently C, N, or $C(R^{22})$, where R^{22} is selected from hydrogen, C_1 - C_{20} hydrocarbyl, and C_1 - C_{20} substituted hydrocarbyl. In some embodiments, each of A^1 and $A^{1'}$ is carbon. When Q is carbon, each of A^1 and $A^{1'}$ can be selected from nitrogen and $C(R^{22})$. When Q is nitrogen, each of A^1 and $A^{1'}$ can be carbon. In some embodiments, Q = nitrogen and $A^1 = A^{1'} =$ carbon. When Q is nitrogen or oxygen, the heterocyclic Lewis base of Formula (I) might not have any hydrogen atoms bound to the A^1 or $A^{1'}$ atoms, which may be preferred because it is thought that hydrogens in those positions may undergo unwanted decomposition reactions that reduce the stability of the catalytically active species.

[0123] The heterocyclic Lewis base (of Formula (I)) represented by $A^1QA^{1'}$ combined with the curved line joining A^1 and $A^{1'}$ can be selected from the following, with each R^{23} group selected from hydrogen, heteroatoms, C_1 - C_{20} alkyls, C_1 - C_{20} alkoxides, C_1 - C_{20} amides, and C_1 - C_{20} substituted alkyls.



15

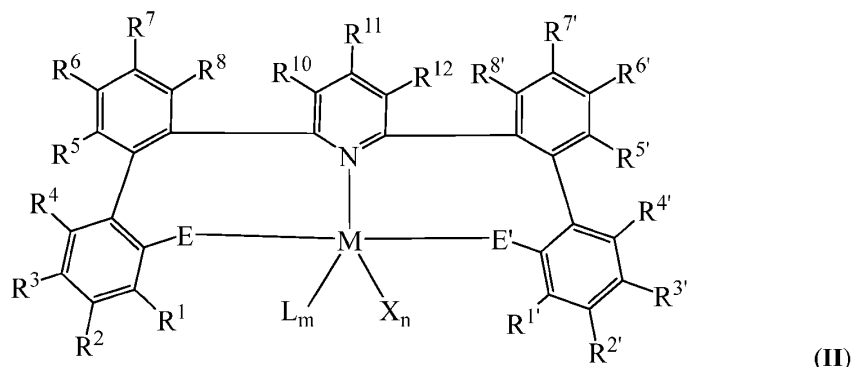
[0124] In some embodiments, the heterocyclic Lewis base (of Formula (I)) represented by $A^1QA^{1'}$ combined with the curved line joining A^1 and $A^{1'}$ is a six membered ring containing zero or one ring heteroatoms or a five membered ring containing zero, one two or three ring heteroatoms. Alternately, the heterocyclic Lewis base (of Formula (I)) represented by $A^1QA^{1'}$ combined with the curved line joining A^1 and $A^{1'}$ is not a six membered ring containing two or more ring heteroatoms.

20

- [0125] In some embodiments of Formula (I), Q is C, N or O, such as Q is N.
- [0126] In some embodiments of Formula (I), each of A¹ and A^{1'} is independently carbon, nitrogen, or C(R²²), with R²² selected from hydrogen, C₁-C₂₀ hydrocarbyl, substituted C₁-C₂₀ hydrocarbyl. In some embodiments, each of A¹ and A^{1'} is carbon.
- 5 [0127] In some embodiments of Formula (I), A¹QA^{1'} of Formula (I) is part of a heterocyclic Lewis base, such as a pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, or a substituted variant of thereof.
- [0128] In some embodiments of Formula (I), A¹QA^{1'} are part of a heterocyclic Lewis base containing 2 to 20 non-hydrogen atoms that links A² to A^{2'} via a 3-atom bridge with Q being
10 the central atom of the 3-atom bridge. In some embodiments, each A¹ and A^{1'} is a carbon atom and the A¹QA^{1'} fragment forms part of a pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, or a substituted variant of thereof group, or a substituted variant thereof.
- [0129] In at least one embodiment of Formula (I), Q is carbon and each of A¹ and A^{1'} is N
15 or C(R²²), where R²² is selected from hydrogen, C₁-C₂₀ hydrocarbyl, substituted C₁-C₂₀ hydrocarbyl, a heteroatom or a heteroatom-containing group. In such embodiments, the A¹QA^{1'} fragment forms part of a cyclic carbene, N-heterocyclic carbene, cyclic amino alkyl carbene, or a substituted variant thereof.
- [0130] In some embodiments of Formula (I), A³---A² is a divalent group containing 2
20 to 20 non-hydrogen atoms that links A¹ to the E-bonded aryl group via a 2-atom bridge, where the A³---A² is a linear alkyl or forms part of a cyclic group (such as an optionally substituted ortho-phenylene group, or ortho-arylene group) or a substituted variant thereof.
- [0131] A^{2'}---A^{3'} is a divalent group containing 2 to 20 non-hydrogen atoms that links
25 A^{1'} to the E'-bonded aryl group via a 2-atom bridge, where the A^{2'}---A^{3'} is a linear alkyl or forms part of a cyclic group (such as an optionally substituted ortho-phenylene group, or ortho-arylene group), or a substituted variant thereof.
- [0132] In some embodiments of Formula (I), M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls.
- [0133] In some embodiments of Formula (I), M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'}
30 are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
- [0134] In some embodiments of Formula (I), M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'}

are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are C₆-C₂₀ aryls.

[0135] In some embodiments, a catalyst compound is represented by Formula (II):



wherein:

- 5 M is a group 3, 4, 5, or 6 transition metal or a lanthanide (such as a group 4 transition metal that is Hf, Zr or Ti);
- E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group, such as O, such as both E and E' are O;
- 10 each L is independently a Lewis base;
- each X is independently an anionic ligand;
- n is 1, 2 or 3;
- m is 0, 1, or 2;
- n+m is not greater than 4;
- 15 each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring
- 20 atoms, and where substitutions on the ring can join to form additional rings:
- any 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;
- any two X groups may be joined together to form a dianionic ligand group;
- each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹, and R¹² is independently hydrogen,
- 25 C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R⁵ and R⁶, R⁶ and R⁷, R⁷ and R⁸, R^{5'} and R^{6'}, R^{6'} and R^{7'}, R^{7'} and R^{8'}, R¹⁰ and R¹¹, or R¹¹ and R¹² may be joined to form one or more substituted hydrocarbyl rings,

unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0136] In Formula (I) or (II), E and E' are each selected from oxygen or NR⁹, where R⁹ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group. In some embodiments, E and E' are oxygen. When E and/or E' are NR⁹, R⁹ can be selected from C₁ to C₂₀ hydrocarbyls, alkyls, or aryls. In one embodiment E and E' are each selected from O, S, or N(alkyl) or N(aryl), where the alkyl can be a C₁ to C₂₀ alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like, and aryl is a C₆ to C₄₀ aryl group, such as phenyl, naphthalenyl, benzyl, methylphenyl, and the like.

[0137] In some embodiments, A³---A² and A^{2'}---A^{3'} are independently a divalent hydrocarbyl group, such as C₁ to C₁₂ hydrocarbyl group.

[0138] In some embodiments of catalyst compounds of Formula (I) or (II), when E and E' are oxygen, each phenolate group can be substituted in the position that is next to the oxygen atom (*i.e.*, R¹ and R^{1'} in Formula (I) and (II)). Thus, when E and E' are oxygen, each of R¹ and R^{1'} is independently a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, such as each of R¹ and R^{1'} is independently a non-aromatic cyclic alkyl group with one or more five- or six-membered rings (such as cyclohexyl, cyclooctyl, adamantyl, or 1-methylcyclohexyl, or substituted adamantyl), such as a non-aromatic cyclic tertiary alkyl group (such as 1-methylcyclohexyl, adamantyl, or substituted adamantyl).

[0139] In some embodiments of the catalyst compound of Formula (I) or (II), each of R¹ and R^{1'} is independently a tertiary hydrocarbyl group. In other embodiments of Formula (I) or (II), each of R¹ and R^{1'} is independently a cyclic tertiary hydrocarbyl group. In other embodiments of the catalyst compound of Formula (I) or (II), each of R¹ and R^{1'} is independently a polycyclic tertiary hydrocarbyl group.

[0140] In some embodiments of the catalyst compound of Formula (I) or (II), each of R¹ and R^{1'} is independently a tertiary hydrocarbyl group. In other embodiments of the catalyst compound of Formula (I) or (II), each of R¹ and R^{1'} is independently a cyclic tertiary hydrocarbyl group. In other embodiments of the catalyst compound of Formula (I) or (II), each of R¹ and R^{1'} is independently a polycyclic tertiary hydrocarbyl group.

[0141] The linker groups (*i.e.*, A³---A² and A^{2'}---A^{3'} in Formula (I)) can each be

part of an ortho-phenylene group, such as a substituted ortho-phenylene group. It may be preferred for the R^7 and $R^{7'}$ positions of Formula (II) to be hydrogen or C_1 to C_{20} alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or an isomer thereof, such as isopropyl, etc. For applications targeting polymers with high tacticity, it may be preferred for the R^7 and $R^{7'}$ positions of Formula (II) to be a C_1 to C_{20} alkyl, such as for both R^7 and $R^{7'}$ to be a C_1 to C_3 alkyl.

[0142] In some embodiments of Formula (I) or (II), M is a group 4 metal, such as Hf or Zr.

[0143] In some embodiments of Formula (I) and (II), each of E and E' is O.

10 [0144] In some embodiments of Formula (I) and (II), each of R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^1 and R^2 , R^2 and R^3 , R^3 and R^4 , $R^{1'}$ and $R^{2'}$, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$ may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or
15 unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings, such as hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.

[0145] In some embodiments of Formula (I) and (II), each of R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl,
20 nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, substituted phenyl (such as methylphenyl and dimethylphenyl), benzyl, substituted benzyl (such as methylbenzyl), naphthalenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, and isomers thereof.

25 [0146] In some embodiments of Formula (I) and (II), each of R^4 and $R^{4'}$ is independently hydrogen or a C_1 to C_3 hydrocarbyl, such as methyl, ethyl or propyl.

[0147] In embodiments of Formula (I) and (II), R^9 is hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, or a heteroatom-containing group, such as hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof. In some embodiments, R^9 is C_1 to C_6
30 alkyl (such as methyl, ethyl, propyl, or butyl), phenyl, 2-methylphenyl, 2,6-dimethylphenyl, or 2,4,6-trimethylphenyl.

[0148] In embodiments of Formula (I) and (II), each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms (such as alkyls or aryls), hydrides, amides, alkoxides, sulfides, phosphides, halides, alkyl sulfonates, and a

combination thereof, (two or more X's may form a part of a fused ring or a ring system), such as each X is independently selected from halides, aryls, and C₁ to C₅ alkyl groups, such as each X is independently a hydrido, dimethylamido, diethylamido, methyltrimethylsilyl, neopentyl, phenyl, benzyl, methyl, ethyl, propyl, butyl, pentyl, fluoro, iodo, bromo, or chloro group.

- 5 [0149] Alternatively, each X may be, independently, a halide, a hydride, an alkyl group, or an alkenyl group.

[0150] In some embodiments of Formula (I) and (II), each L is a Lewis base, independently, selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, halocarbons, and phosphines, such as ethers, thioethers, or a combination thereof, optionally two or more L's may form a part of a fused ring or a ring system, such as each L is independently selected from ether or thioether groups, such as each L is an ethyl ether, tetrahydrofuran, dibutyl ether, or dimethylsulfide group.

[0151] In some embodiments of Formula (I) and (II), each of R¹ and R^{1'} is independently cyclic tertiary alkyl groups.

- 15 [0152] In some embodiments of Formula (I) and (II), n is 1, 2 or 3, such as 2.

[0153] In some embodiments of Formula (I) and (II), m is 0, 1 or 2, such as 0.

[0154] In some embodiments of Formula (I) and (II), each of R¹ and R^{1'} is not hydrogen.

- [0155] In some embodiments of Formula (I) and (II), M is Hf or Zr, each of E and E' is O; each of R¹ and R^{1'} is independently a C₁-C₄₀ hydrocarbyl, a substituted C₁-C₄₀ hydrocarbyl, a heteroatom or a heteroatom-containing group, each of R², R³, R⁴, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₂₀ hydrocarbyl, substituted C₁-C₂₀ hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings; each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms (such as alkyls or aryls), hydrides, amides, alkoxides, sulfides, phosphides, halides, and a combination thereof, (two or more X's may form a part of a fused ring or a ring system); each L is, independently, selected from the group consisting of ethers, thioethers, and halo carbons (two or more L's may form a part of a fused ring or a ring system).

[0156] In some embodiments of Formula (II), each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently hydrogen, C₁-C₄₀ hydrocarbyl, substituted C₁-C₄₀ hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more adjacent R groups may be joined

to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0157] In some embodiments of Formula (II), each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.

[0158] In some embodiments of Formula (II), each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, substituted phenyl (such as methylphenyl and dimethylphenyl), benzyl, substituted benzyl (such as methylbenzyl), naphthalenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, or isomers thereof.

[0159] In some embodiments of Formula (II), M is Hf or Zr, each of E and E' is O; each of R¹ and R^{1'} is independently a C₁-C₄₀ hydrocarbyl, a substituted C₁-C₄₀ hydrocarbyl, a heteroatom or a heteroatom-containing group;

each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₂₀ hydrocarbyl, substituted C₁-C₂₀ hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings;

R⁹ is hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, or a heteroatom-containing group, such as hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof;

each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms (such as alkyls or aryls), hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two or more X's may form a part of a fused ring or a ring system);

n is 2; m is 0; and each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more adjacent R groups may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and

where substitutions on the ring can join to form additional rings, such as each of R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, substituted phenyl (such as methylphenyl and dimethylphenyl), benzyl, substituted benzyl (such as methylbenzyl), naphthalenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, and isomers thereof.

[0160] In some embodiments of Formula (II), M is Zr or Hf, both E and E' are oxygen, and both R^1 and $R^{1'}$ are C₄-C₂₀ cyclic tertiary alkyls.

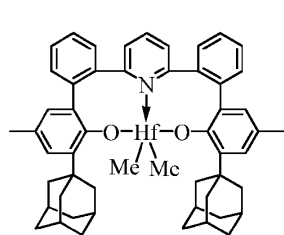
[0161] In some embodiments of Formula (II), M is Zr or Hf, both E and E' are oxygen, and both R^1 and $R^{1'}$ are adamantan-1-yl or substituted adamantan-1-yl.

[0162] In some embodiments of Formula (II), M is Zr or Hf, both E and E' are oxygen, and each of R^1 , $R^{1'}$, R^3 and $R^{3'}$ are adamantan-1-yl or substituted adamantan-1-yl.

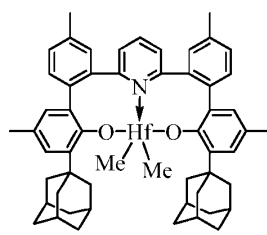
[0163] In some embodiments of Formula (II), M is Zr or Hf, both E and E' are oxygen, both R^1 and $R^{1'}$ are C₄-C₂₀ cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C₁-C₂₀ alkyls.

[0164] In some embodiments, a catalyst compound is one or more of: dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-adamantan-1-yl)-5-(tert-butyl)-[1,1'-biphenyl]-2-olate], dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-adamantan-1-yl)-5-(tert-butyl)-[1,1'-biphenyl]-2-olate], dimethylzirconium[6,6'-(pyridine-2,6-diylbis(benzo[b]thiophene-3,2-diyl))bis(2-adamantan-1-yl)-4-methylphenolate], dimethylhafnium[6,6'-(pyridine-2,6-diylbis(benzo[b]thiophene-3,2-diyl))bis(2-adamantan-1-yl)-4-methylphenolate], dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-5-methyl-[1,1'-biphenyl]-2-olate)], dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-5-methyl-[1,1'-biphenyl]-2-olate)], dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-4',5-dimethyl-[1,1'-biphenyl]-2-olate)], dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-4',5-dimethyl-[1,1'-biphenyl]-2-olate)], or combinations thereof.

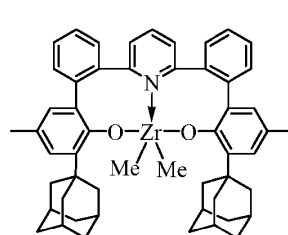
[0165] In some embodiments, a catalyst compound is one or more of:



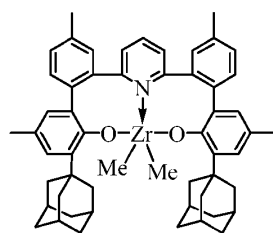
Complex 1



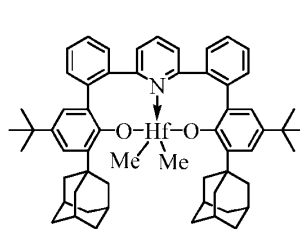
Complex 2



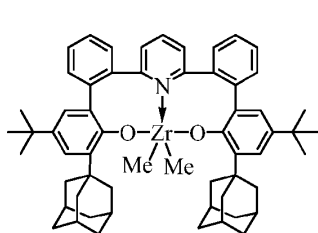
Complex 3



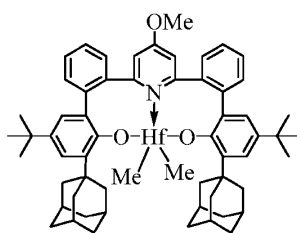
Complex 4



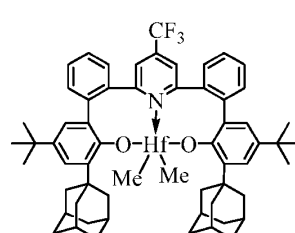
Complex 5



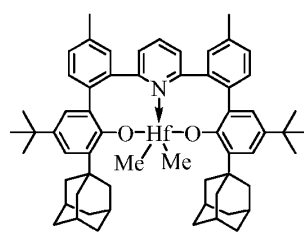
Complex 6



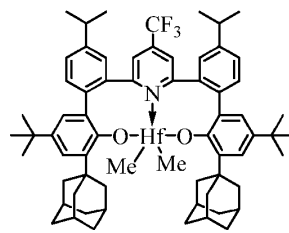
Complex 7



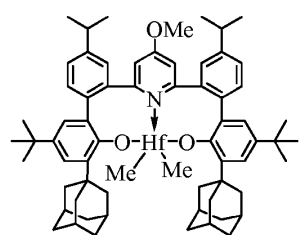
Complex 8



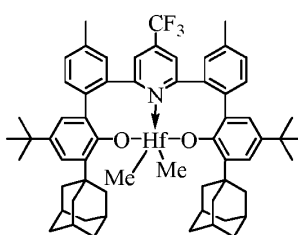
Complex 9



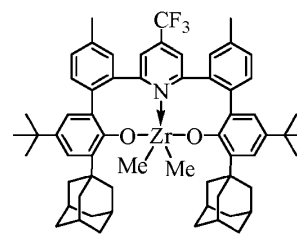
Complex 10



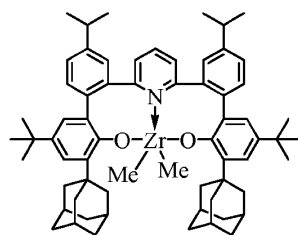
Complex 11



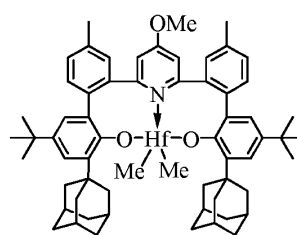
Complex 12



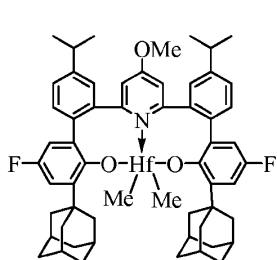
Complex 13



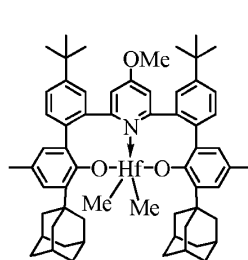
Complex 14



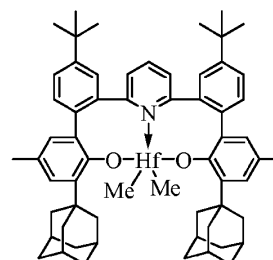
Complex 15



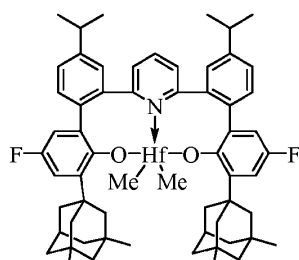
Complex 16



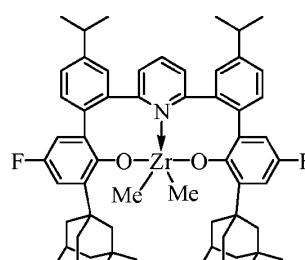
Complex 17



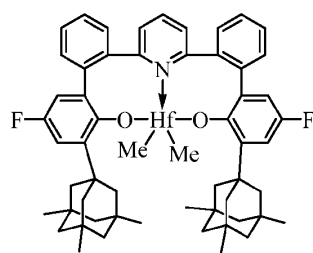
Complex 18



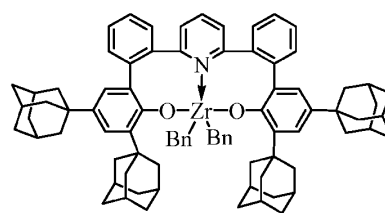
Complex 19



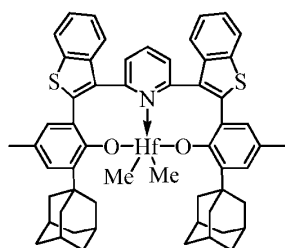
Complex 20



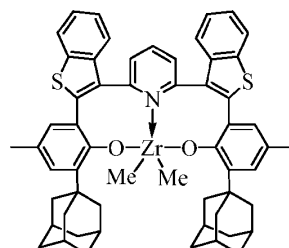
Complex 21



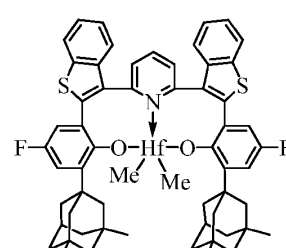
Complex 22



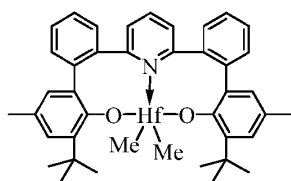
Complex 23



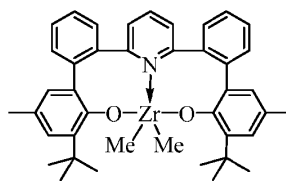
Complex 24



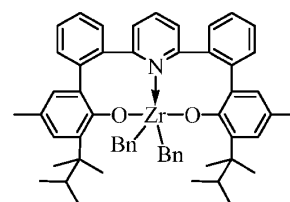
Complex 25



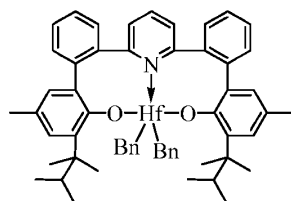
Complex 26



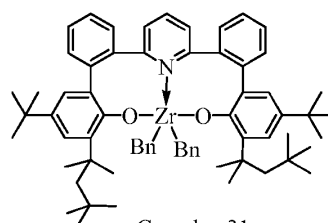
Complex 27



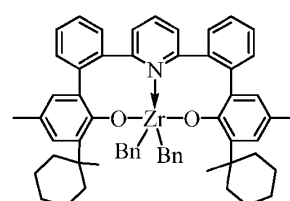
Complex 29



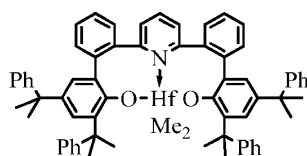
Complex 30



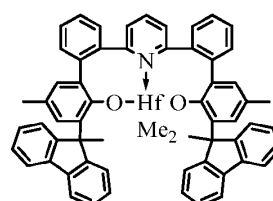
Complex 31



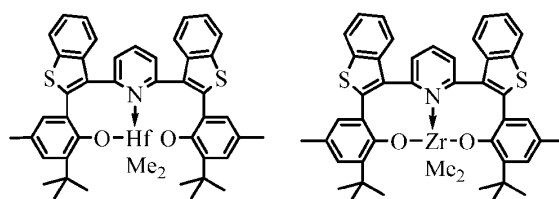
Complex 32



Complex 33

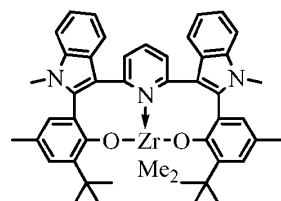


Complex 34

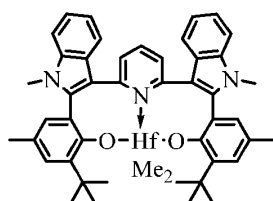


Complex 35

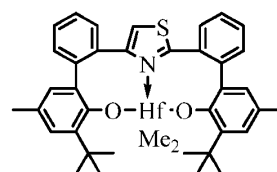
Complex 36



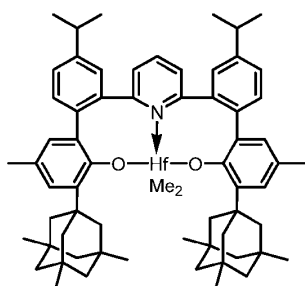
Complex 37



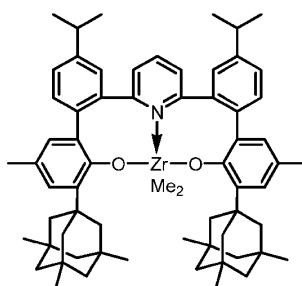
Complex 38



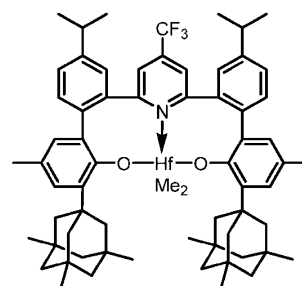
Complex 39



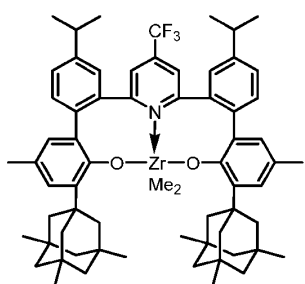
Complex 40



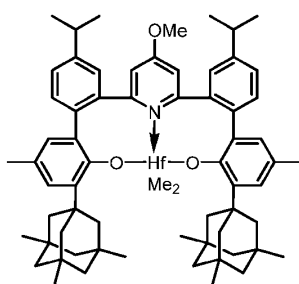
Complex 41



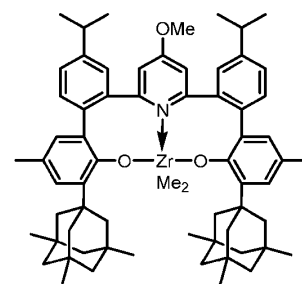
Complex 42



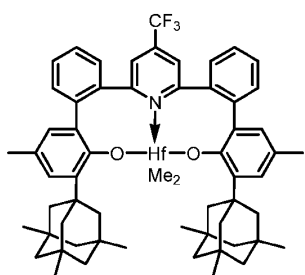
Complex 43



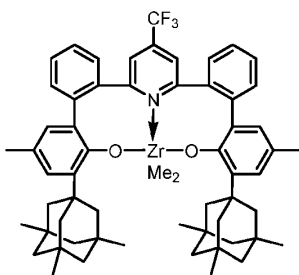
Complex 44



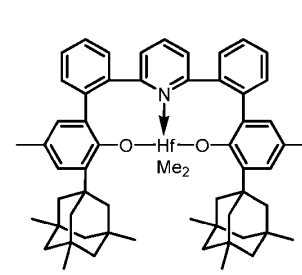
Complex 45



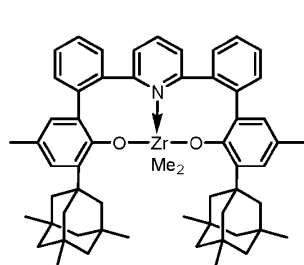
Complex 46



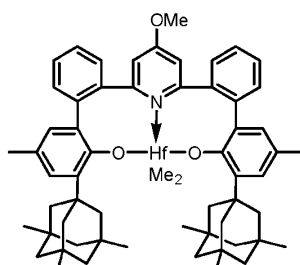
Complex 47



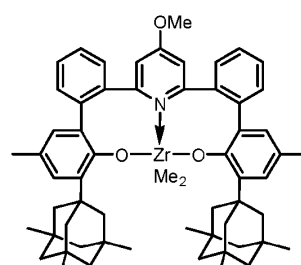
Complex 48



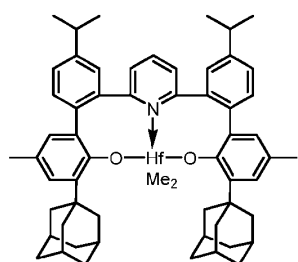
Complex 49



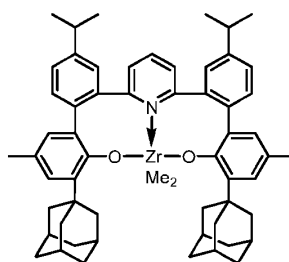
Complex 50



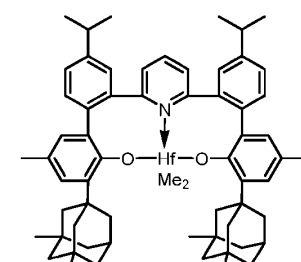
Complex 51



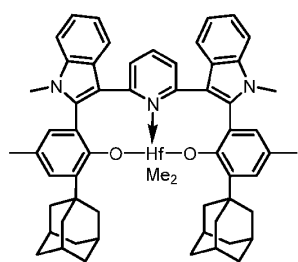
Complex 52



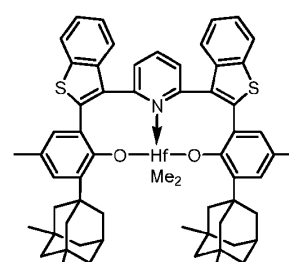
Complex 53



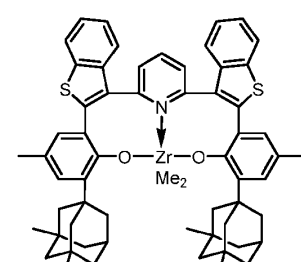
Complex 54



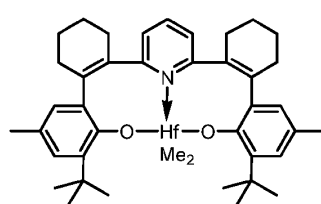
Complex 56



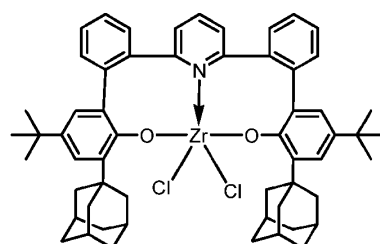
Complex 57



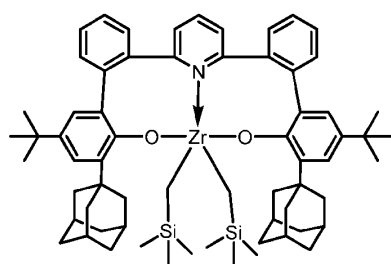
Complex 58



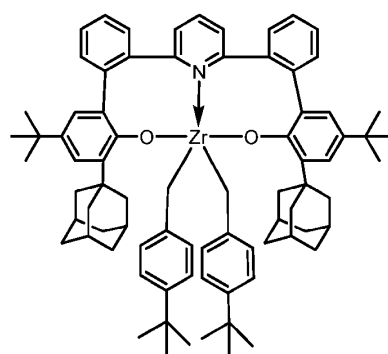
Complex 59



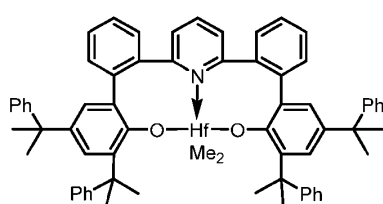
Complex 60



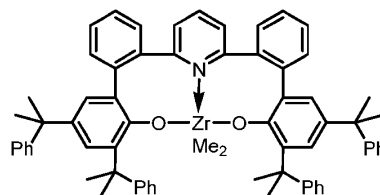
Complex 62



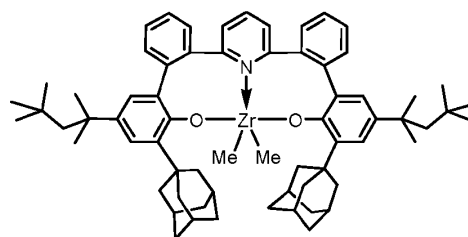
Complex 63



Complex 64



Complex 65



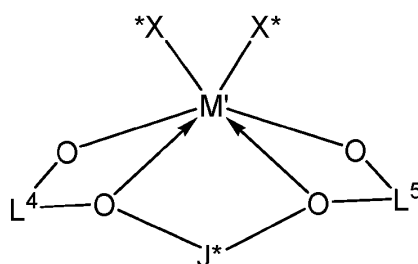
Complex 66

5 [0166] In an embodiment of the present disclosure transition metal complexes useful herein are certain “non-metallocene” olefin polymerization catalysts. The term “non-metallocene catalyst”, also known as “post-metallocene catalyst” describe transition metal complexes that do not feature any pi-coordinated cyclopentadienyl anion donors (or the like) and are useful the polymerization of olefins when combined with common activators. Families of non-

10 metallocene complexes that may be useful for the present invention are described in *Angew. Chem. Int. Ed.*, 2014, v.53, pp. 2-25; *Chem. Rev.*, 2003, v.103, pp. 283-315; *Angew. Chem. Int. Ed.*, 1999, v.38, pp. 428-447; *ACS Catal.*, 2011, v.1, pp. 887-900; *Polymer J.*, 2007, v.39(3), pp. 193-207; and US Patent Nos. 6,841,502, 7,018,949, 7,256,296, 7,964,681.

[0167] Additional transition metal complexes useful herein include chelated transition

15 metal complexes, such as those represented by the following Formula (IV):



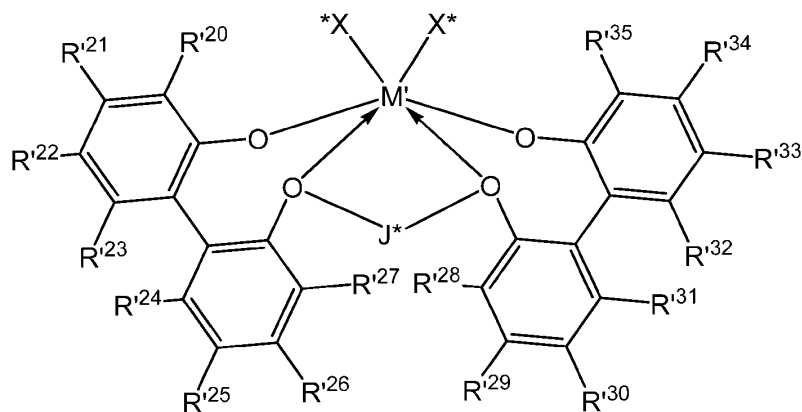
(IV)

where: (1) J* is a divalent bridging group comprising C, Si, or both; (2) M' is a group 4 metal, preferably hafnium or zirconium; (3) O is oxygen; (4) each X* is independently a univalent anionic ligand, or two X*'s are joined and bound to the metal atom to form a metallocycle ring, or two X*'s are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand; and (5) L⁴ and L⁵ are independently, a substituted monocyclic or polycyclic aromatic groups.

[0168] In some embodiments, J* is a divalent substituted or unsubstituted C₃₋₆ aliphatic or cycloaliphatic group.

[0169] In some embodiments, L⁴ and L⁵ are independently a monocyclic or polycyclic aromatic group substituted with any combination alkyl, aryl, alkoxy, or amino substituents which may optionally be substituted with halogens.

[0170] In yet further embodiments, suitable catalyst compounds useful herein include biphenyl phenol transition metal complexes, such as those having the following structural Formula (IVa):



(IVa)

where: (1) J* is a divalent bridging group comprising C, Si, or both; (2) M is a group 4 metal, preferably hafnium or zirconium; (3) O is oxygen; (4) each X* is independently a univalent anionic ligand, or two X*'s are joined and bound to the metal atom to form a metallocycle ring, or two X*'s are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand; and

(5) each R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , R^{28} , R^{29} , R^{30} , R^{31} , R^{32} , R^{33} , R^{34} , R^{35} is independently hydrogen, halo, C₁-C₅₀ hydrocarbyl, substituted hydrocarbyl, halocarbyl or substituted halocarbyl.

[0171] In particular embodiments, each R^{20} and R^{35} may be or may comprise a bulky
5 substituent, such as substituted or unsubstituted aryl, carbazolyl, fluorenyl and/or anthracenyl.

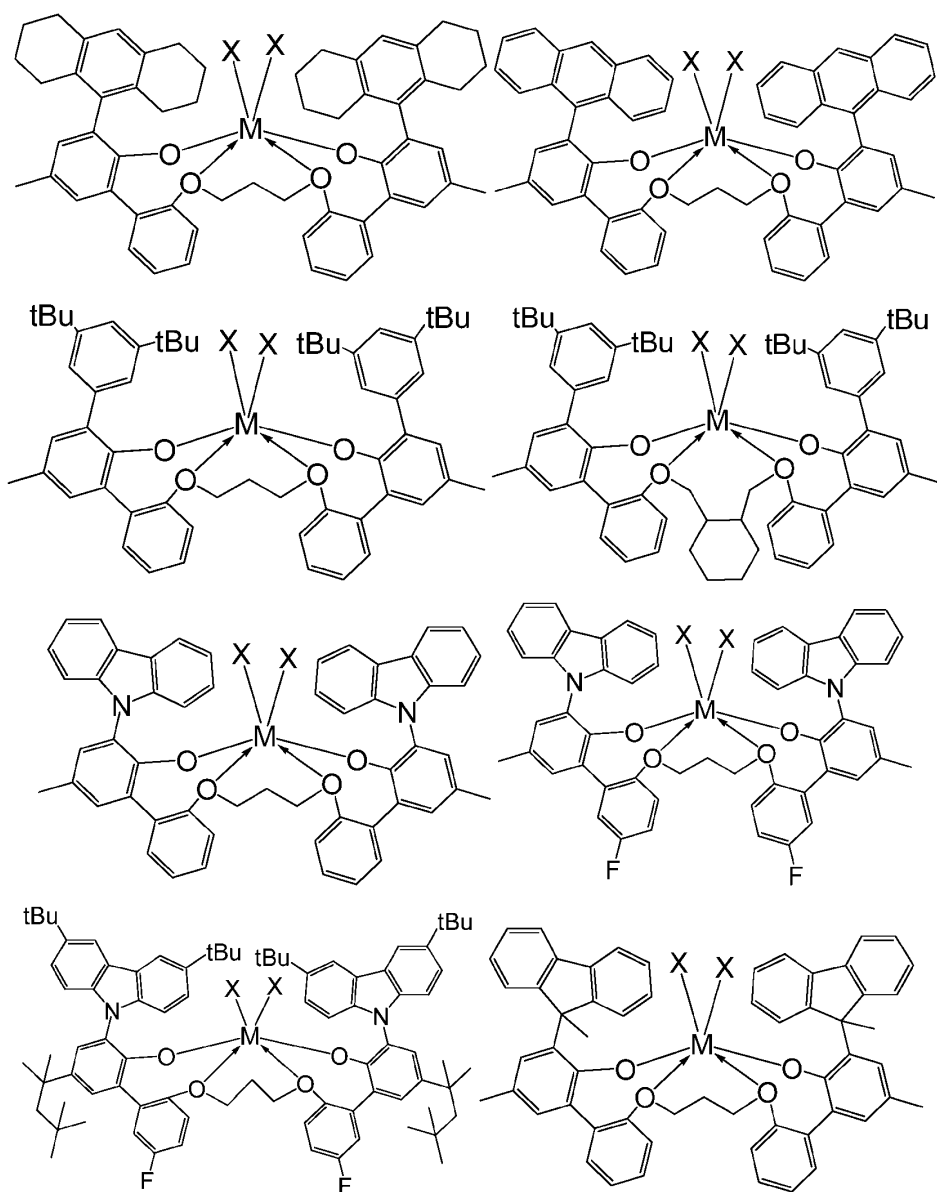
[0172] In other particular embodiments, each R^{20} and R^{35} independently may be
3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, 3,5-di(*tert*-butyl)phenyl, carbazol-9-yl,
3,6-di-*tert*-butylcarbazol-9-yl, 2,3,4,5,6,7,8,9-octahydrocarbazol-1-yl, anthracen-9-yl,
1,2,3,4,5,6,7,8-octahydroanthracen-9-yl, naphthalenyl, fluoren-9-yl, 9-methylfluoren-9-yl,
10 1,2,3,4,5,6,7,8-octahydrofluoren-9-yl, or 9-methyl-1,2,3,4,5,6,7,8-octahydrofluoren-9-yl.

[0173] In other particular embodiments, R^{22} and R^{33} are independently C₁-C₁₀
hydrocarbyl, alternatively C₁-C₁₀ alkyls such as methyl, ethyl and all isomers of propyl, butyl,
pentyl, hexyl, heptyl, octyl, nonyl and decyl.

[0174] In other particular embodiments, R^{25} and R^{30} are independently C₁-C₁₀ substituted
15 or unsubstituted hydrocarbyl, halo, C₁-C₁₀ alkoxy, and C₂-C₂₀ dialkylamino. Alternatively
 R^{25} and R^{30} are independently C₁-C₁₀ alkyls such as methyl, ethyl and all isomers of propyl,
butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl (including cyclic and linear or branched
cyclic combinations); halogens such as fluoro, chloro, bromo; C₁-C₁₀ alkoxy such as methoxy,
ethoxy, and all isomers of propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, nonoxy, and
20 decoxy (including cyclic and linear or branched cyclic combinations); C₂-C₂₀ dialkylamino
such as dimethyl amino, diethyl amino, and all isomers of dipropylamino, dibutylamino,
dipentylamino, dihexylamino, diheptylamino, dioctylamino, dinonylamino, didecylamino
(including cyclic and linear or branched cyclic combinations) and mixed alkyls such as
methylethylamino, methylbutyl amino and the like.

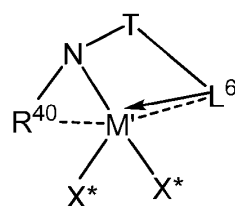
[0175] In other particular embodiments, J* may be propan-1,3-diyl, butan-1,4-diyl,
25 cyclohexanediyl, cyclohexen-4,5-diyl, or bis(methylene)cyclohexan-1,2-diyl.

[0176] Non-limiting examples of particularly useful biphenyl phenol transition metal
complexes are illustrated below, wherein M is hafnium or zirconium and X is methyl, benzyl,
or chloro:



5 [0177] Additional particularly useful biphenyl phenol transition metal complexes are described in US 2006/0025548; US 2006/0052554; WO 2003/091262; WO 2005/108406; WO 2007/136494; WO 2007/136495; WO 2007/136496; WO 2009/064482; and WO 2013/096573, and are incorporated by reference.

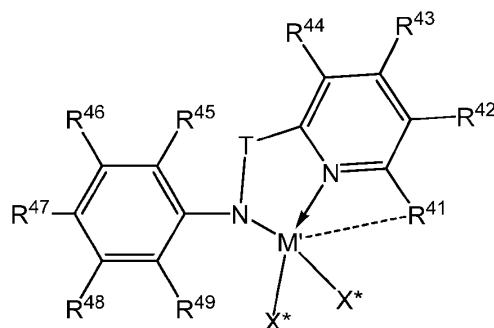
[0178] In yet further embodiments, transition metal complexes useful herein include those
10 represented by the following Formula (V):



(V)

- wherein (1) M' is a group 4 metal, preferably hafnium; (2) L^6 is a C_5 - C_{20} heteroaryl group containing a Lewis base functionality, especially pyridine-2-yl or substituted pyridine-2-yl group or a divalent derivative thereof; (3) R^{40} is selected from a C_1 - C_{30} alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl and substituted derivatives thereof or a divalent derivative thereof; (4) T is a divalent bridging group comprising carbon and or silicon, preferably a C_1 - C_{20} hydrocarbyl substituted methylene or silane group; (5) each X^* is independently a univalent anionic ligand, or two X^* s are joined and bound to the metal atom to form a metallocycle ring, or two X^* s are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand; (6) N is nitrogen; and (7) bonds, optional bonds and dative bonds are represented by lines, dotted lines and arrows, respectively.

[0179] In yet further embodiments, catalyst compounds useful herein are pyridyl amide metal complexes, such as those having the following Formula (Va):



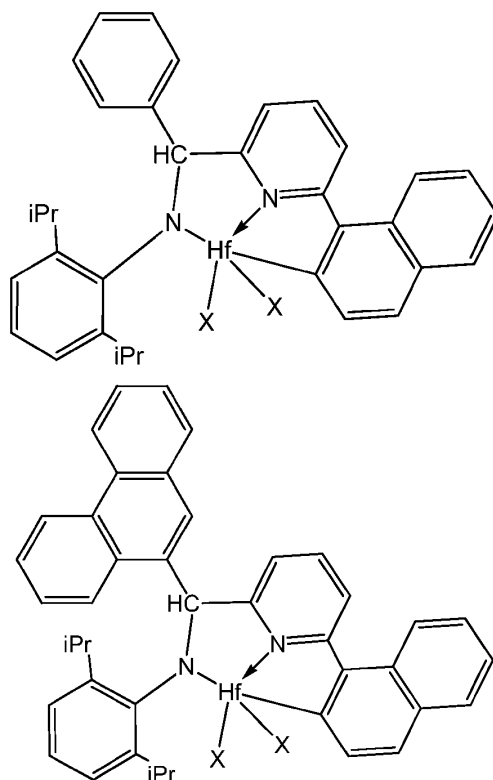
(Va)

- wherein M' , T , N and X^* are as previously defined as in formula (5); each R^{41} , R^{42} , R^{43} , and R^{44} are independently hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl or silyl group, or one or more adjacent R^{41} - R^{44} may be joined together to form a fused ring derivative; R^{45} - R^{49} are independently hydrogen, or C_1 - C_{10} alkyl, most preferably R^{45} and R^{49} are alkyl such as isopropyl or *tert*-butyl; T is preferably $CR^{50}R^{51}$ where R^{50} and R^{51} are independently hydrogen, halogen, a C_1 - C_{20} hydrocarbyl, most preferably, one of R^{50} and R^{51} is hydrogen and the other is a C_6 - C_{20} aryl group, especially 2-isopropyl, phenyl or a fused

polycyclic aryl group, most preferably anthracenyl; and bonds, optional bonds and dative bonds are represented by lines, dotted lines and arrows, respectively.

[0180] Non-limiting examples of pyridyl amide catalysts useful herein are illustrated below, wherein X is preferably methyl, benzyl or chloro:

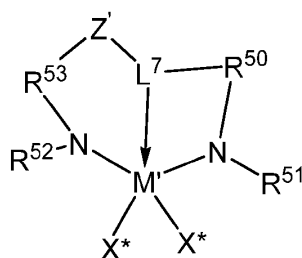
5



10

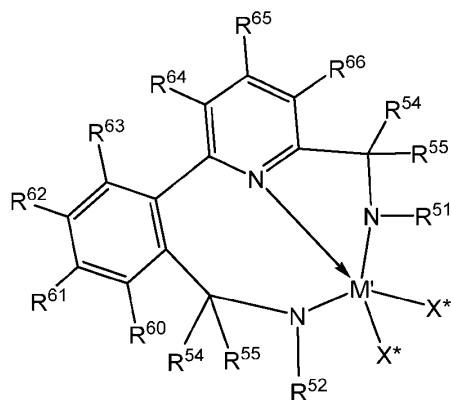
[0181] Additional pyridyl amide transition metal complexes particularly useful herein are described in US 2004/0220050; WO 2002/038628; WO 2002/046249; WO 2003/040201; WO 2004/024739; WO 2004/024740; WO 2004/026925 and WO 2010/0227990 and are incorporated by reference.

[0182] In yet further embodiments, useful catalyst compounds include those having the following structural Formula (VI):



(VI)

- wherein (1) M' is a group 4 metal, preferably hafnium; (2) N is nitrogen; (3) L^7 is a group that links R^{50} to Z' by a three atom bridge with the central of the three atoms being a group 15 or 16 element that preferably forms a dative bond to M, and is a C_5 - C_{20} heteroaryl group containing a Lewis base functionality, especially a divalent pyridinyl or substituted pyridinyl group; (4) Z' is a divalent linker group, $(R^{56})_pC-C(R^{57})_q$, where R^{56} and R^{57} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, and wherein adjacent R^{56} and R^{57} groups may be joined to form an aromatic or saturated, substituted or unsubstituted hydrocarbyl ring, wherein the ring has 5, 6, 7 or 8 ring carbon atoms and where the substituents on the ring can join to form additional rings, and p is 1 or 2 and q is 1 or 2; (5) R^{50} and R^{53} are each, independently, $ER^{54}R^{55}$ with E being carbon, silicon or germanium, and each R^{54} and R^{55} being independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen and phosphino, and R^{54} and R^{55} 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; (6) R^{51} and R^{52} are independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, silylcarbyls and substituted silylcarbyl groups; and (7) each X^* is independently a univalent anionic ligand, or two X^* s are joined and bound to the metal atom to form a metallocycle ring, or two X^* s are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.
- [0183] In yet further embodiments, useful catalyst compounds include pyridyl diamide metal complexes represented by the following Formula (VIa):



(VIa)

wherein M' , X^* , N, R^{51} , R^{52} , R^{54} , and R^{55} are as previously defined as in Formula (VI); R^{60} , R^{61} , R^{62} , R^{63} , R^{64} , R^{65} , R^{66} are independently selected from the group consisting of hydrogen,

hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein any one or more adjacent R^{60} - R^{66} may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, wherein the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings.

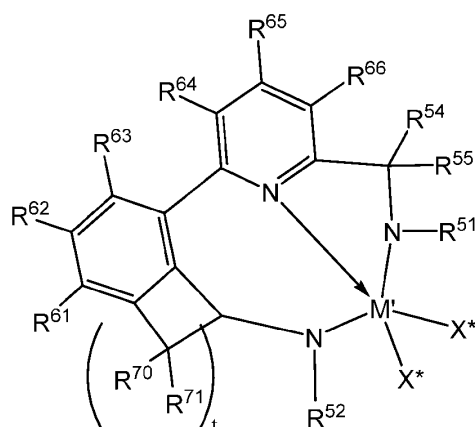
5 [0184] In an embodiment of the invention, R^{60} to R^{66} are hydrogen.

[0185] In an embodiment of the invention, R^{62} is joined with R^{63} to form a phenyl ring fused to the existing phenyl ring (*e.g.*, a naphthalenyl group), and R^{60} , R^{61} , R^{64} , R^{65} , and R^{66} are independently hydrogen or an alkyl group, preferably hydrogen.

[0186] In an embodiment of the invention, each R^{54} and R^{55} are independently hydrogen,
 10 an alkyl group or an aryl group or substituted aryl group; preferably one or both R^{54} or R^{55} is hydrogen, or one R^{54} or R^{55} is hydrogen and the other is an aryl group or substituted aryl group. Preferred but non limiting aryl groups for R^{54} or R^{55} include phenyl, 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl, and naphthalenyl.

[0187] In an embodiment of the invention, R^{52} and R^{51} are independently aryl or
 15 substituted aryl; preferably R^{51} is a substituted phenyl group such as, but not limited to 2,6-diisopropylphenyl, 2,6-diethylphenyl, 2,6-dimethylphenyl, mesityl, and the like, and preferably R^{52} is phenyl or a substituted phenyl group such as, but not limited to 2-tolyl, 2-ethylphenyl, 2-propylphenyl, 2-trifluoromethylphenyl, 2-fluorophenyl, mesityl, 2,6-diisopropylphenyl, 2,6-diethylphenyl, 2,6-dimethylphenyl, 3,5-di-*tert*-butylphenyl, and the
 20 like.

[0188] In yet further embodiments, useful catalyst compounds include pyridyl diamide metal complexes, such as those represented by the following Formula (VIb):



(VIb)

wherein M^+ , X^* , N , R^{51} , R^{52} , R^{54} , R^{55} , R^{61} - R^{66} are as previously defined as in Formulae (VI) and (VIa); each R^{70} - R^{71} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein any one or more adjacent R^{70} - R^{71} may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, wherein the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings, and t is 2 or 3 (corresponding to cyclopentyl and cyclohexyl rings, respectively).

[0189] In an embodiment of the invention, R^{61} - R^{66} are hydrogen.

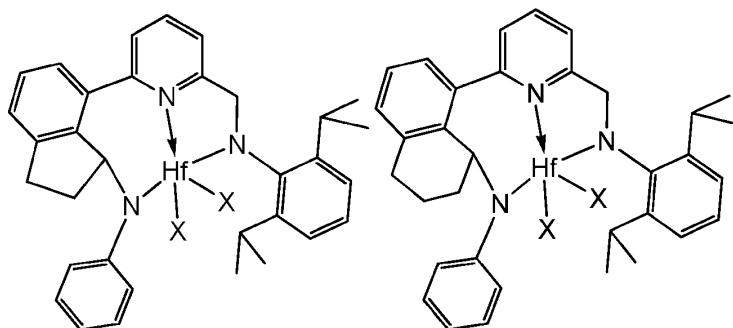
[0190] In an embodiment of the invention, each R^{70} and R^{71} are independently hydrogen, and t is 2 or 3, preferably 2.

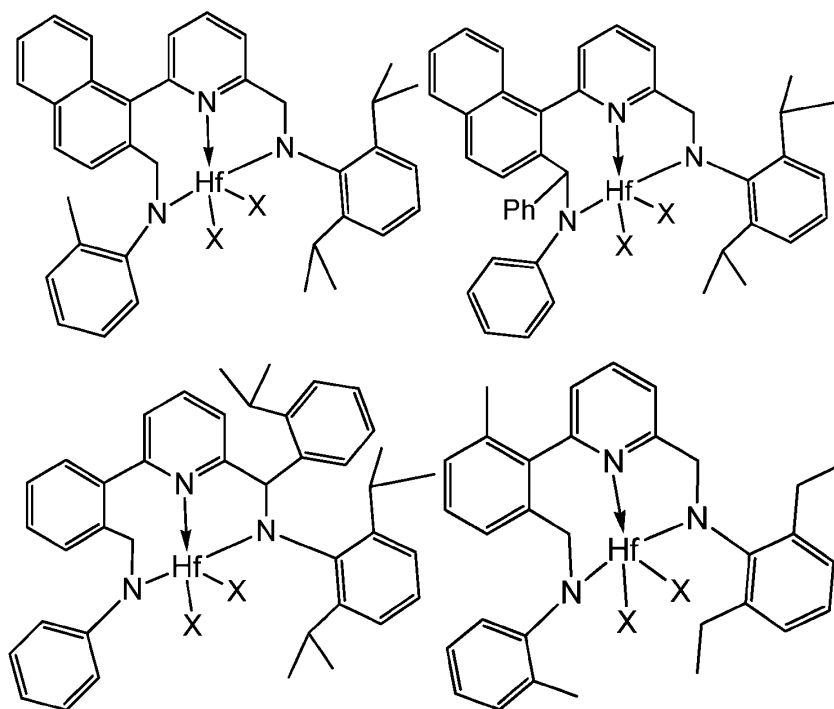
[0191] In an embodiment of the invention, each R^{54} and R^{55} are independently hydrogen, an alkyl group or an aryl group or substituted aryl group; preferably one or both R^{54} or R^{55} is hydrogen, or one R^{54} or R^{55} is hydrogen and the other is an aryl group or substituted aryl group. Preferred but non limiting aryl groups include phenyl and 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl and naphthalenyl.

[0192] In an embodiment of the invention, R^{52} and R^{51} are independently aryl or substituted aryl; preferably R^{51} is a substituted phenyl group such as, but not limited to 2,6-diisopropylphenyl, 2,6-diethylphenyl, 2,6-dimethylphenyl, mesityl, and the like, and preferably R^{52} is phenyl or a substituted phenyl group such as, but not limited to 2-tolyl, 2-ethylphenyl, 2-propylphenyl, 2-trifluoromethylphenyl, 2-fluorophenyl, mesityl, 2,6-diisopropylphenyl, 2,6-diethylphenyl, 2,6-dimethylphenyl, 3,5-di-tert-butylphenyl, and the like.

[0193] In an embodiment of the invention, R^{54} , R^{55} , R^{61} - R^{66} , each R^{70} - R^{71} are hydrogen, R^{52} is phenyl, R^{51} is 2,6-diisopropylphenyl and t is 2.

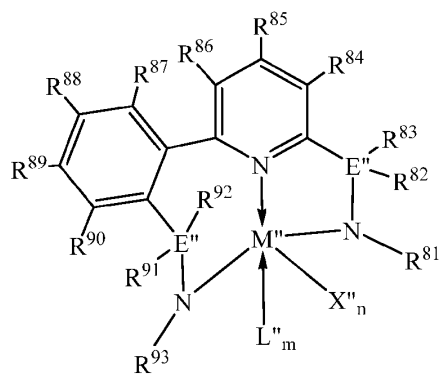
[0194] Non-limiting examples of pyridyl diamide catalysts that are useful herein are illustrated below, wherein X is methyl, benzyl, or chloro:





[0195] Additional pyridyl diamide transition metal complexes useful herein are described in US 2010/0022726; US 2011/0301310; US 2012/0071616; US 2014/0316089; 5 WO 2012/134613; WO 2012/134614; and WO 2012/134615 are incorporated by reference.

[0196] Transition metal complexes (also referred to as catalyst complexes or pre-catalyst complexes) useful herein include pyridyldiamido transition metal complexes represented by the Formula (VII):



(VII)

10 wherein:

M'' is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

E'' is selected from carbon, silicon, or germanium, preferably carbon;

X'' is an anionic leaving group, preferably alkyl, aryl, hydride, alkylsilane, fluoride, chloride, bromide, iodide, triflate, carboxylate, alkylsulfonate;

L'' is a neutral Lewis base, preferably ether, amine, thioether;

R⁸¹ and R⁹³ are each independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups, preferably aryl;

R⁸², R⁸³, R⁸⁴, R⁸⁵, R⁸⁶, R⁸⁷, R⁸⁸, R⁸⁹, R⁹⁰, R⁹¹, and R⁹² are each independently selected from the group consisting of hydrogen, hydrocarbyls, alkoxy, silyl, amino, aryloxy, substituted hydrocarbyls, halogen, and phosphino;

n is 1 or 2;

m is 0, 1, or 2; and

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;

R⁸⁷ and R⁸⁸ may be joined to form a ring, preferably an aromatic ring, a six-membered aromatic ring with the joined R⁸⁷ and R⁸⁸ group being -CH=CHCH=CH-;

R⁹⁰ and R⁹¹ may be joined to form a ring, preferably a five-membered ring with the joined R⁹⁰ and R⁹¹ group being -CH₂CH₂-, a six-membered ring with the joined R⁹⁰ and R⁹¹ group being -CH₂CH₂CH₂-.

[0197] In a preferred embodiment, R⁸⁴, R⁸⁵, and R⁸⁶ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁸⁴ and R⁸⁵ and/or R⁸⁵ and R⁸⁶) may be joined to form a substituted or unsubstituted hydrocarbyl or 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.

[0198] In another preferred embodiment, R⁸⁷, R⁸⁸, R⁸⁹, and R⁹⁰ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁸⁷ and R⁸⁸, and/or R⁸⁹ and R⁹⁰) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or 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.

[0199] In still another preferred embodiment, n + m is not greater than 4.

[0200] In yet another preferred embodiment, R⁸² and R⁸³ are each, independently, selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R⁸² and R⁸³ 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 R^2 and R^3 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.

- 5 [0201] In still yet another preferred embodiment, R^{91} and R^{92} are each, independently, selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{91} and R^{92} 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 R^{91} and
- 10 R^{92} 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.

- [0202] In a preferred embodiment, R^{81} and R^{93} 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
- 15 methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof.

- [0203] Preferred R^{83} -E- R^{82} groups and preferred R^{92} -E- R^{91} groups include CH_2 , CMe_2 , $SiMe_2$, $SiEt_2$, $SiPr_2$, $SiBu_2$, $SiPh_2$, $Si(aryl)_2$, $Si(alkyl)_2$, $CH(aryl)$, $CH(Ph)$, $CH(alkyl)$, and $CH(2\text{-isopropylphenyl})$, where alkyl is a C_1 to C_{40} alkyl group (preferably C_1 to C_{20} alkyl, preferably one or more of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl,
- 20 undecyl, dodecyl, and isomers thereof), aryl is a C_5 to C_{40} aryl group (preferably a C_6 to C_{20} aryl group, preferably phenyl or substituted phenyl, preferably phenyl, 2-isopropylphenyl, or 2-tertbutylphenyl).

- [0204] In a preferred embodiment, each X'' may be independently selected from halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, triflate, alkylsulfonate, arylsulfonate, and alkynyl. In another embodiment, two L'' groups may be
- 25 linked to form a dianionic leaving group, for example, oxalate.

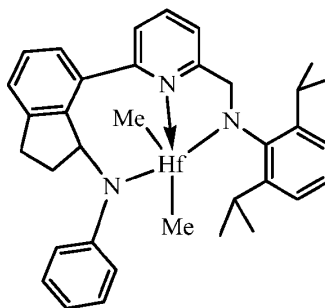
- [0205] In another embodiment of the invention, each L'' is independently selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines, preferably ethers.

- 30 [0206] In any embodiment of the invention described herein, M'' is preferably a Group 4 metal, preferably Zr or Hf.

[0207] In any embodiment of the invention described herein, each E'' is preferably carbon.

[0208] In any embodiment of the invention described herein, the transition metal complex

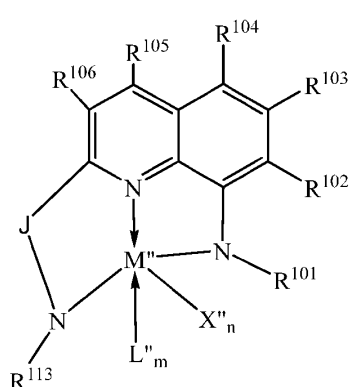
is represented by the formula:



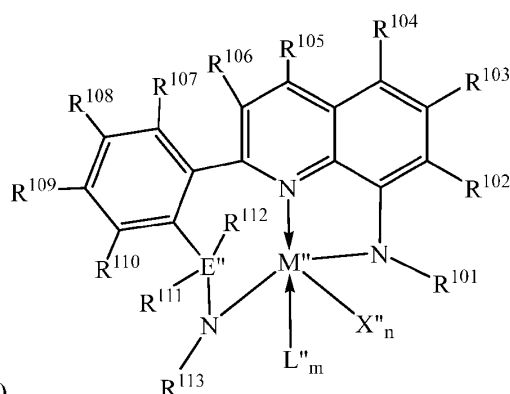
[0209] The pyridyl diamine ligands described herein are generally prepared in multiple steps in accordance with the disclosure of US 9,290,519.

- 5 [0210] In a preferred embodiment of the invention, the transition metal complex is not a metallocene. A metallocene catalyst is defined as an organometallic compound with at least one π -bound cyclopentadienyl moiety (or substituted cyclopentadienyl moiety) and more frequently two π -bound cyclopentadienyl moieties or substituted cyclopentadienyl moieties.

- [0211] Transition metal complexes useful herein include quinolinyldiamido transition metal complexes represented by Formula (VIII), preferably by Formula (IX):
- 10



(VIII)



(IX)

wherein:

M'' is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal (preferably a group 4 metal);

J is group comprising a three-atom-length bridge between the quinoline and the amido

- 15 nitrogen, preferably 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;

R^{101} and R^{113} are independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups;

R^{102} , R^{103} , R^{104} , R^{105} , R^{106} , R^{107} , R^{108} , R^{109} , R^{110} , R^{111} , and R^{112} are independently hydrogen, hydrocarbyl, alkoxy, silyl, amino, aryloxy, substituted hydrocarbyl, halogen, or phosphino;

n is 1 or 2;

m is 0, 1, or 2, where;

$n+m$ is not greater than 4; and

any two adjacent R groups (*e.g.*, R^{101} and R^{102} , R^{102} and R^{103} , etc.) may be joined to form a substituted hydrocarbyl, unsubstituted hydrocarbyl, substituted heterocyclic ring, or unsubstituted 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;

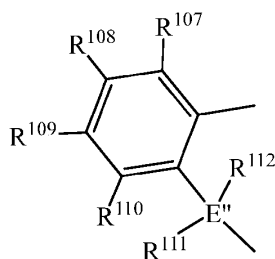
any two X'' groups may be joined together to form a dianionic group;

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.

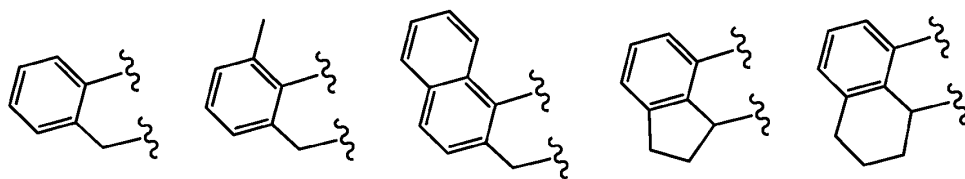
[0212] Preferably, M'' is a Group 4 metal, such as zirconium or hafnium.

[0213] In a preferred embodiment, J is an aromatic substituted or unsubstituted hydrocarbyl (preferably a hydrocarbyl) having from 3 to 30 non-hydrogen atoms, preferably J is represented by the formula:



where R^{107} , R^{108} , R^{109} , R^{110} , R^{111} , R^{112} , and E'' are as defined above, and any two adjacent R groups (*e.g.*, R^{107} and R^{108} , R^{108} and R^{109} , R^{109} and R^{110} , R^{110} and R^{111} , 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 (preferably 5 or 6 atoms), and said ring may be saturated or unsaturated (such as partially unsaturated or aromatic), preferably J is an arylalkyl (such as arylmethyl, etc.) or dihydro-1H-indenyl, or tetrahydronaphthalenyl group.

[0214] In embodiments of the invention, J is selected from the following structures:



where  indicates connection to the complex.

[0215] In embodiments of the invention, E'' is carbon.

[0216] In embodiments of the invention, X'' is 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 NMe₂), or alkylsulfonate.

[0217] In embodiments of the invention, L'' is an ether, amine or thioether.

[0218] In embodiments of the invention, R¹⁰⁷ and R¹⁰⁸ are joined to form a six-membered aromatic ring with the joined R¹⁰⁷R¹⁰⁸ group being -CH=CHCH=CH-.

[0219] In embodiments of the invention, R¹⁰ and R¹¹ are joined to form a five-membered ring with the joined R¹⁰R¹¹ group being -CH₂CH₂-.

[0220] In embodiments of the invention, R¹¹⁰ and R¹¹¹ are joined to form a six-membered ring with the joined R¹¹⁰R¹¹¹ group being -CH₂CH₂CH₂-.

[0221] In embodiments of the invention, R¹⁰¹ and R¹¹³ may be 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.

[0222] In a preferred embodiment of the invention, the quinolinyldiamido transition metal complex represented by the Formula II above where:

M'' is a Group 4 metal (preferably hafnium);

E'' is selected from carbon, silicon, or germanium (preferably carbon);

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

L'' is an ether, amine, or thioether;

R¹⁰¹ and R¹¹³ are independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups (preferably aryl);

R^{102} , R^{103} , R^{104} , R^{105} , R^{106} , R^{107} , R^{108} , R^{109} , R^{110} , R^{111} , and R^{112} are independently hydrogen, hydrocarbyl, alkoxy, silyl, amino, aryloxy, substituted hydrocarbyls, halogen, and phosphino;

n is 1 or 2;

5 m is 0, 1, or 2;

$n+m$ is from 1 to 4; and

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;

10 R^{107} and R^{108} may be joined to form a ring (preferably an aromatic ring, a six-membered aromatic ring with the joined $R^{107}R^{108}$ group being $-\text{CH}=\text{CHCH}=\text{CH}-$);

R^{110} and R^{111} may be joined to form a ring (preferably a five-membered ring with the joined $R^{110}R^{111}$ group being $-\text{CH}_2\text{CH}_2-$, a six-membered ring with the joined $R^{110}R^{111}$ group being $-\text{CH}_2\text{CH}_2\text{CH}_2-$).

15 **[0223]** In embodiments of Formula **VIII** and **IX**, R^{104} , R^{105} , and R^{106} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^{104} and R^{105} and/or R^{105} and R^{106}) may be joined to form a substituted hydrocarbyl, unsubstituted hydrocarbyl, unsubstituted heterocyclic ring or substituted heterocyclic ring, where the ring
20 has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings.

[0224] In embodiments of Formula **VIII** and **IX**, R^{107} , R^{108} , R^{109} , and R^{110} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^{107} and R^{108} , and/or R^{109} and R^{110}) may be joined to form a saturated, substituted
25 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.

[0225] In embodiments of Formula **VIII** and **IX**, R^{102} and R^{103} are each, independently, selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls,
30 alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{102} and R^{103} 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 R^{102} and R^{103} 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.

[0226] In embodiments of Formula **VIII** and **IX**, R^{111} and R^{112} are each, independently, selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{111} and R^{112} 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 R^{111} and R^{112} 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.

[0227] In embodiments of Formula **VIII** and **IX**, R^{101} and R^{113} 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.

[0228] In embodiments of Formula **IX**, preferred R^{112} -E- R^{111} groups include CH_2 , CMe_2 , $SiMe_2$, $SiEt_2$, $SiPr_2$, $SiBu_2$, $SiPh_2$, $Si(aryl)_2$, $Si(alkyl)_2$, $CH(aryl)$, $CH(Ph)$, $CH(alkyl)$, and $CH(2\text{-isopropylphenyl})$, where alkyl is a C_1 to C_{40} alkyl group (preferably C_1 to C_{20} alkyl, preferably 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 (preferably a C_6 to C_{20} aryl group, preferably phenyl or substituted phenyl, preferably phenyl, 2-isopropylphenyl, or 2-tertbutylphenyl).

[0229] Preferably, the R groups above and other R groups mentioned hereafter, contain from 1 to 30, preferably 2 to 20 carbon atoms, especially from 6 to 20 carbon atoms.

[0230] Preferably, M is Ti, Zr, or Hf, and E is carbon, with Zr or Hf based complexes being especially preferred.

[0231] In any embodiment described herein, E'' is carbon and R^{112} and R^{111} 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 hydrocarbyl groups with from one to ten carbons.

[0232] In any embodiment described herein of Formula **IX**, R^{111} and R^{112} are independently selected from hydrogen, methyl, ethyl, phenyl, isopropyl, isobutyl, and trimethylsilyl.

[0233] In any embodiment described herein of Formula **IX**, R^{107} , R^{108} , R^{109} , and R^{110} are independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, phenyl, cyclohexyl, fluoro, chloro, methoxy, ethoxy, phenoxy, and trimethylsilyl.

[0234] In any embodiment described herein of Formula **VIII** or **IX**, R^{102} , R^{103} , R^{104} , R^{105} , and R^{106} are independently selected from the group consisting of hydrogen, hydrocarbyls, alkoxy, silyl, amino, substituted hydrocarbyls, and halogen.

5 [0235] In any embodiment described herein of Formula **VIII** or **IX**, each L'' is independently selected from Et_2O , $MeOtBu$, Et_3N , $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide.

[0236] In any embodiment described herein of Formula **VIII** or **IX**, each X'' is independently selected from methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, dimethylamido, diethylamido, dipropylamido, 10 and diisopropylamido.

[0237] In any embodiment described herein of Formula **VIII** or **IX**, R^{101} 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, 2,6-dicyclopentylphenyl, or 2,6-dicyclohexylphenyl.

15 [0238] In any embodiment described herein of Formula **I** or **II**, R^{113} 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.

[0239] In any embodiment described herein of Formula **IX**, wherein J is dihydro-1H-indenyl and R^1 is 2,6-dialkylphenyl or 2,4,6-trialkylphenyl.

[0240] In any embodiment described herein of Formula **VIII** or **IX**, R^{101} is 2,6-diisopropylphenyl and R^{113} is a hydrocarbyl group containing 1, 2, 3, 4, 5, 6, or 7 carbon atoms.

[0241] 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 are present in the reaction zone where the process(es) described herein occur. It may be preferable to use the same activator for the transition metal compounds, however, two different activators, such as a support-bound activator and a non-coordinating anion activator or an alumoxane, can be used in combination. If one or more transition metal compounds contain 25 an X group which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane can be contacted with the transition metal compounds prior to addition of the non-coordinating anion activator.

[0242] The two transition metal compounds (pre-catalysts) may be used in any ratio. In some embodiments, 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, such as 9:1, 8:2, 7:3, 6:4, or 1:1. The particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired.

- 5 In a particular embodiment, when using the two pre-catalysts, where both are activated with the same activator, useful mole percents, based upon 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.

Methods to Prepare Bis(phenolate) Catalyst Compounds.

- 10 [0243] General methods to prepare bis(phenolate) catalyst compounds can be found in US 11,254,763, incorporated herein by reference.

Optional Scavengers, Co-Activators, Chain Transfer Agents

- [0244] In addition to support-bound activator, scavengers or co-activators may be used. A scavenger is a compound that is typically added to facilitate polymerization by scavenging
15 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.

- [0245] Co-activators can include alumoxanes such as methylalumoxane, modified
20 alumoxanes such as modified methylalumoxane, and aluminum alkyls such as trimethylaluminum, tri-isobutylaluminum, triethylaluminum, and tri-isopropylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-n-decylaluminum or tri-n-dodecylaluminum. Co-activators are typically used in combination with Lewis acid activators and ionic activators when the pre-catalyst is not a dihydrocarbyl or dihydride complex. Sometimes co-activators
25 are also used as scavengers to deactivate impurities in feed or reactors.

[0246] 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 dialkyl zinc, such as diethyl zinc.

- 30 [0247] Chain transfer agents may be used in the compositions and or processes described herein. Useful chain transfer agents are typically hydrogen, alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, such as methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, trimethylaluminum, triisobutylaluminum,

trioctylaluminum, or a combination thereof.

[0248] In some embodiments, little or no co-activator (such as alumoxane) is used in the polymerization processes described herein.

[0249] Alumoxanes are generally oligomeric compounds containing $-Al(R^1)-O-$ sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. A useful alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number US 5,041,584). Another useful alumoxane is solid polymethylaluminoxane as described in US 8,404,880; US 8,975,209 and US 9,340,630.

[0250] When the additional activator is an alumoxane (modified or unmodified), typically the maximum amount of activator is at up to a 5,000-fold molar excess Al/M (including the aluminum of the support-bound activator) over the catalyst compound (per metal catalytic site). The minimum Al/M is a 1:1 molar ratio. Alternate ranges include from 1:1 to 500:1, alternately from 1:1 to 200:1, alternately from 1:1 to 100:1, or alternately from 1:1 to 50:1.

Polymerization Processes

[0251] In some embodiments, the present disclosure relates to polymerization processes where monomer (such as ethylene or propylene), and optionally comonomer, are contacted with a catalyst system comprising an activator, a support and at least one catalyst compound, as described above. The catalyst compound, support, and activator may be combined in any order, and are combined typically prior to contacting with the monomer.

[0252] Monomers useful herein include substituted or unsubstituted C_2 to C_{40} alpha olefins, such as C_2 to C_{20} alpha olefins, such as C_2 to C_{12} alpha olefins, such as ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In some embodiments, the monomer comprises propylene and an optional comonomers comprising one or more ethylene or C_4 to C_{40} olefins, such as C_4 to C_{20} olefins, such as C_6 to C_{12} olefins. The C_4 to C_{40} olefin monomers may be linear, branched, or cyclic. The C_4 to C_{40} cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may

optionally include heteroatoms and/or one or more functional groups. In another embodiment, the monomer comprises ethylene 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
5 unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups.

[0253] Exemplary C₂ to C₄₀ olefin monomers and optional comonomers include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, cyclopentene, cycloheptene, cyclooctene, cyclododecene, substituted derivatives
10 thereof, and isomers thereof, such as hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 5-methylcyclopentene, cyclopentene, norbornene, 5-ethylidene-2-norbornene, and their respective homologs and derivatives.

[0254] In at least one embodiment, one or more dienes are present in the polymer produced herein at up to 10 weight %, such as at 0.00001 to 1.0 weight %, such as 0.002 to 0.5 weight %,
15 such as 0.003 to 0.2 weight %, 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 or 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.

[0255] Example diolefin monomers of the present disclosure include any hydrocarbon
20 structure, such as C₅ 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 diolefin monomers may be selected from non-conjugated diene monomers. For example, the diolefin monomers are linear di-vinyl monomers, such as those containing from 5 to 30 carbon atoms. Examples of some dienes include pentadiene,
25 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, such as dienes can include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene,
30 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, divinylbenzene, and low molecular weight polybutadienes (Mw less than 1000 g/mol). Cyclic dienes may include cyclopentadiene, vinylnorbornene, norbornadiene, and dicyclopentadiene.

[0256] Polymerization processes of present disclosure can be carried out in any manner

known in the art. Any suspension, bulk, slurry, or gas phase polymerization process known in the art can be used. Particularly, any suspension, slurry, high pressure tubular or autoclave process, or gas phase polymerization process known in the art can be used under polymerizable conditions. Such processes can be run in a batch, semi-batch, or continuous mode. Gas phase polymerization processes and slurry processes may be utilized. In some embodiments, the process is not a homogeneous polymerization process, *e.g.*, a process where at least 90 wt% of the product is soluble in the reaction media. In some embodiments, 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 some embodiments, the process is a slurry 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).

15 [0257] In some embodiments, the polymerization is performed in the slurry phase. 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 as described above. 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 employed 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 is typically operated above the reaction diluent critical temperature and pressure. Often, a hexane or an isobutane medium is employed.

20 [0258] In an embodiment, a polymerization process is referred to as a particle form polymerization, or a slurry process, where the temperature is kept below the temperature at which the polymer goes into solution. An example of this polymerization is described in for instance US 3,248,179. A temperature in the particle form process can be about 85°C to about 110°C. Two polymerization methods for the slurry process may be those employing 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 4,613,484, which is

30

herein fully incorporated by reference.

[0259] In a class of embodiments, the polymerization is performed in the gas phase, such as, in a fluidized bed gas phase process. Generally, in a fluidized bed gas phase process used for producing polymers, a gaseous stream containing one or more monomers is continuously
5 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 Patent 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
10 5,668,228; all of which are fully incorporated herein by reference.

[0260] Useful reactor types and/or processes for the production of polyolefin polymers include, but are not limited to, UNIPOL™ Gas Phase Reactors and processes (available from Univation Technologies); INEOS™ Gas Phase Reactors and Processes; Continuous Flow Stirred-Tank (CSTR) reactors (slurry); Plug Flow Tubular reactors (slurry); Slurry: (*e.g.*, Slurry
15 Loop (single or double loops)) (available from Chevron Phillips Chemical Company) and (Series Reactors) (available from Mitsui Chemicals)); BORSTAR™ Process and Reactors (slurry combined with gas phase); and Multi-Zone Circulating Reactors (MZCR) such as SPHERIZONE™ Reactors and Process available from Lyondell Basell.

[0261] Suitable diluents/solvents for polymerizations herein include non-coordinating,
20 inert liquids. Examples include straight and branched-chain hydrocarbons, such as propane, isobutane, butane, pentane, isopentane, neopentane, 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™ fluids); perhalogenated hydrocarbons, such as perfluorinated
25 C₄₋₁₀ 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 some embodiments, aliphatic hydrocarbon solvents are used as the solvent, such as
30 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. In another embodiment, the solvent is not aromatic, for example 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.

[0262] In some embodiments, 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. For example, the polymerization is run in a bulk process.

- 5 [0263] Some example polymerizations can be run at any temperature and/or pressure suitable to obtain the desired ethylene polymers. Typical temperatures and/or pressures include a temperature of about 0°C to about 300°C, such as about 20°C to about 200°C, such as about 35°C to about 150°C, such as about 40°C to about 120°C, such as about 45°C to about 80°C; and at a pressure of about 0.35 MPa to about 10 MPa, such as about 0.45 MPa to about 6 MPa, such as about 0.5 MPa to about 4 MPa.

[0264] In a typical polymerization, the run time of the reaction is up to 300 minutes, such as in the range of about 5 to 250 minutes, such as about 10 to 120 minutes.

- [0265] In some embodiments, 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).

- [0266] In some embodiments, the polymerization, such as gas phase polymerization: 1) is conducted at temperatures of 0 to 300°C (such as 60 to 120°C, such as 70 to 110°C, such as 75 to 100°C, such as 80 to 95°C); 2) is conducted at a pressure of atmospheric pressure to 10 MPa (such as 0.35 to 10 MPa, such as 0.45 to 6 MPa, such as 0.5 to 4 MPa); 3) the polymerization can occur in one reaction zone; 4) the catalyst productivity is at least 1,000 g polymer/g supported catalyst/hr (such as at least 2,000 g polymer/g supported catalyst/hr, such as at least 5,000 g polymer/g supported catalyst/hr, such as at least 8,000 g polymer/g supported catalyst/hr, such as at least 10,000 g polymer/g supported catalyst/hr, such as at least 15,000 g polymer/g supported catalyst/hr, such as at least 20,000 g polymer/g supported catalyst/hr) and 5) optionally 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)). In some embodiments, 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. Room temperature is 23°C unless otherwise noted.

[0267] Unless otherwise indicated, “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 $\text{gPgc}^{-1}\text{hr}^{-1}$.

- 5 [0268] In at least one embodiment, according to the present disclosure, a catalyst system has a catalyst productivity of greater than about $500 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as greater than about $2,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as greater than about $20,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as about $10,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $60,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as about $15,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $50,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as about $15,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $30,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as about
 10 $15,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $20,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, alternatively about $20,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $30,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, alternatively about $30,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $50,000 \text{ gPgc}^{-1}\text{hr}^{-1}$, such as about $30,000 \text{ gPgc}^{-1}\text{hr}^{-1}$ to about $40,000 \text{ gPgc}^{-1}\text{hr}^{-1}$.

- [0269] Other additives may also be used in the polymerization, as desired, such as one or more scavengers, hydrogen, aluminum alkyls, silanes, or chain transfer agents (such as
 15 alkylalumoxanes, a compound represented by the formula AlR_3 or ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, such as methyl, ethyl, propyl, butyl, penyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof).

Polyolefin Products

- 20 [0270] The present disclosure also relates to compositions of matter produced by the methods described herein. The processes described herein may be used to produce polymers of olefins or mixtures of olefins. Polymers that may be prepared include polyethylene, polypropylene, homopolymers of C_4 - C_{20} olefins, copolymers of C_4 - C_{20} olefins, copolymers of ethylene with C_3 - C_{20} olefins, copolymers of propylene with C_4 - C_{20} olefins, terpolymers of
 25 C_4 - C_{20} olefins, terpolymers of ethylene and propylene with C_4 - C_{20} olefins, and terpolymers of ethylene and propylene with 5-ethylidene-2-norbornene.

- [0271] In some embodiments, the process described herein produces propylene homopolymers or propylene copolymers, such as propylene-ethylene and / or propylene-alphaolefin (such as C_4 to C_{20}) copolymers (such as propylene-hexene copolymers or
 30 propylene-octene copolymers) having a M_w/M_n of between 1 to 10 (such as 2-5, such as 2-4, such as 2-3).

[0272] In some embodiments, the polymers produced herein are copolymers of ethylene for example having from 0 to 25 mole% (alternately from 0.1 to 10 mole%, alternately from 0.2 to 5 mole%, such as 1 to 3 mole%) of one or more C_3 to C_{20} olefin comonomer (such as C_3

to C₁₂ alpha-olefin, such as propylene, butene, hexene, octene, decene, dodecene, such as propylene, butene, hexene, octene), or are copolymers of propylene for example having from 0 to 25 mole% (such as from 0.1 to 10 mole%, such as from 0.2 to 5 mole%, such as from 1 to 3 mole%) of one or more of C₂ or C₄ to C₂₀ olefin comonomer (such as ethylene or C₄ to C₁₂ alpha-olefin, such as ethylene, butene, hexene, octene, decene, dodecene, such as ethylene, butene, hexene, octene).

[0273] In some embodiments, the monomer is ethylene and the comonomer is hexene, such as from 0 to 8 mole% hexene, such as 1 to 5 mole%.

[0274] Polymers produced herein can have a weight average molecular weight (M_w) of 5,000 to 1,000,000 g/mol, such as 25,000 to 750,000 g/mol, such as 100,000 to 500,000 g/mol, such as 200,000 to 400,000 g/mol, alternatively 400,000 g/mol to 800,000 g/mol, such as 600,000 g/mol to 800,000 g/mol.

[0275] Polymers produced herein can have a number average molecular weight (M_n) of 5,000 to 1,000,000 g/mol, such as 100,000 to 500,000 g/mol, such as 100,000 to 200,000 g/mol, alternatively 200,000 to 300,000 g/mol, alternatively 300,000 g/mol to 400,000 g/mol.

[0276] Polymers produced herein can have an M_w/M_n of greater than 1 to 40, such as 2 to 20, such as 2 to 10, such as 2 to 5, 2 to 4, such as 2 to 3.

[0277] In some embodiments, 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).

[0278] In at least one embodiment, a polymer of the present disclosure can have a melt temperature (T_m (°C)) of about 120°C to about 150°C, such as about 122.5°C to about 150°C, such as about 135°C to about 147°C, such as about 140°C to about 145°C, alternatively about 145°C to about 150°C, alternatively about 150°C to about 160°C, such as about 150°C to about 155°C. Differential Scanning Calorimetry (DSC) measurements can be performed on a TA-Q100 instrument to determine the melt temperature of the polymers. Samples can be pre-annealed at 220°C for 15 minutes and then allowed to cool to room temperature overnight. The samples can then be heated to 220°C at a rate of 100°C/minute and then cooled at a rate of 50°C/minute. Melt temperature can be collected during the heating period.

GPC 4-D

[0279] Unless otherwise indicated, for purposes of the Claims, the distribution and the

moments of molecular weight (M_w , M_n , M_z , M_w/M_n , etc.), the comonomer content 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 with a multiple-channel band filter based infrared detector ensemble IR5 with band region covering about 2700 cm^{-1} to about 3000 cm^{-1} (representing saturated C-H stretching vibration), an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10- μm Mixed-B LS columns are used to provide polymer separation. Reagent grade 1,2,4-trichlorobenzene (TCB) (from Sigma-Aldrich) comprising ~300 ppm antioxidant BHT can be used as the mobile phase at a nominal flow rate of ~1.0 mL/min and a nominal injection volume of ~200 μL . The whole system including transfer lines, columns, and detectors can be contained in an oven maintained at ~145°C. A given amount of sample can be weighed and sealed in a standard vial with ~10 μL flow marker (heptane) added thereto. After loading the vial in the auto-sampler, the oligomer or polymer may automatically be dissolved in the instrument with ~8 mL added TCB solvent at ~160°C with continuous shaking. The sample solution concentration can be from ~0.2 to ~2.0 mg/mL, with lower concentrations used for higher molecular weight samples. The concentration, c , at each point in the chromatogram can be calculated from the baseline-subtracted IR5 broadband signal, I , using the equation: $c = \alpha I$, where α is the mass constant determined with polyethylene or polypropylene standards. The mass recovery can be 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. 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 gm/mole. The MW at each elution volume is calculated with following equation:

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

where the variables with subscript "PS" stand for polystyrene while those without a subscript are for the test samples. In this method, $\alpha_{PS} = 0.67$ and $K_{PS} = 0.000175$, α and K for other materials are as calculated by GPC ONE™ software (Polymer Characterization, S.A., Valencia, Spain). 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.

[0280] 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. In particular, this provides the methyls per 1000 total carbons (CH₃/1000TC) as a function of molecular weight. The short-chain branch (SCB) content per 1000TC (SCB/1000TC) is then computed as a function of molecular weight by applying a chain-end correction to the CH₃/1000TC function, assuming each chain to be linear and terminated by a methyl group at each end. The weight % comonomer is then obtained from the following expression in which f is 0.3, 0.4, 0.6, 0.8, and so on for C₃, C₄, C₆, C₈, and so on co-monomers, respectively:

$$w_2 = f * \text{SCB}/1000\text{TC}.$$

The bulk composition of the polymer from the GPC-IR and GPC-4D analyses is obtained by considering the entire signals of the CH₃ and CH₂ channels between the integration limits of the concentration chromatogram. First, the following ratio is obtained

$$\text{Bulk IR ratio} = \frac{\text{Area of CH}_3 \text{ signal within integration limits}}{\text{Area of CH}_2 \text{ signal within integration limits}}.$$

Then the same calibration of the CH₃ and CH₂ signal ratio, as mentioned previously in obtaining the CH₃/1000TC as a function of molecular weight, is applied to obtain the bulk CH₃/1000TC. A bulk methyl chain ends per 1000TC (bulk CH₃end/1000TC) is obtained by weight-averaging the chain-end correction over the molecular-weight range. Then

$$w_{2b} = f * \text{bulk CH}_3/1000\text{TC}$$

$$\text{bulk SCB}/1000\text{TC} = \text{bulk CH}_3/1000\text{TC} - \text{bulk CH}_3\text{end}/1000\text{TC}$$

and bulk SCB/1000TC is converted to bulk w_2 in the same manner as described above.

[0281] 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 (*Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press, 1972.):

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

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, $P(\theta)$ 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,

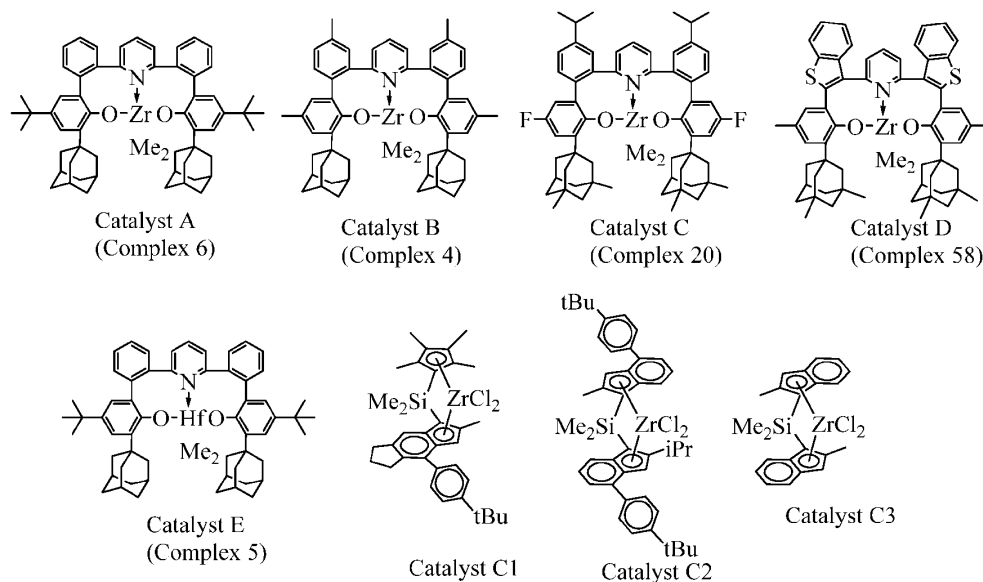
$n = 1.500$ for TCB at 145°C and $\lambda = 665 \text{ nm}$. For analyzing polyethylene homopolymers, ethylene-hexene copolymers, and ethylene-octene copolymers, $dn/dc = 0.1048 \text{ ml/mg}$ and $A_2 = 0.0015$; for analyzing ethylene-butene copolymers, $dn/dc = 0.1048 \cdot (1 - 0.00126 \cdot w_2) \text{ ml/mg}$ and $A_2 = 0.0015$ where w_2 is weight percent butene comonomer.

- 5 [0282] 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
- 10 is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the equation $[\eta] = \eta_s/c$, where c is concentration and is determined from the IR5 broadband channel output. The viscosity MW at each point is calculated as $M = K_{ps} M^{\alpha_{ps}+1} / [\eta]$, where α_{ps} is 0.67 and K_{ps} is 0.000175.

EXPERIMENTAL

- 15 [0283] All manipulations were carried out with careful exclusion of oxygen and moisture in the drybox filled with nitrogen atmosphere. Solvents were purchased of anhydrous grade and were sparged with nitrogen and stored over molecular sieves for 1 day prior to usage. All reagents unless mentioned otherwise were purchased from commercial vendors (Millipore Sigma, Fisher Scientific, Strem Chemicals, Grace Chemicals or Oakwood Chemical) and used
- 20 as received unless otherwise noted.

[0284] The catalysts tested were as follows:



[0285] Catalyst A (Complex 6), Catalyst B (Complex 4), Catalyst C (Complex 20) and Catalyst E (Complex 5) were prepared as described in US 11,254,763. Catalyst D (Complex 58 in the cited patent application) was prepared as described in WO 2021/162746. Catalyst C₂ and C₃ were obtained from commercial sources. Catalyst C₁ was prepared according to EP 4017887.

Supported catalyst preparation

Preparation of support materials

Comparative support - Silica supported MAO (SMAO)

[0286] In a celstir, 10.0 g of 200°C calcined silica (DM-L403, Asahi Glass) was suspended in ca 100 mL of dry toluene and cooled in the freezer to -20°C. After ca 30 minutes of cooling, a 30% solution of MAO (15.8 g in toluene) was slowly added to the stirring silica mixture (over 10 minutes). The reactions were allowed to warm up to room temperature with stirring for 1.5 hours. After 1.5 hours, the temperature was raised to 100°C and the reactions were allowed to stir for additional 2.5 hours. The temperature was then decreased down to 55°C and the mixture was then filtered over glass frit. The SMAO was then washed with toluene 2 x 50 mL and pentane 2 x 50 mL and was dried *in vacuo* for 1 hour. Yield: 14.1 g

Preparation and isolation of trispentafluorophenylalane

[0287] 0.21 g of AlMe₃ (in ca 5 mL of toluene) was slowly added to stirred slurry of 1.5 g of tris(pentafluorophenyl)boron in pentane (ca 30 mL). Upon completion, the mixture became

homogenous, and it was stirred for 1 hour at room temperature uncapped to allow BMe_3 removal as a gas. Upon completion, the mixture was placed in a freezer at -35°C . After 1 day, the precipitated crystalline material was filtered, washed with additional pentane ($2 \times 10 \text{ mL}$) and dried *in vacuo* to afford spectroscopically pure alane as a crystalline white powder that is isolated as toluene adduct in 68% yield.

Comparative support – boron based (SBA-B)

[0288] 3.0 g of Grace Sylopol 952 x 1836 silica (600°C calcination; determined to have 0.891 mmol $-\text{OH}/\text{g}$ via titration with BnMgCl) was slurried in 30 mL of toluene in a small CelstirTM. While stirring, 0.206 g (1.38 mmol) of diethylaniline was added, followed by addition of 0.691 g (1.35 mmol) of trispentafluorophenylboron. The reaction mixture was stirred for 1 hour at room temperature. In order to cap the remaining Si-OH groups, a BHT:TEAL complex (2:1) was prepared. In a separate vial, 0.256 g of TEAL (2.25 mmol) was dissolved in 2 mL of toluene. While stirring, 991.5 mg of BHT was slowly added as a toluene solution (ca 5mL). The reaction mixture showed noticeable bubbling. Upon completion, the pale-yellow solution was stirred for 30 minutes. After 30 minutes, the TEAL/BHT solution was slowly added to the silica slurry. The slurry was stirred for 2 hours, and was then filtered, washed with toluene ($2 \times 15 \text{ mL}$) and pentane ($2 \times 15 \text{ mL}$) and dried *in vacuo* to give 3.9 g of free-flowing solids.

Inventive support – aluminum based (SBA-Al1)

[0289] 3.0 g of Grace Sylopol 952 x 1836 silica (600°C calcination; determined to have 0.891 mmol $-\text{OH}/\text{g}$ via titration with BnMgCl) was slurried in 30 mL of toluene in a small CelstirTM. While stirring, 0.206 g (1.38 mmol) of diethylaniline was added, followed by addition of 0.837 g (1.35 mmol) of trispentafluorophenylaluminum (toluene adduct). The reaction mixture was stirred for 1 hour at room temperature. In order to cap the remaining Si-OH groups, a BHT:TEAL complex (2:1) was prepared. In a separate vial, 0.256 g of TEAL (2.25 mmol) was dissolved in 2 mL of toluene. While stirring, 991.5 mg of BHT was slowly added as a toluene solution (ca 5 mL). The reaction mixture showed noticeable bubbling. Upon completion, the pale-yellow solution was stirred for 30 minutes. After 30 minutes, the TEAL/BHT solution was slowly added to the silica slurry. The slurry was stirred for 2 hours, and was then filtered, washed with toluene ($2 \times 15 \text{ mL}$) and pentane ($2 \times 15 \text{ mL}$) and dried *in vacuo* to give 3.9 g of free-flowing solids.

Inventive support – in-situ aluminum based (SBA-Al2)

[0290] In a small round bottom flask, 0.165 g (2.29 mmol) of AlMe_3 (in ca 5 mL of toluene) was slowly added to a stirred slurry of 1.17 g (2.29 mmol) of tris(pentafluorophenyl)boron in

pentane (ca 30 mL). Upon completion, the mixture became homogenous, and it was stirred for 1 hour at room temperature uncapped to allow BMe_3 removal as a gas. The anticipated Al content is 2.29 mmol in solution based on TMA quantity used. In a separate Celstir™, 10.0 g of Sylopol 952 x 1836 (600°C calcination; 0.891 mmol -OH / g) was slurried in toluene (30 mL). While stirring, the solution of $\text{Al}(\text{C}_6\text{F}_5)_3$ prepared in the first step was transferred to the silica slurry. This was followed by addition of diethylaniline (0.342 g, 2.29 mmol) in minimal toluene. The silica slurry was further stirred for 30 minutes. In a third-round bottom flask, 0.764 g TEAL (6.71 mmol, based on monomer) was suspended in 30 mL of toluene. While stirring, a toluene solution of BHT (ca 20 mL, containing 2.957 g of BHT, 13.4 mmol) was slowly added to the TEAL mixture. The reaction was allowed to proceed for 30 minutes. After 30 minutes, the TEAL:BHT complex was slowly added to the silica slurry at room temperature. The reaction mixture was then stirred overnight. After 18 hours, the mixture was filtered, the solid was washed with toluene (2 x 50 mL) and pentane (2 x 50 mL) and dried *in vacuo* to afford the 13.2 g of support material as white free flowing powder.

15 Preparation of supported catalysts.

[0291] **Catalyst A / SMAO and Catalyst E / SMAO (comparative)** was prepared according to examples outlined in US 11,225,539 B2. Ziegler Natta (ZN) catalyst used is a 4th generation phthalate catalyst obtained from commercial sources.

[0292] **Catalyst A / SBA-B (comparative)** -- 17 mg of organometallic precursor A was added to 0.55 g of SBA-B in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as an off-white free flowing powder.

[0293] **Catalyst A / SBA-A11** -- 33 mg of organometallic precursor A was added to 1.0 g of SBA-A11 in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as an off-white free flowing powder.

[0294] **Catalyst A / SBA-A12** -- 16.5 mg of organometallic precursor A was added to 1 g of SBA-A12 in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as an off-white free flowing powder.

[0295] **Catalyst B / SBA-A12** -- 21 mg of organometallic precursor B was added to 1 g of

SBA-AI2 in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as a free-flowing powder.

[0296] **Catalyst C / SBA-AI2** -- 24 mg of organometallic precursor C was added to 1 g of SBA-AI2 in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as a free-flowing powder.

[0297] **Catalyst D / SBA-AI2** -- 25 mg of organometallic precursor D was added to 1 g of SBA-AI2 in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as a free-flowing powder.

[0298] **Catalyst E / SBA-AI2** - 29 mg of organometallic precursor D was added to 1.2 g of SBA-AI2 in toluene. The mixture was allowed to shake for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and was dried *in vacuo* to afford the final catalyst as a free-flowing powder.

[0299] **Catalyst C₁ / SMAO (comparative)** -- 0.95 g of SMAO was suspended in 5 mL of toluene and placed on the shaker. TIBAL (0.33 mL of 1M solution) was then added, and the mixture was allowed to shake for 15 minutes at room temperature. Metallocene solid C₁ (21.0 mg) was then added to the shaking mixture as a toluene solution (ca 1 mL). The solution was further shaken for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (1 x 10 mL) and pentane (2 x 10 mL) and dried *in vacuo* to afford supported catalyst as a red free-flowing powder.

[0300] **Catalyst C₂ / SMAO (comparative)** -- 0.95 g of SMAO was suspended in 5 mL of toluene and placed on the shaker. TIBAL (0.33 mL of 1M solution) was then added, and the mixture was allowed to shake for 15 minutes at room temperature. Metallocene solid C₂ (22.8 mg) was then added to the shaking mixture as a toluene solution (ca 1 mL). The solution was further shaken for 4 hours. After 4 hours, the mixture was filtered, and the solid was washed with toluene (1 x 10 mL) and pentane (2 x 10 mL) and dried *in vacuo* to afford supported catalyst as a red free-flowing powder.

[0301] **Catalyst C₃ / SMAO (comparative)** -- 2.0 g of SMAO was slurried in 15 mL of toluene in a 40 mL vial equipped with a mechanical stirrer. TIBAL (1.05 mL of 1M in hexane) was slowly added with stirring. The mixture was mechanically agitated for about 20 minutes. After 20 minutes 11.0 mg of catalyst C dissolved in 5.0 mL of toluene was slowly added. The reactions are mechanically stirred for 3 hours. After 3 hours, the solids were filtered on a glass

frit, washed with toluene (2 x 10 mL) and pentane (2 x 10 mL) and dried *in vacuo*.

Density Functional Theory Calculations and Results

[0302] In order to demonstrate the thermodynamic driving force and stability of Support-Al relative to Support-B, density functional theory (DFT) calculations (M06-2X level) were carried out. DFT calculations confirm the striking difference between boron and aluminum in the SBA type scaffold. As shown in FIG. 1, (MeO)₃SiOH molecule was used as a proxy for silica support. Modelled activator structures are shown at the right side of FIG. 1.

[0303] DFT calculations confirm that the most reasonable mechanism for support-bound activator formation involves 2 steps: Lewis acid binding and polarization of Si-OH⁺, followed by proton abstraction by aniline. Modelling insights revealed that this mechanism is significantly more favorable for aluminum species as indicated by highly exergonic nature of the reaction. Such high thermodynamic driving force is advantageous, as it will prevent reversible steps that will ensure full activation and mitigate the risk of activator leeching from support. The more efficient aniline abstraction in an aluminum-based system likely leads to higher population of activator sites – hence the aluminum-based activator could show productivity improvement over boron-based activator.

Computational details.

[0304] Ground state geometry optimizations and frequency calculation was carried out using M06-2X level of theory with 6-31G** basis set as implemented in Jaguar. Vibrational analysis was carried out to confirm zeroth order saddle point (a local minimum). Energetics were calculated at 298K at 1 atm with 6-311G**++ basis set. Reported energies utilize thermodynamic corrections to energy from the gas phase optimized structures and are reported in gas phase.

Polymerization procedure (propylene bulk slurry)

[0305] A 1L autoclave reactor equipped with a mechanical stirrer was used for polymer preparation. Prior to the run, the reactor was placed under nitrogen purge while maintaining 90°C temperature for 30 minutes. Upon cooling back to ambient temperature, propylene feed (500 mL), scavenger (0.2 mL of 1M TIBAL, triisobutylaluminum) and optionally hydrogen (charged from a 50 mL bomb at a desired pressure) were introduced to the reactor and were allowed to mix for 5 minutes. Desired amount of supported catalyst (typically 12.5 – 25.0 mg) was then introduced to the reactor by flushing the pre-determined amount of catalyst slurry (5 wt% in mineral oil) from a catalyst tube with 100 mL of liquid propylene. The reactor was kept for 5 minutes at room temperature (pre-poly stage), before raising the temperature to 70°C. The reaction was allowed to proceed at that temperature for a desired time period (typically

30 minutes). After the given time, the temperature was reduced to 25°C, the excess propylene was vented off and the polymer granules were collected and dried overnight. The polymerization results are outlined in Table 1.

Table 1 Bulk slurry polymerization of propylene

Ex.	Cat.	Support	Cat. (mg)	T _p (°C)	H ₂ (mmol)	Time (min)	Yield (g)	Productivity (g/g·h)	M _n	M _w	T _m
I1	A	SBA-A11	12.6	70	2	20	205	48,766	-	-	-
I2	A	SBA-A11	4.7	60	2	30	56	23,640	-	-	-
I3	A	SBA-A12	12.4	70	0	30	81	12,999	337,178	769,655	138
I4	A	SBA-A12	12.8	70	12.5	30	113	17,741	275,256	699,653	140
I5	B	SBA-A12	25.2	70	12.5	20	170	20,267	288,306	691,948	139
I6	B	SBA-A12	12.3	70	0	30	72	11,771	342,199	769,457	140
I7	B	SBA-A12	13.2	70	12.5	30	127	19,317	294,718	692,534	-
I8	C	SBA-A12	12.5	70	0	30	23	3,747	103,064	240,017	152
I9	C	SBA-A12	12.6	70	12.5	30	146	23,215	101,778	218,127	152
I10	D	SBA-A12	12.6	70	0	30	16	2,505	109,566	252,177	153
I11	D	SBA-A12	13.1	70	12.5	30	221	33,881	101,225	215,971	153
I12	E	SBA-A12	12.5	70	2	30	4	697	125,402	630,045	155
I13	E	SBA-A12	25.7	70	12.5	30	12	937	127,611	464,048	155
C1	A	SMAO	25.0	70	0	60	54	2,148	410,935	727,957	-
C2	A	SMAO	25.2	70	12.5	60	73	2,893	385,084	687,023	-
C3	A	SBA-B	4.9	70	2	30	31	12,714	351,895	842,905	-
C4	E	SMAO	25.5	70	0	60	0	16	-	-	-
C5	C1	SMAO	12.6	70	2	30	58	9,231	-	-	158
C6	C2	SMAO	12.3	70	2	60	91	7,440	-	-	153
C7	C3	SMAO	12.6	70	2	30	22	3,430	-	-	149
C8	ZN / C-donor	MgCl ₂	4.9	70	12.5	30	101	40,934	63,404	367,313	-
C9	ZN / C-donor	MgCl ₂	4.9	70	12.5	30	100	40,918	61,280	364,438	-

- [0306] The results outlined in Table 1 demonstrate superior activation efficiency of 8-8 catalysts. The productivities under industrially relevant conditions exceed 20,000 g/g x hr and are similar to conventional Ziegler Natta catalysts. The examples also highlight differences between conventional metallocenes of commercial relevance (C_1 and C_2 symmetric) and inventive 8-8 catalysts. In the case of 8-8 catalysts, significant improvement in catalyst productivity is observed relative to metallocenes (3 – 4-fold). In addition, catalyst A on SBA-Al demonstrated orders of magnitude improvement in productivity over Catalyst A on SMAO which further reinforces the need for careful choice of activator system for post-metallocene catalysts. As shown in FIG. 2, excellent particle morphology was observed.
- 10 [0307] In addition to slurry polymerization of propylene, catalyst A on SBA-Al1 was also tested in both isopentane slurry and gas phase (salt bed) for polymerization of ethylene. The catalyst showed significant improvement relative to a boron version in both slurry and gas phase polymerization of ethylene. The productivities and comparisons against commercially relevant metallocene catalysts (MCN-1, bis(1-methyl-3-butyl-cyclopentadienyl)zirconium chloride and MCN-2, bis(propylcyclopentadienyl)zirconium dichloride) are shown FIG. 6A and FIG. 6B. In all cases, the novel support showed improved productivity over commercially used metallocenes under identical conditions.
- 15 [0308] To summarize, the combination of $Al(C_6F_5)_3$ along with silica and Lewis base is a highly efficient method for supportation of 8-8 catalyst systems and constitutes a definite improvement over previously explored boron analogs. The supported catalysts demonstrate productivities that are 3 – 4-fold higher relative to conventional metallocenes and are on par with Ziegler Natta catalyst, as shown in FIG. 4. The combination of excellent monomer incorporation, high productivity and molecular weight positions 8-8 catalysts as catalyst systems for various polymers.
- 20 [0309] Overall, support-bound activators of the present disclosure can provide improved activation of post-metallocene catalysts, such as 8-8 catalysts. Catalyst systems having a support-bound activator of the present disclosure can provide reduced or eliminated reactor fouling, while maintaining slurry phase or gas phase polymerization conditions in the reactor. In addition, supported post-metallocene catalysts utilizing a support-bound activator of the present disclosure can have high productivity for olefin polymerizations while maintaining or improving upon other beneficial properties provided by post-metallocene catalysts such as improved polymer molecular weight, comonomer incorporation, stereoregularity, and temperature stability, as compared to post-metallocene catalysts used in solution phase polymerizations.
- 30

[0310] The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the present disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

5 [0311] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit
10 may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

15 [0312] 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,
20 it is not intended that the present disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including" for purposes of United States law. 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,"
25 "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[0313] While the present disclosure has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit
30 of the present disclosure.

CLAIMS

What is claimed is:

1. A modified support material, comprising:
a support material particle having surface oxygen atoms;
a haloarylaluminate having at least one haloaryl substituent, the haloarylaluminate coupled with at least one of the surface oxygen atoms;
a cationic group; and
optionally one or more main group metal compounds coupled with one or more of the surface oxygen atoms that are different than the surface oxygen atoms coupled with the haloarylaluminate.
2. The modified support material of claim 1, wherein the support material particle is a porous silica particle and the haloarylaluminate is covalently bonded to the first portion of the surface oxygen atoms.
3. The modified support material of claims 1 or 2, wherein the haloarylaluminate coupled with the first portion of the surface oxygen atoms and having at least one haloaryl substituent is represented by Formula (Ia or Ib):



wherein:

each of R¹, R², and R³ is independently C₁-C₄₀-alkyl, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl, C₁-C₄₀-aryleneoxy, C₁-C₄₀-alkylaryleneoxy, C₁-C₄₀-arylalkyleneoxy, or any two of R¹, R², and R³ may be joined to form saturated or unsaturated C₅-C₂₀ ring, wherein at least one of R¹, R², or R³ is C₆-C₄₀-haloaryl.

4. The modified support material of claim 3, wherein each of R^1 , R^2 , and R^3 is independently C₆-C₄₀-haloaryl.
5. The modified support material of claim 4, wherein each of R^1 , R^2 , and R^3 is independently selected from the group consisting of phenyl substituted with at least one halogen atom, naphthalenyl substituted with at least one halogen atom, and anthracenyl group substituted with at least one halogen atom.
6. The modified support material of claim 5, wherein each of R^1 , R^2 , and R^3 is perfluorinated phenyl.
7. The modified support material of claim 5, wherein each of R^1 , R^2 , and R^3 is perfluorinated naphthalenyl.
8. The modified support material of claims 1-2, wherein the main group metal compound is present, is coupled with the surface oxygen atoms, and is represented by Formula (D or E)



or



wherein:

M is a group 2 or 13 metal; each of R of Formula (D) or (E) is independently C₁-C₁₀-alkyl; X is F or OR¹ where R¹ is substituted or unsubstituted C₁-C₄₀-alkyl, C₁-C₄₀-alkoxy, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl; v is 2 or 3; and m = 1, 2, or 3 but not larger than v.

9. The modified support material of any of claims 1 to 8, wherein the cationic group is represented by Formula (IIIa):



wherein:

L is a neutral Lewis base; and

H is hydrogen.

10. The modified support material of claim 8, wherein $(L-H)^+$ is an ammonium.

11. The modified support material of claim 10, wherein the ammonium is represented by Formula (IVa):



wherein:

E is nitrogen; and

each of R^1 , R^2 , and R^3 of Formula (IVa) is independently C_1 to C_{50} hydrocarbyl optionally substituted with an alkoxy group, a silyl group, a halogen, or a halogen-containing group.

12. The modified support material of any of claims 1 to 11, wherein the cationic group is selected from the group consisting of

N,N-di(methyl)anilinium,

N,N-di(ethyl)anilinium,

N,N-di(propyl)anilinium,

N,N-di(butyl)anilinium,

N,N-di(pentyl)anilinium,

N,N-di(hexyl)anilinium,

N,N-di(heptyl)anilinium,

N,N-di(octyl)anilinium,

N,N-di(nonyl)anilinium, and

N,N-di(decyl)anilinium.

13. A process to prepare a modified support material comprising:

combining:

a support material particle having surface oxygen atoms such as silica, alumina, titania, magnesia, zirconia or clay;

a first aluminum Lewis acid agent represented by Formula (Va)



wherein:

each of R^1 , R^2 , and R^3 is independently C₁-C₄₀-alkyl, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl, C₁-C₄₀-aryleneoxy, C₁-C₄₀-alkylaryleneoxy, C₁-C₄₀-arylalkyleneoxy, or any of the R^1 , R^2 and R^3 may be joined to form saturated or unsaturated C₅-C₂₀ ring, wherein at least one of R^1 , R^2 , or R^3 is C₆-C₄₀-haloaryl;

a neutral Lewis base represented by Formula (VIa)



wherein:

Q is either nitrogen or phosphorus

R^1 , R^2 , and R^3 of Formula (VIa) is independently substituted or unsubstituted C₁-C₄₀-alkyl, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl, C₁-C₄₀-aryleneoxy, C₁-C₄₀-alkylaryleneoxy, or C₁-C₄₀-arylalkyleneoxy; and

an optional second aluminum Lewis acid compound, different from the first aluminum compound, represented by Formula (VIIa)



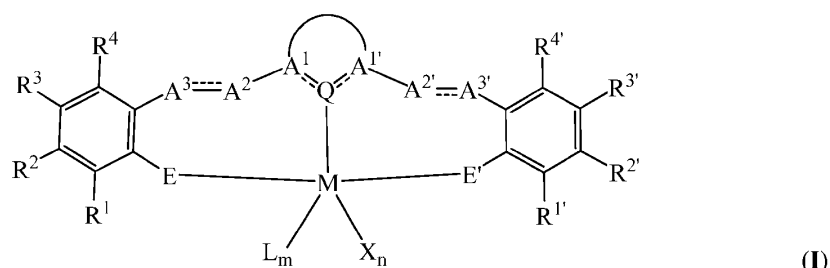
each of R^1 independently C₁-C₄₀-alkyl, C₆-C₄₀ aryl or hydride, and

R^2 and R^3 are independently C₁-C₄₀-alkyl, C₁-C₄₀-haloalkyl, C₆-C₄₀-aryl, C₆-C₄₀-haloaryl, C₂-C₄₀-alkynyl, C₂-C₄₀-haloalkynyl, C₂-C₄₀-alkenyl, C₂-C₄₀-haloalkenyl, C₁-C₄₀-aryleneoxy, C₁-C₄₀-alkylaryleneoxy, C₁-C₄₀-arylalkyleneoxy; Optionally any R^2 and R^3 may be joined to form saturated or unsaturated C₅-C₂₀ ring.

14. A catalyst system, comprising:

the modified support material of any of claims 1 to 12; and
a catalyst compound.

15. The catalyst system of claim 14, wherein the catalyst compound is represented by Formula (I):



wherein:

M of Formula (I) is a group 3, 4, 5, or 6 transition metal or a lanthanide;

E and E' of Formula (I) are each independently O, S, or NR⁹ wherein R⁹ is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl or a heteroatom-containing group;

Q of Formula (I) is a group 14, 15, or 16 atom that forms a dative bond to metal M;

A¹QA^{1'} of Formula (I) is part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A² to A^{2'} via a 3-atom bridge with Q being the central atom of the 3-atom bridge,

A¹ and A^{1'} of Formula (I) are independently C, N, or CR²², wherein R²² is hydrogen, C₁-C₂₀ hydrocarbyl, or C₁-C₂₀ substituted hydrocarbyl;

A³—A² of Formula (I) is a divalent group containing 2 to 40 non-hydrogen atoms that links A¹ to the E-bonded aryl group via a 2-atom bridge;

A^{2'}—A^{3'} of Formula (I) is a divalent group containing 2 to 40 non-hydrogen atoms that links A^{1'} to the E'-bonded aryl group via a 2-atom bridge;

each L of Formula (I) is a Lewis base;

each X of Formula (I) is an anionic ligand;

n of Formula (I) is 1, 2, or 3;

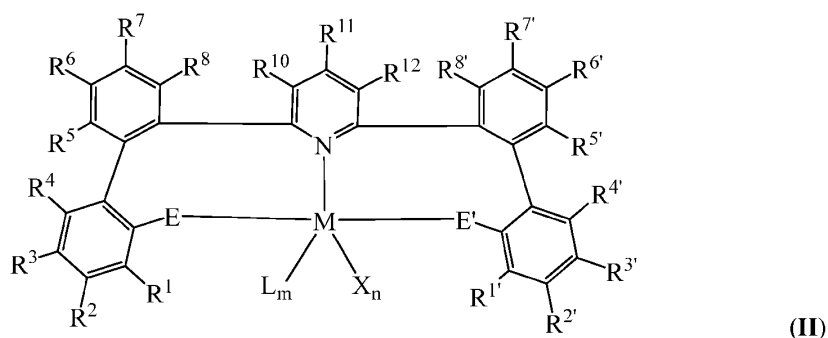
m of Formula (I) is 0, 1, or 2;

n+m of Formula (I) is not greater than 4;

each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} of Formula (I) is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} of Formula (I) may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and wherein substitutions on the one or more rings can join to form additional rings;

when m is 2, any 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; and
 when n is 2 or 3, any two X groups may be joined together to form a dianionic ligand group.

16. The catalyst system of claim 15, wherein the catalyst compound is represented by Formula (II):



wherein:

M of Formula (II) is a group 3, 4, 5, or 6 transition metal or a lanthanide;

E and E' of Formula (II) are each independently O, S, or NR⁹, wherein R⁹ is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group;

each L of Formula (II) is independently a Lewis base;

each X of Formula (II) is independently an anionic ligand;

n of Formula (II) is 1, 2, or 3;

m of Formula (II) is 0, 1, or 2;

n+m of Formula (II) is not greater than 4;

each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} of Formula (II) is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom, or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} of Formula (II) may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the one or more rings can join to form additional rings;

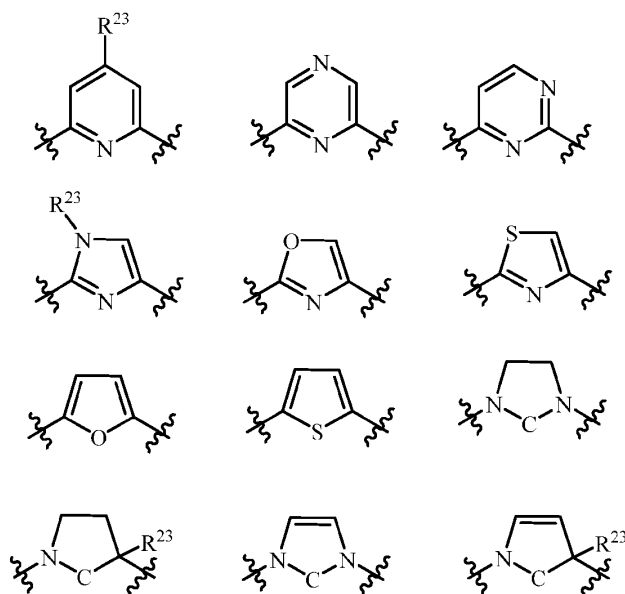
when m is 2, any two L groups may be joined together to form a bidentate Lewis base;

an X group of Formula (II) may be joined to an L group of Formula (II) to form a monoanionic bidentate group;

when n is 2 or 3, any two X groups of Formula (II) may be joined together to form a dianionic ligand group; and

each of R^5 , R^6 , R^7 , R^8 , $R^{5'}$, $R^{6'}$, $R^{7'}$, $R^{8'}$, R^{10} , R^{11} , and R^{12} of Formula (II) is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom, or a heteroatom-containing group, or one or more of R^5 and R^6 , R^6 and R^7 , R^7 and R^8 , $R^{5'}$ and $R^{6'}$, $R^{6'}$ and $R^{7'}$, $R^{7'}$ and $R^{8'}$, R^{10} and R^{11} , or R^{11} and R^{12} of Formula (II) may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

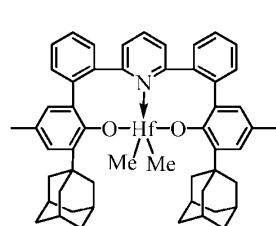
17. The catalyst system of claim 16, wherein M of Formula (II) is Hf, Zr, or Ti.
18. The catalyst system of claim 17, wherein each of E and E' of Formula (II) is oxygen.
19. The catalyst system of claim 15, wherein for the catalyst compound represented by Formula (I):
 - M is Zr or Hf;
 - Q is nitrogen;
 - both A¹ and A^{1'} are carbon;
 - both E and E' are oxygen; and
 - each of R¹ and R^{1'} is independently C₄-C₂₀ cyclic tertiary alkyls or substituted C₄-C₂₀ cyclic tertiary alkyls.
20. The catalyst system of claim 19, wherein both R¹ and R^{1'} of Formula (I) are t-butyl, adamantan-1-yl or substituted adamantan-1-yl.
21. The catalyst system of claim 15, wherein for the catalyst compound represented by Formula (I):
 - M is Zr or Hf;
 - both E and E' are oxygen;
 - each of R¹ and R^{1'} is independently C₄-C₂₀ cyclic tertiary alkyls or substituted C₄-C₂₀ cyclic tertiary alkyls; and
 - A¹QA^{1'} combined with the curved line joining A¹ and A^{1'} can be selected from the following,



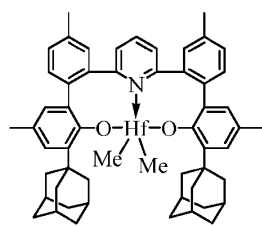
with each R^{23} group selected from hydrogen, heteroatoms, C_1 - C_{20} alkyls, C_1 - C_{20} alkoxides, C_1 - C_{20} amides, and C_1 - C_{20} substituted alkyls.

22. The catalyst system of claim 20, wherein both R^1 and $R^{1'}$ are *t*-butyl, adamantan-1-yl or substituted adamantan-1-yl.

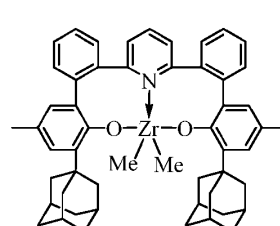
23. The catalyst system of claim 14, wherein the catalyst compound is selected from the group consisting of Complexes 1 - 66:



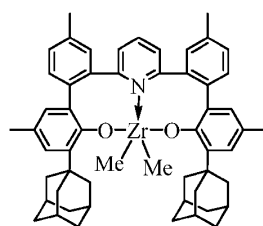
Complex 1



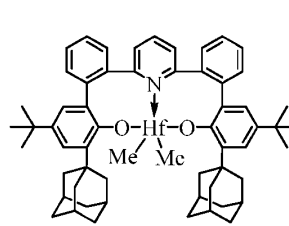
Complex 2



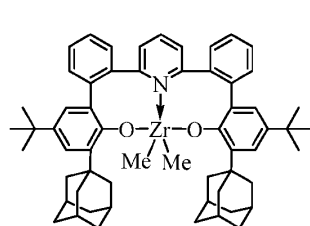
Complex 3



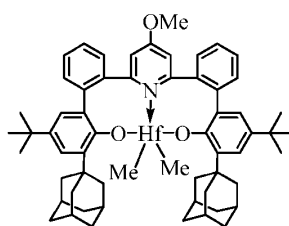
Complex 4



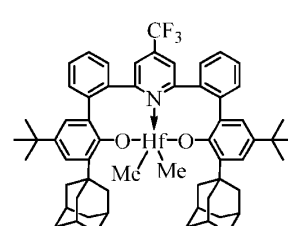
Complex 5



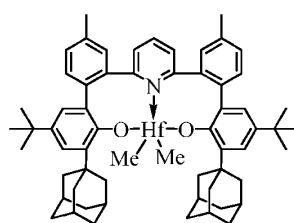
Complex 6



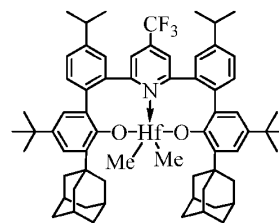
Complex 7



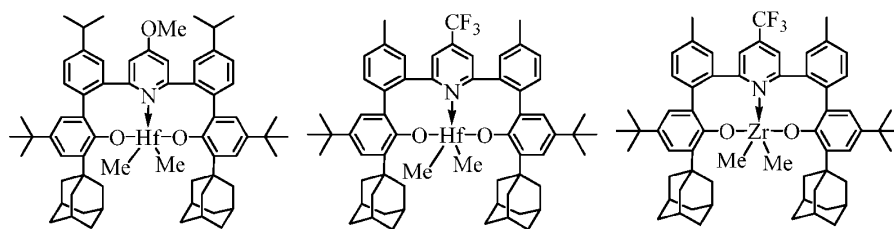
Complex 8



Complex 9



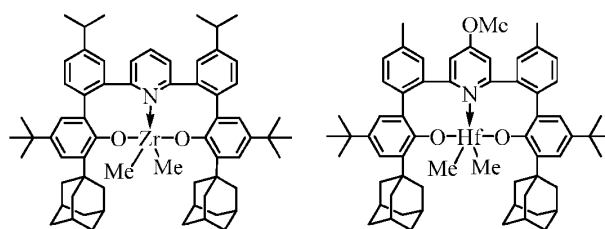
Complex 10



Complex 11

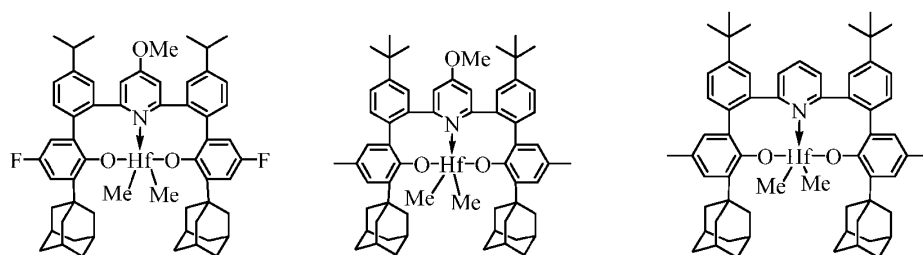
Complex 12

Complex 13



Complex 14

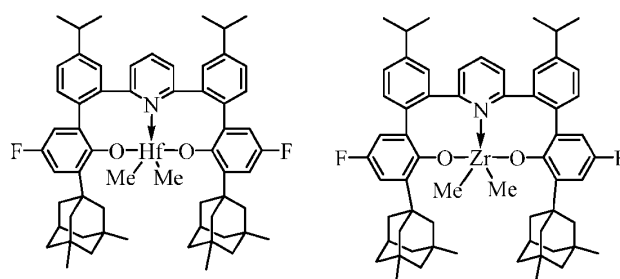
Complex 15



Complex 16

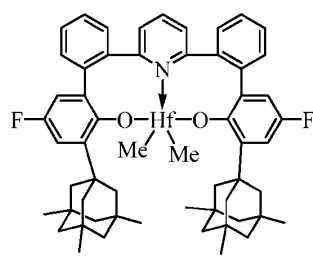
Complex 17

Complex 18

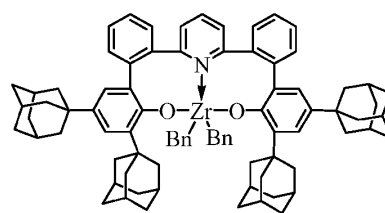


Complex 19

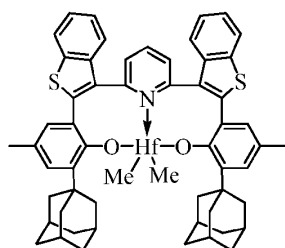
Complex 20



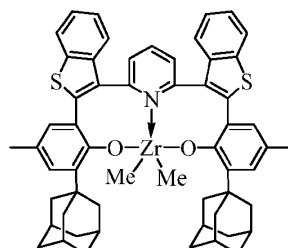
Complex 21



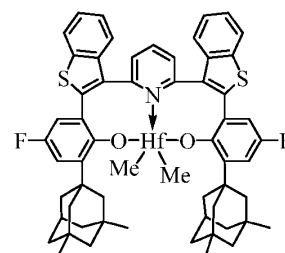
Complex 22



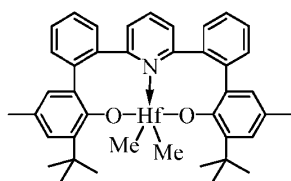
Complex 23



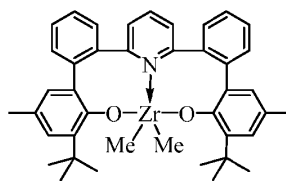
Complex 24



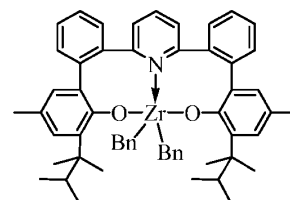
Complex 25



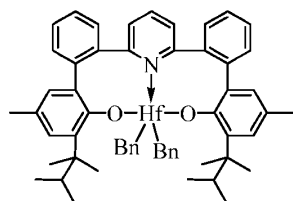
Complex 26



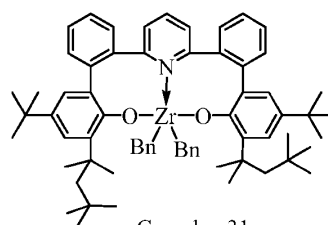
Complex 27



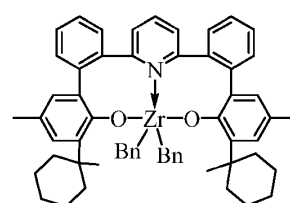
Complex 29



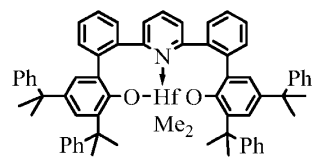
Complex 30



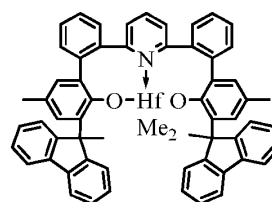
Complex 31



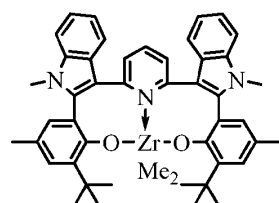
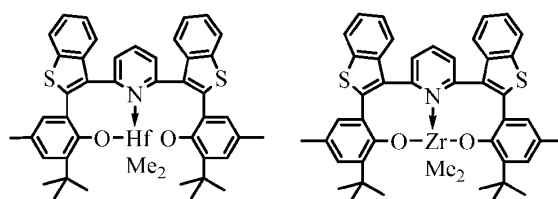
Complex 32



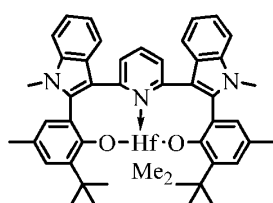
Complex 33



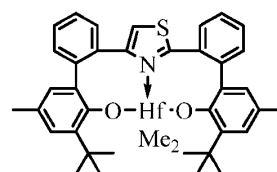
Complex 34



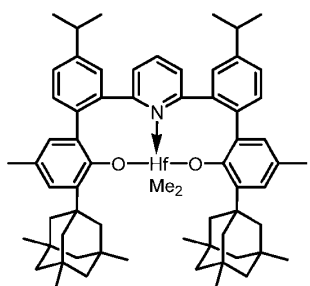
Complex 37



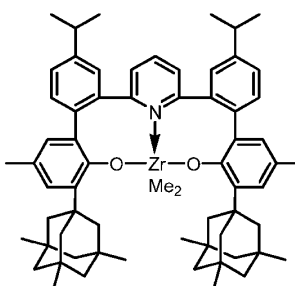
Complex 38



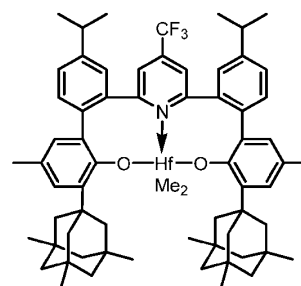
Complex 39



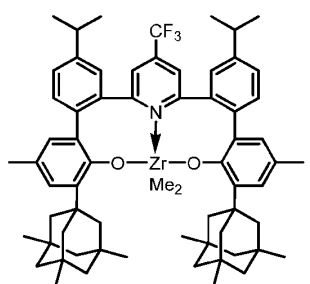
Complex 40



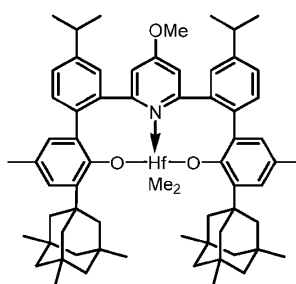
Complex 41



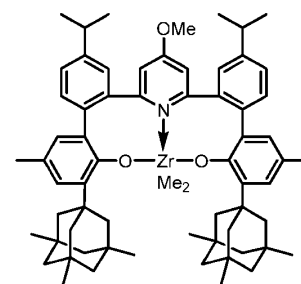
Complex 42



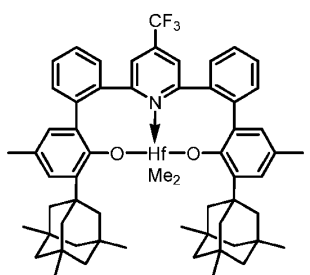
Complex 43



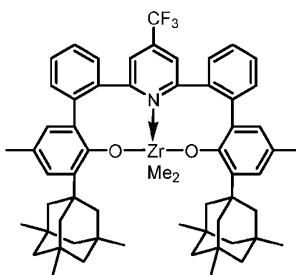
Complex 44



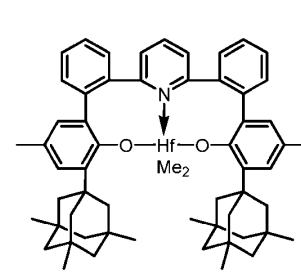
Complex 45



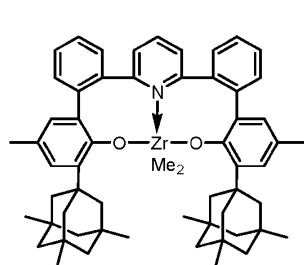
Complex 46



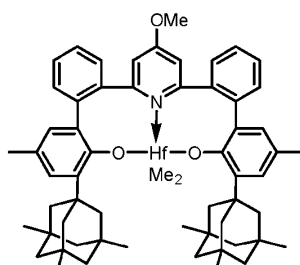
Complex 47



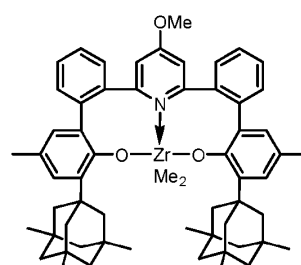
Complex 48



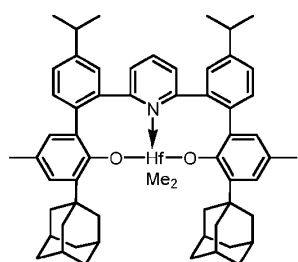
Complex 49



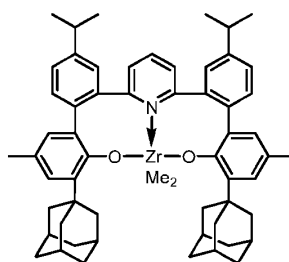
Complex 50



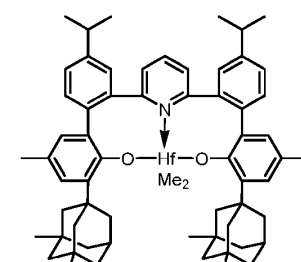
Complex 51



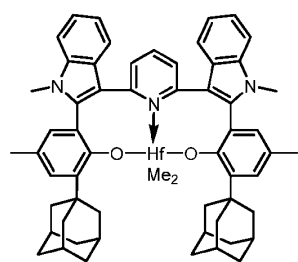
Complex 52



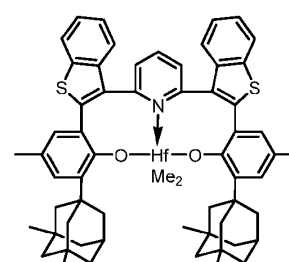
Complex 53



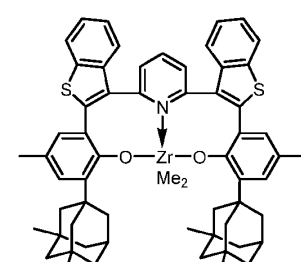
Complex 54



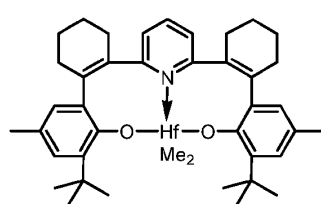
Complex 56



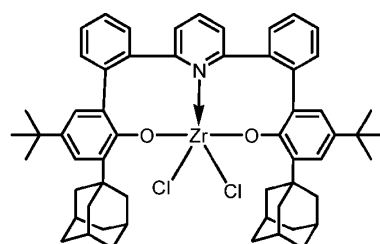
Complex 57



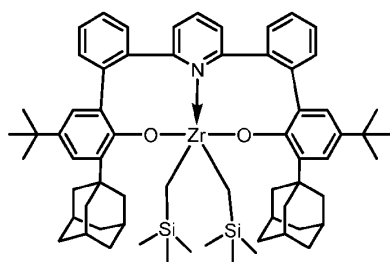
Complex 58



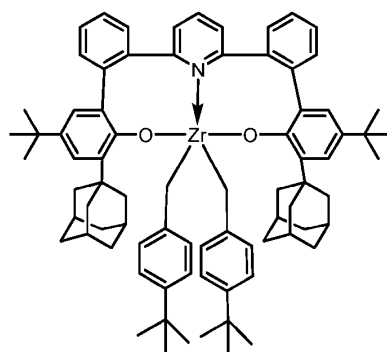
Complex 59



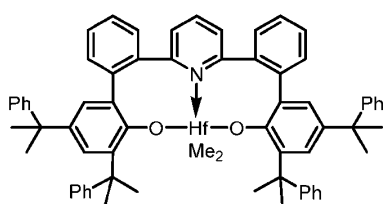
Complex 60



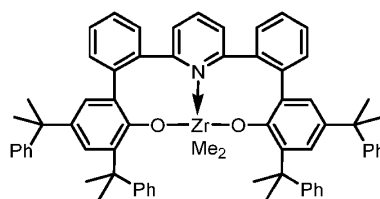
Complex 62



Complex 63

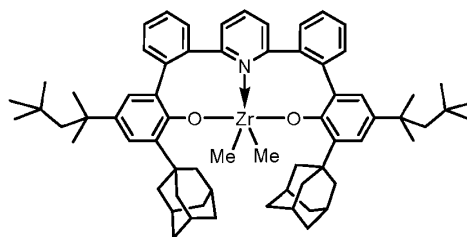


Complex 64



Complex 65

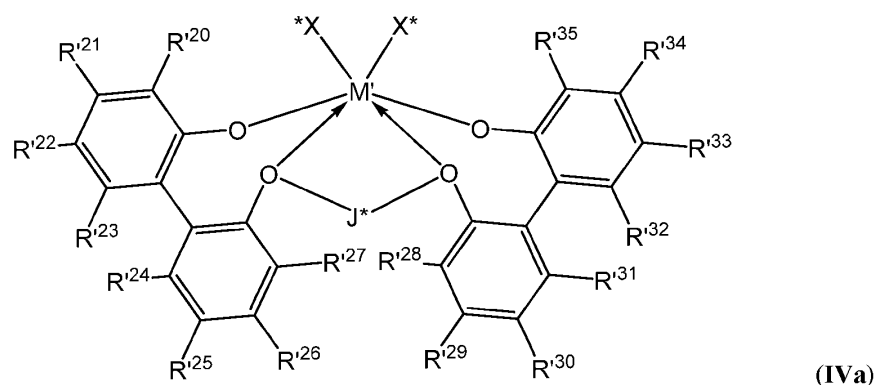
and



Complex 66

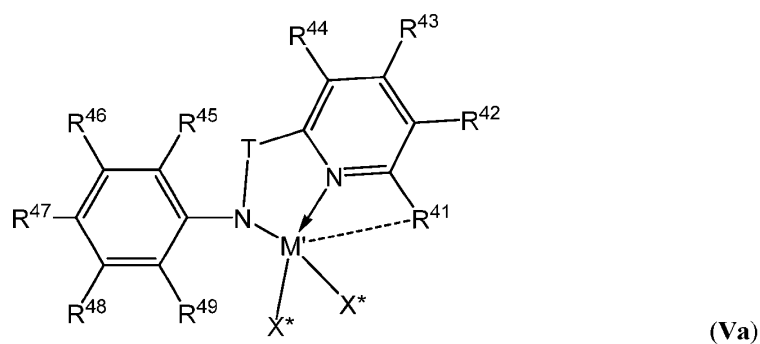
24. A process to polymerize olefins, the process comprising introducing one or more olefins with the catalyst system of any of claims 14 to 23 and obtaining a polymer.

25. The catalyst system of claim 12, wherein the catalyst compound is represented by Formula (IVa):



wherein: (1) J* of Formula (IVa) is a divalent bridging group comprising C, Si, or both; (2) M' of Formula (IVa) is a group 4 metal; (3) O of Formula (IVa) is oxygen; (4) each X* of Formula (IVa) is independently a univalent anionic ligand, or two X*s are joined and bound to the metal atom to form a metallocycle ring, or two X*s are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand; and (5) each of R'²⁰, R'²¹, R'²², R'²³, R'²⁴, R'²⁵, R'²⁶, R'²⁷, R'²⁸, R'²⁹, R'³⁰, R'³¹, R'³², R'³³, R'³⁴, R'³⁵ of Formula (IVa) is independently hydrogen, halo, C₁-C₅₀ hydrocarbyl, substituted hydrocarbyl, halocarbyl or substituted halocarbyl.

26. The catalyst system of claim 14, wherein the catalyst compound is represented by Formula (Va):



wherein (1) M' of Formula (Va) is a group 4 metal, (2) T of Formula (Va) is a divalent bridging group comprising carbon or silicon; (3) each X* of Formula (Va) is independently a univalent anionic ligand, or two X*s are joined and bound to the metal atom to form a metallocycle ring, or two X*s are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand; (4) N of Formula (Va) is nitrogen; (5) each of R'⁴¹, R'⁴², R'⁴³, and R'⁴⁴ of Formula (Va) is independently hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl or silyl group, or one or more adjacent R'⁴¹-R'⁴⁴ may be joined together to form a fused ring

derivative; each of R^{45} , R^{46} , R^{47} , R^{48} , or R^{49} of Formula (Va) is independently hydrogen, or C_1 - C_{10} alkyl; T of Formula (Va) is $CR^{50}R^{51}$ wherein each of R^{50} and R^{51} is independently hydrogen, halogen, a C_1 - C_{20} hydrocarbyl.

27. A catalyst system of claim 14, wherein the catalyst compound is represented by Formula (II) or (III):



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

M is Ti, Zr, Hf

n is 0 or 1;

T is an optional bridging group, and when T is present, the catalyst represented can be in a racemic or a meso form;

L_1 and L_2 are independently cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, optionally substituted, that are each bonded to M, or L_1 and L_2 are independently cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, which are optionally substituted, in which any two adjacent substituents on L^1 and L^2 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;

q is 1 or 2;

R' is a cyclic, linear, or branched C_1 to C_{40} alkyl or substituted alkyl group;

X_1 and X_2 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 X_1 and X_2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms.