POLYOLEFIN CATALYSTS AND METHODS THEREOF

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CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to US Provisional Application No. 63/561,632 filed March 5, 2024, the disclosure of which is incorporated herein by reference.

FIELD

[0002] The present disclosure relates to catalyst compounds, catalyst systems containing such compounds, and uses thereof.

BACKGROUND

[0003] Polyolefin materials are widely implemented within industrial and commercial applications. Such materials have become ubiquitous in society in various forms, ranging from plastic containers and foodstuffs to various components of automobile and engineering equipment. The wide range of use and application of polyolefin materials highlights the financial incentive to produce these polymers in mass via an industrially scalable process.

[0004] A commonly associated polymer within the field of polyolefin materials is polyethylene (PE). Different methods of PE synthesis can be specifically designed to induce the material to exhibit different macromolecular characteristics and physical properties, as exemplified in the production of low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE). Additionally, various different polymerization methods can be expanded into other olefin monomer systems to produce polymers having various chemical compositions, molecular weights, polydispersities, tacticities, crystallinities, physical properties, and thermal properties.

[0005] In some cases, it is desirable to controllably tune and/or control various chemical, macromolecular, and physical properties of polyolefin materials to satisfy a particular purpose. As such, large amounts of interest and investigation have been directed towards developing new catalyst systems to be implemented for polyolefin synthesis. Such catalyst systems typically comprise, at least, a catalyst complex and an activator compound. When implemented into polyolefin synthesis, the components of the catalyst system should be carefully considered

as they can influence the various properties of the formed polyolefin. In addition, aspects of the catalyst composition (*e.g.*, catalyst activity, chemical tolerance, thermal stability, chemical stability, and shelf life) should be considered when developing new olefin polymerization catalyst systems.

[0006] Typically, in the synthesis of polyolefins, olefin monomers are brought into contact with the catalyst system via one or more gas phase, solution phase, and bulk phase polymerization processes. However, it should be considered that the polymerization implemented be industrially feasible, in that large quantities of polyolefins are produced at elevated rates of production (*e.g.*, catalyst activity). In addition, it can be desirable to produce polyolefins having higher molecular weights to satisfy physical property requirements related to an intended application.

[0007] While there exist reports of catalyst systems able to produce high molecular weight polyolefins, the polymeric materials produced often have high molecular weights accompanied with broad molecular weight distributions, and thus can often have processing difficulties due to hardness provided by a minor amount of very high molecular weight polymer component in the produced polyolefin product. Additionally, such catalyst systems often have low catalyst activity (*e.g.*, amount of polymer produce per a period of time).

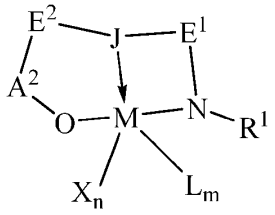
[0008] Thus, there is a need to develop new catalyst compounds and systems having high catalyst activity and the capability of forming high molecular weight polyolefins without adverse influence on material properties and processability.

[0009] References for citing in an Information Disclosure Statement (37 C.F.R. 1.97(h)): Baier, M. C., et al., *Angew. Chem. Int. Ed.* **2014**, *53*, 9722-9744.; US2020/0095349; Kulyabin, P. S., et al., *Chemistry – A European Journal*, **2019**, *25* (44), 10478-10489.; Hagadorn, J. R. et al., *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)*, **2011**, *52* (1); U.S. Pat. Nos. 5,041,584; 9,340,630; 8,404,880; 8,975,209; 5,447,895; 8,658,556.

SUMMARY

[0010] The present disclosure relates to catalyst compounds, catalyst systems containing such compounds, and uses thereof.

[0011] In some embodiments, a compound is represented by the formula:



wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

A^2 is selected from the group consisting of unsubstituted aryl, substituted aryl, unsubstituted heteroaryl, and substituted heteroaryl group;

J is a heterocyclic Lewis base;

E^1 is selected from the group consisting of unsubstituted hydrocarbyl, substituted hydrocarbyl, and unsubstituted or substituted silylcarbyl;

E^2 is selected from the group consisting of unsubstituted hydrocarbyl, substituted hydrocarbyl, and unsubstituted or substituted silylcarbyl;

J and E^2 are optionally fused to form one or more unsubstituted hydrocarbyl rings, substituted hydrocarbyl rings, unsubstituted heterocyclic rings, or substituted heterocyclic rings;

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 4 or less;

R^1 is selected from the group consisting of unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and unsubstituted or substituted C_1-C_{40} heteroatom-containing group;

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

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

[0012] In some embodiments, a catalyst system includes an activator and a catalyst compound of the present disclosure.

[0013] In some embodiments, a polymerization process includes introducing one or more C_2-C_{20} alpha-olefin monomers and a catalyst system into a reactor, the catalyst system including an activator and a catalyst compound of the present disclosure.

DETAILED DESCRIPTION

[0014] The present disclosure relates to catalyst compounds, catalyst systems containing such compounds, and uses thereof.

[0015] Catalyst compounds, and catalyst systems containing such compounds, of the present disclosure provide high catalyst activity, and polyolefins formed using such catalyst compounds, and systems thereof, can have high molecular weight values.

[0016] Catalyst compounds of the present disclosure are phenolate-heterocyclic-amido ligands coordinated to group 4 transition metals. The complexes contain a tridentate ligand featuring a central neutral heterocyclic donor group, an anionic phenolate donor, and an anionic amido donor. The tridentate ligand coordinates to the metal center to form five-membered and seven-membered rings. These complexes have been discovered to be useful as catalyst compounds for the polymerization of olefins. For example, catalyst compounds of the present disclosure can provide high molecular weight polymers at high catalyst activity useful for commercial production.

[0017] In some embodiments, the present disclosure provides a catalyst system comprising an activator and a catalyst of the present disclosure.

[0018] In some embodiments, the present disclosure provides a polymerization process comprising a) introducing one or more olefin monomers with a catalyst system comprising: i) an activator and ii) a catalyst compound of the present disclosure.

[0019] In some embodiments, the present disclosure provides a polyolefin formed by a catalyst system and or method of the present disclosure.

[0020] In some embodiments, the present disclosure provides for a process for the production of an ethylene alpha-olefin copolymer comprising polymerizing ethylene and (optionally) at least one C_3-C_{20} alpha-olefin by contacting the ethylene and (optionally) the at least one C_3-C_{20} alpha-olefin with a catalyst system, for example in at least one continuous stirred tank reactor or loop reactor.

[0021] In some embodiments, the present disclosure provides for a process for the production of a propylene alpha-olefin copolymer comprising polymerizing propylene and (optionally) at least one ethylene and/or (optionally) C_4-C_{20} alpha-olefin by contacting the propylene and the at least one ethylene and/or at least one C_4-C_{20} alpha-olefin with a catalyst system, for example in at least one continuous stirred tank reactor or loop reactor.

Definitions

[0022] 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 3 metal" is an element from group 4 of the Periodic Table, *e.g.* Sc, Y, or Nd.

[0023] Room temperature is about 23°C unless otherwise noted.

[0024] 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

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 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 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.

[0025] Ethylene shall be considered an α-olefin.

[0026] Unless otherwise specified, the term "C_n" means hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer.

[0027] 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 C_1-C_{50} alkyl group refers to an alkyl group comprising carbon atoms at a total number thereof in the range from 1 to 50.

[0028] The terms "group," "radical," and "substituent" may be used interchangeably.

[0029] 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 C_1-C_{100} radicals that may be linear, branched, or cyclic or combinations thereof, and when cyclic, aromatic or non-aromatic. Combinations of linear, branched and/or cyclic groups are included. 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, pentyl, iso-amyl, hexyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like, alkyenyl groups such as ethenyl, propenyl, and the like, aryl groups, such as phenyl, tolyl, benzyl, naphthalenyl, and the like, cycloalkyl groups such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl,

norbornyl, adamantanyl, substituted adamantanyl such as 3-methyladamantanyl or 3,5-dimethyladamantanyl, fluorenyl, substituted fluorenyl such as 9-methylfluorenyl. When two adjacent or geminal hydrocarbyls are joined together, they can form a hydrocarbyl ring.

[0030] 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, 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 least one heteroatom has been inserted within a hydrocarbyl ring. When two adjacent or geminal substituted hydrocarbyls or one substituted hydrocarbyl and one hydrocarbyl are joined together, they can form a substituted hydrocarbyl ring. A substituted hydrocarbyl ring by definition can include heterocyclic and substituted heterocyclic rings.

[0031] 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, -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. A substituted hydrocarbyl, alternatively, can have at least one heteroatom or heteroatom group inserted between two adjacent carbon atoms of the hydrocarbyl group. For example, -NR*-, -O-, -Se-, -Te-, -PR*-, -AsR*-, -SbR*-, -S, -BR*-, -SiR^*_2-, -GeR^*_2-, -SnR^*_2-, -PbR^*_2- and the like, may be inserted between two carbon atoms. R* is as defined as above.

[0032] "Heteroatom containing groups" when used to define a substituent refer to groups where the heteroatom is directly bonded to the substrate. For example, when a heteroatom containing group is bonded to an aryl ring, the heteroatom is directly bonded the aryl ring. The term heteroatom containing group and functional group may be used interchangeably.

[0033] An unsubstituted hydrocarbyl contains only carbon and hydrogen atoms. The terms hydrocarbyl and unsubstituted hydrocarbyl are used interchangeably.

[0034] Silylcarbyl radicals (also called silylcarbyls) are groups in which the silyl functionality is bonded directly to the indicated atom or atoms. Examples when bonded to one atom include SiH_3, SiH_2R^*, $SiHR^*_2$, SiR^*_3, $SiH_2(OR^*)$, $SiH(OR^*)_2$, $Si(OR^*)_3$, $SiH_2(NR^*_2)$, $SiH(NR^*_2)_2$, $Si(NR^*_2)_3$, and the like where R* is independently a hydrocarbyl and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Examples when bonded to two atoms include SiH_2, $SiHR^*$, SiR^*_2, $SiR^*(OR^*)$, $SiH(OR^*)$, $Si(OR^*)_2$, $SiH(NR^*_2)$, $SiR^*(NR^*_2)$, $Si(NR^*_2)_2$, and the like where R* is as defined as above.

[0035] The term "aryl" or "aryl group" means an aromatic ring including 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, and includes variants thereof, such as pyridyl, 4-methylpyridyl, furanyl, benzofuranly, thiophenyl, benzo[b]thiophenyl, and the like. 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 aryl also includes substituted aryls, and the term heteroaryl includes substituted heteroaryls.

[0036] The term "substituted aryl," means an aryl group having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group. The term "substituted heteroaryl," means an heteroaryl group having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group. Heteroaryl groups are also referred to as heterocyclic groups.

[0037] The term "heteroatom" refers to any group 13-17 element, excluding carbon. A heteroatom may include B, Si, Ge, Sn, N, P, As, O, S, Se, Te, F, Cl, Br, and I. The term "heteroatom-containing group" may include the aforementioned elements with hydrogens attached, such as BH, BH_2, SiH_2, OH, NH, NH_2, etc. or a heteroatom-containing group that has one or more hydrogen atoms replaced by a hydrocarbyl or substituted hydrocarbyl group(s) such as BR', BR'_2, SiR'_2, OR', NR', NR'_2, etc. where R' represents the hydrocarbyl or substituted hydrocarbyl groups.

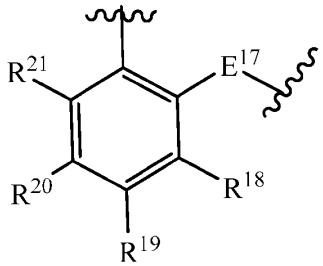
[0038] The term "heterocyclic Lewis base" refers to Lewis bases that are also heterocycles. Examples of heterocyclic Lewis bases may include pyridine, imidazole, thiazole, and furan.

[0039] The terms "alkyl radical" and "alkyl" are used interchangeably throughout this disclosure. For purposes of this disclosure, "alkyl radical" is defined to be C_1-C_{100} alkyls that may be linear, branched, or cyclic, or combinations thereof. 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, methylcyclohexyl, and the like. Substituted alkyl radicals are radicals in which at least one hydrogen atom of the alkyl radical has been substituted with at least a non-hydrogen group, such as a 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.

[0040] 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).

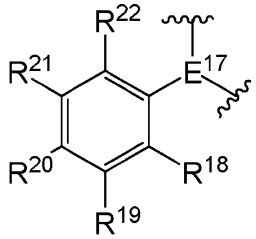
[0041] A " phenolate" is a phenolate group where optionally one, two, three, four or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a heteroatom or heteroatom-containing group, such as halogen (such as Br, 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-). For example, a "substituted phenolate" group in the catalyst compounds described herein is represented by the formula:



where R^{18} is hydrogen, C_1-C_{40} hydrocarbyl (such as C_1-C_{40} alkyl) or C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, E^{17} is oxygen, sulfur, and each

of R^{19}, R^{20}, and R^{21} is independently selected from hydrogen, C_1-C_{40} hydrocarbyl (such as C_1-C_{40} alkyl) or C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or two or more of R^{18}, R^{19}, R^{20}, and R^{21} are joined together to form a C_4-C_{62} 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.

[0042] An "amido" is an aniline group where optionally 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 aniline group (Ph-N(R^)- group, where R^ is hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom or a heteroatom-containing group). For example, a "substituted amido" group in the catalyst compounds described herein is represented by the formula:



where R^{18} is hydrogen, C_1-C_{40} hydrocarbyl (such as C_1-C_{40} alkyl) or C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, E^{17} is nitrogen, and each of R^{19}, R^{20}, R^{21}, and R^{22} is independently selected from hydrogen, C_1-C_{40} hydrocarbyl (such as C_1-C_{40} alkyl) or C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or two or more of R^{18}, R^{19}, R^{20}, R^{21}, and R^{22} are joined together to form a C_4-C_{62} cyclic or polycyclic ring structure, or a combination thereof, and the wavy lines show where the substituted amido group forms bonds to the rest of the catalyst compound.

[0043] 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.

[0044] A heterocyclic ring, also referred to as a heterocycle, is a ring having a heteroatom in the ring structure as opposed to a "heteroatom-substituted ring" where a hydrogen on a ring

atom is replaced with a heteroatom. For example, tetrahydrofuran is a heterocyclic ring and 4-N,N-dimethylamino-phenyl is a heteroatom substituted ring. 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.

[0045] 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}).

[0046] The following abbreviations may be used herein: Me is methyl, MAO is methylalumoxane, THF is tetrahydrofuran, RT is room temperature (and is 23°C unless otherwise indicated), tol is toluene, Cp is cyclopentadienyl, NMR is nuclear magnetic resonance, and TMA is trimethylaluminum.

[0047] A "catalyst system" is a combination of at least one catalyst compound, an activator, an optional coactivator, and an optional support material. 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.

[0048] 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.

[0049] 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, aryloxide, alkyl, alkenyl, thiolate, carboxylate, amido, benzyl, hydrido, amidinate, amidate, and phenyl. Two anionic donors may be joined to form a dianionic group.

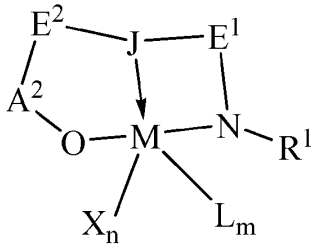
[0050] A "neutral Lewis base" or "neutral donor group" is an uncharged (neutral) group which donates one or more pairs of electrons to a metal ion. Non-limiting examples of neutral Lewis bases include ethers, thioethers, amines, phosphines, ethyl ether, tetrahydrofuran, dimethylsulfide, triethylamine, pyridine, alkenes, alkynes, alenes, and carbenes. Lewis bases may be joined together to form bidentate or tridentate Lewis bases.

[0051] 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, C_1-C_{40} hydrocarbyl, C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, and Ph is optionally substituted phenyl.

[0052] Lanthanide metals (La-Lu), include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

Catalyst Compounds

[0053] In some embodiments, a catalyst can be represented by Formula **(I)**:



(I)

wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

A^2 is selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl group;

J is a heterocyclic Lewis base;

E^1 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and unsubstituted or substituted silylcarbyl;

E^2 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and unsubstituted or substituted silylcarbyl, wherein J and E^2 are optionally joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings;

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;

R^1 is selected from the group consisting of unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and unsubstituted or substituted C_1-C_{40} heteroatom-containing groups;

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

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

[0054] In at least one embodiment, the catalyst compounds represented by Formula **(I)** features one seven-membered and one five-membered metallocycle rings. The seven-membered metallocycle ring contains the atoms from the metal M, an oxygen atom (*e.g.*, part of a group, such as phenolate), two atoms of the aryl, substituted aryl, heteroaryl or substituted heteroaryl group A^2, one atom of the hydrocarbyl, substituted hydrocarbyl or silylcarbyl group E^2, and two atoms from the bridging Lewis base group J. The five-membered metallocycle ring contains the atoms from the metal M, a nitrogen, an atom of the hydrocarbyl, substituted hydrocarbyl or silylcarbyl group E^1, and two atoms from the bridging Lewis base group J.

[0055] In some embodiments, the metal M is a group 4 metal, such as zirconium or hafnium.

[0056] In at least one embodiment, the catalyst compounds represented by Formula **(I)** features one seven-membered and one five-membered metallocycle rings. The seven-membered metallocycle ring contain the atoms from the metal M, a phenolate oxygen, two atoms of the aryl group A^2, one atom of the hydrocarbyl or substituted hydrocarbyl group E^2, and two atoms from the bridging Lewis base group J. The five-membered metallocycle ring contains the atoms from the metal M, a nitrogen (from the amido group), an atom from the hydrocarbyl or substituted hydrocarbyl group E^1, and two atoms from the bridging Lewis base group J.

[0057] In at least one embodiment, each L of the catalysts represented by Formula **(I)** can be independently selected from the group consisting of ethers, amines, phosphines, thioethers, esters, Et_2O, MeO^tBu, Et_3N, $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide. In at least one embodiment, m of the catalysts represented by Formula **(I)** is 0. In at least one embodiment, each X of the catalysts represented by Formula **(I)** can be independently selected from the group consisting of methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate, dimethylamido, diethylamido, dipropylamido, and diisopropylamido, such as chloro, such as methyl. In at least one embodiment, n of the catalysts represented by Formula **(I)** is 2.

[0058] In some embodiments, X is selected from methyl or benzyl, n is 2, and m is zero.

[0059] In some embodiments, E^1 can be selected from the group consisting of $C(R^{15})(R^{16})$ and $Si(R^{15})(R^{16})$. Each of R^{15} and R^{16} may be independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and C_1-C_{40} heteroatom containing group, or R^{15} and R^{16} may be joined to form one or more C_3-C_{20} hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0060] In some embodiments, E^2 can be selected from the group consisting of $C(R^{25})(R^{26})$, $Si(R^{25})(R^{26})$, and $C=C(R^{25})(R^{26})$. Each of R^{25} and R^{26} may be independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and a C_1-C_{40} heteroatom containing group, or R^{25} and R^{26} may be joined to form one or more C_3-C_{20} hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0061] In some embodiments, E^1 and E^2 are independently selected from $-CH_2$, $-CMe_2$, $-CEt_2$, -CHMe, -CHEt, $-CPh_2$, -CHPh, $-SiMe_2$, $-SiEt_2$, $-SiPh_2$, and -SiMePh, such as $-CH_2$.

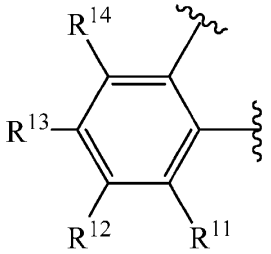
[0062] In some embodiments, E^1 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, and E^2 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, $C=CH_2$, $C=CMe_2$, $C=CEt_2$, $C=CPh_2$, C=CHMe, C=CHEt, and C=CHPh.

[0063] In some embodiments, E^1 is CH_2 and E^2 is selected from CH_2 and $C=CMe_2$.

[0064] In at least one embodiment, R^1 is selected from a substituted or unsubstituted C_6-C_{40} aryl such as a phenyl group, a methylphenyl group, a dimethylphenyl group, a trimethylphenyl group, a tetramethylphenyl group, a pentamethylphenyl group, an ethylphenyl group, a diethylphenyl group, a triethylphenyl group, an isopropylphenyl group, a diisopropylphenyl group, a triisopropylphenyl group, a *tert*-butylphenyl group, a di-*tert*-butylphenyl group, a tri-*tert*-butylphenyl group, a methylisopropylphenyl group, a methyl-*tert*-butlyphenyl group, an ethylisopropylphenyl group, an ethyl-*tert*-butylphenyl group, a methylnaphthalenyl group, an ethylnaphthalenyl group, an isopropylnaphthalenyl group, and a *tert*-butylnaphthalenyl group. Alternatively, R^1 is selected from the group consisting of methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0065] In some embodiments, R^1 is selected from 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and 2,6-diisopropyl-4-methylphenyl.

[0066] In at least one embodiment, A^2 of Formula (**I**) is represented by the formula:



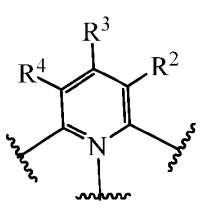
wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and a substituted or unsubstituted C_1-C_{40} heteroatom-containing group. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. In some embodiments, R^{11} is a C_5-C_{30} cycloalkyl, or C_5-C_{30} substituted cycloalkyl, such as cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, fluorenyl, 9-methylfluorenyl, adamantanyl, or substituted adamantanyl. In some embodiments, R^{11} can be C_1-C_{10} alkyl, such as *tert*-butyl, *tert*-pentyl, and *tert*-octyl (2,4,4-trimethylpent-2-yl), or R^{11} can be a heteroatom-containing group such as trimethylsilyl, carbazol-9-yl or substituted carbazol-9-yl. Alternatively, R^{11} can be aryl, such as defined for R^1. In some embodiments, R^{13} is a C_1-C_{20} hydrocarbyl such as for example methyl, *tert*-butyl, n-octyl and the like.

[0067] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, substituted adamantanyl, carbazol-9-yl, substituted carbazol-9-yl, fluoren-9-yl, substituted fluoren-9-yl, phenyl, and substituted phenyl.

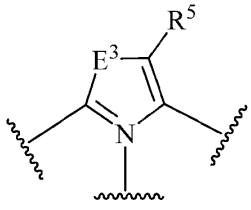
[0068] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, 3-methyladamantan-1-yl, 3,5-dimethyladamantan-1-yl, carbazol-9-yl 2,7-di-tert-butylcarbazol-9-yl, fluoren-9-yl, 9-methylfluoren-9-yl, phenyl, 3,5-di-tert-butylphenyl, 3,5-di-isopropylphenyl, 3,5-dimethylphenyl.

[0069] In some embodiments, R^{13} is selected from methyl or *tert*-butyl.

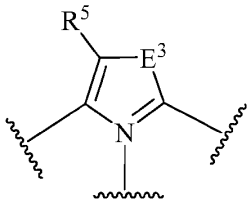
[0070] In some embodiments, J of Formula (**I**) can be represented by the formula:



(IA) or



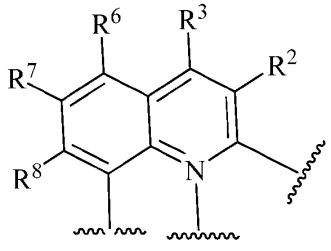
(IB) or



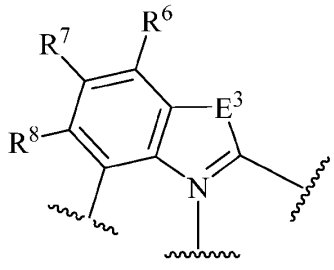
(IC)

wherein E^3 is selected from the group consisting of O, S, and $N(R^{10})$, and each of R^2, R^3, R^4, R^5 and R^{10} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and C_1-C_{40} heteroatom-containing group, or one or more of R^2 and R^3 or R^3 and R^4 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings. In at least one embodiment, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl. In at least one embodiment, E^3 can be selected from group 16 atoms (*e.g.*, sulfur (such as J = thiazole); oxygen (such as J = oxazole)) or $N(R^{10})$, where R^{10} is hydrogen or C_1-C_{10} hydrocarbyl, C_1-C_{10} substituted hydrocarbyl, a heteroatom, or a C_1-C_{10} heteroatom-containing group). In at least one embodiment, J of Formula **(I)** has the structure of **(IA)** above.

[0071] In some embodiments, J and E^2 of Formula **(I)** are joined to form a ring represented by the formulae:



(1D) or

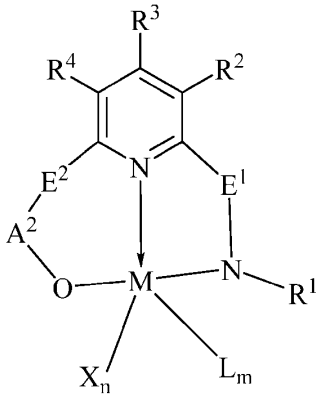


(1E)

wherein E^3 is selected from the group consisting of O, S, and $N(R^{10})$, wherein each of R^2, R^3, R^6, R^7, R^8, and R^{10} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or one or more of R^6 and R^7 or R^7 and R^8 or R^2 and R^3 or R^3 and R^6 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and

where substitutions on the ring can join to form additional rings. In at least one embodiment, each of R^2, R^3, R^6, R^7, R^8, and R^{10} is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^2, R^3, R^6, R^7, R^8, and R^{10} is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0072] In some embodiments, a catalyst can be represented by Formula (**II**):



(II)

wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

A^2 is selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl group;

E^1 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and unsubstituted or substituted silylcarbyl;

E^2 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and unsubstituted or substituted silylcarbyl, wherein E^2 is optionally fused with the Lewis base to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings;

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;

R^1 is selected from the group consisting of unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing groups;

each R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group;

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

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

[0073] In at least one embodiment, the catalyst compounds represented by Formula **(II)** features one seven-membered and one five-membered metallocycle ring. The seven-membered metallocycle ring contain the atoms from the metal M, a phenolate oxygen, two atoms of the aryl or substituted aryl group A^2, one atom of the hydrocarbyl or substituted hydrocarbyl group E^2, and two atoms from the bridging Lewis base. The five-membered metallocycle ring contains the atoms from the metal M, a nitrogen, an atom from the hydrocarbyl or substituted hydrocarbyl group E^1, and two atoms from the bridging Lewis base.

[0074] In some embodiments, the metal M is a group 4 metal, such as zirconium or hafnium.

[0075] In at least one embodiment, each L of the catalysts represented by Formula **(II)** can be independently selected from the group consisting of ethers, amines, phosphines, thioethers, esters, Et_2O, MeO^tBu, Et_3N, $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide. In at least one embodiment, m of the catalysts represented by Formula **(II)** is 0. In at least one embodiment, each X the catalysts represented by Formula **(II)** can be independently selected from the group consisting of methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate, dimethylamido, diethylamido, dipropylamido, and diisopropylamido, such as chloro, such as methyl. In at least one embodiment, n of the catalysts represented by Formula **(II)** is 2.

[0076] In some embodiments, X is selected from methyl, or benzyl, n is 2, and m is zero.

[0077] In some embodiments, E^1 can be selected from the group consisting of $C(R^{15})(R^{16})$ and $Si(R^{15})(R^{16})$. Each of R^{15} and R^{16} may be independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or R^{15} and R^{16} may be joined to form one or more C_3-C_{20} alkyl groups, hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0078] In some embodiments, E^2 can be selected from the group consisting of $C(R^{25})(R^{26})$, $Si(R^{25})(R^{26})$, and $C{=}C(R^{25})(R^{26})$. Each of R^{25} and R^{26} may be independently selected from the

group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and C_1-C_{40} heteroatom-containing group, or R^{25} and R^{26} may be joined to form one or more C_3-C_{20} alkyl groups, hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0079] In some embodiments, E^1 and E^2 are independently selected from $-CH_2$, $-CMe_2$, $-CEt_2$, -CHMe, -CHEt, $-CPh_2$, -CHPh, $-SiMe_2$, $-SiEt_2$, $-SiPh_2$, -SiMePh, such as $-CH_2$.

[0080] In some embodiments, E^1 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, and E^2 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, $C{=}CH_2$, $C{=}CMe_2$, $C{=}CEt_2$, $C{=}CPh_2$, C=CHMe, C=CHEt, and C=CHPh.

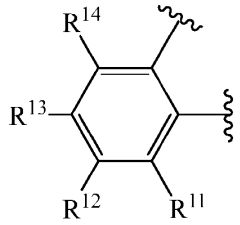
[0081] In some embodiments, E^1 is CH_2 and E^2 is selected from CH_2 and $C{=}CMe_2$.

[0082] In at least one embodiment, R^1 is selected from a substituted or unsubstituted C_6-C_{40} aryl, such as a phenyl group, methylphenyl group, a dimethylphenyl group, a trimethylphenyl group, a tetramethylphenyl group, a pentamethylphenyl group, an ethylphenyl group, a diethylphenyl group, a triethylphenyl group, an isopropylphenyl group, a diisopropylphenyl group, a triisopropylphenyl group, a *tert*-butylphenyl group, a di-*tert*-butylphenyl group, a tri-*tert*-butylphenyl group, a methylisopropylphenyl group, a methyl-*tert*-butlyphenyl group, an ethylisopropylphenyl group, an ethyl-*tert*-butylphenyl group, a methylnaphthalenyl group, an ethylnaphthalenyl group, an isopropylnaphthalenyl group, and a *tert*-butylnaphthalenyl group. Alternatively, R^1 is selected from the group consisting of methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0083] In some embodiments, R^1 is selected from 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and 2,6-diisopropyl-4-methylphenyl.

[0084] In some embodiments, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and C_1-C_{40} heteroatom-containing group, or one or more of R^2 and R^3 or R^3 and R^4 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings. In at least one embodiment, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0085] In at least one embodiment, A^2 of Formula (**II**) is represented by the formula:



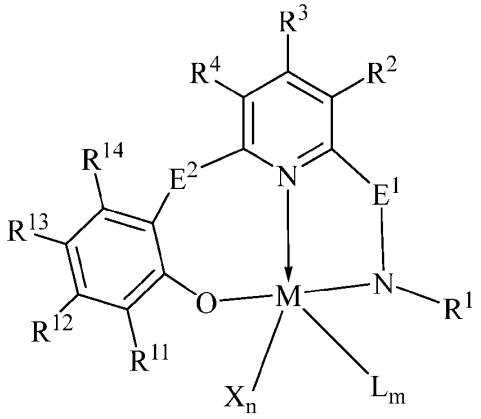
wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. In some embodiments, R^{11} is a C_5-C_{30} cycloalkyl, or C_5-C_{30} substituted cycloalkyl, such as cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, fluorenyl, 9-methylfluorenyl, adamantanyl, or substituted adamantanyl. In some embodiments, R^{11} can be C_1-C_{10} alkyl, such as *tert*-butyl, *tert*-pentyl, and *tert*-octyl (2,4,4-trimethylpent-2-yl), or R^{11} can be a heteroatom-containing group such as trimethylsilyl, carbazol-9-yl or substituted carbazol-9-yl. Alternatively, R^{11} can be aryl or substituted aryl, such as defined for R^1. In some embodiments, R^{13} is a C_1-C_{20} hydrocarbyl such as for example methyl, *tert*-butyl, n-octyl and the like.

[0086] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, substituted adamantanyl, carbazol-9-yl, substituted carbazol-9-yl, fluoren-9-yl, substituted fluoren-9-yl, phenyl, and substituted phenyl.

[0087] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, 3-methyladamantan-1-yl, 3,5-dimethyladamantan-1-yl, carbazol-9-yl 2,7-di-tert-butylcarbazol-9-yl, fluoren-9-yl, 9-methylfluoren-9-yl, phenyl, 3,5-di-tert-butylphenyl, 3,5-di-isopropylphenyl, 3,5-dimethylphenyl.

[0088] In some embodiments, R^{13} is selected from methyl or *tert*-butyl.

[0089] In some embodiments, a catalyst can be represented by Formula (**III**):



(III)

wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

E^1 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and silylcarbyl;

E^2 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and silylcarbyl, wherein E^2 is optionally fused with the Lewis base to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings;

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;

R^1 is selected from the group consisting of C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing groups;

each R^2, R^3, R^4, R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group;

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

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

[0090] In at least one embodiment, the catalyst compounds represented by Formula **(III)** features one seven-membered and one five-membered metallocycle rings. The seven-membered metallocycle ring contain the atoms from the metal M, a phenolate oxygen, two atoms of the aryl group, one atom of the hydrocarbyl or substituted hydrocarbyl group E^2, and

two atoms from the bridging Lewis base. The five-membered metallocycle ring contains the atoms from the metal M, a nitrogen, an atom from the hydrocarbyl or substituted hydrocarbyl group E^1, and two atoms from the bridging Lewis base.

[0091] In some embodiments, the metal M is a group 4 metal, such as zirconium or hafnium.

[0092] In at least one embodiment, each L of the catalysts represented by Formula **(III)** can be independently selected from the group consisting of ethers, amines, phosphines, thioethers, esters, Et_2O, MeO^tBu, Et_3N, $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide. In at least one embodiment, m of the catalysts represented by Formula **(III)** is 0. In at least one embodiment, each X the catalysts represented by Formula **(III)** can be independently selected from the group consisting of methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate, dimethylamido, diethylamido, dipropylamido, and diisopropylamido, such as chloro, such as methyl. In at least one embodiment, n of the catalysts represented by Formula **(III)** is 2.

[0093] In some embodiments, X is selected from methyl, or benzyl, n is 2, and m is zero.

[0094] In some embodiments, E^1 can be selected from the group consisting of $C(R^{15})(R^{16})$ and $Si(R^{15})(R^{16})$. Each of R^{15} and R^{16} may be independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or R^{15} and R^{16} may be joined to form one or more C_3-C_{20} alkyl groups, hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0095] In some embodiments, E^2 can be selected from the group consisting of $C(R^{25})(R^{26})$, $Si(R^{25})(R^{26})$, and $C{=}C(R^{25})(R^{26})$. Each of R^{25} and R^{26} may be independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or R^{25} and R^{26} may be joined to form one or more C_3-C_{20} alkyl groups, hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0096] In some embodiments, E^1 and E^2 are independently selected from $-CH_2$, $-CMe_2$, $-CEt_2$, -CHMe, -CHEt, $-CPh_2$, -CHPh, $-SiMe_2$, $-SiEt_2$, $-SiPh_2$, -SiMePh, such as $-CH_2$.

[0097] In some embodiments, E^1 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, and E^2 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, $C{=}CH_2$, $C{=}CMe_2$, $C{=}CEt_2$, $C{=}CPh_2$, C=CHMe,

C=CHEt, and C=CHPh.

[0098] In some embodiments, E^1 is CH_2 and E^2 is selected from CH_2 and $C{=}CMe_2$.

[0099] In at least one embodiment, R^1 is selected from a substituted or unsubstituted C_6-C_{40} aryl, such as a phenyl group, methylphenyl group, a dimethylphenyl group, a trimethylphenyl group, a tetramethylphenyl group, a pentamethylphenyl group, an ethylphenyl group, a diethylphenyl group, a triethylphenyl group, an isopropylphenyl group, a diisopropylphenyl group, a triisopropylphenyl group, a *tert*-butylphenyl group, a di-*tert*-butylphenyl group, a tri-*tert*-butylphenyl group, a methylisopropylphenyl group, a methyl-*tert*-butlyphenyl group, an ethylisopropylphenyl group, an ethyl-*tert*-butylphenyl group, a methylnaphthalenyl group, an ethylnaphthalenyl group, an isopropylnaphthalenyl group, and a *tert*-butylnaphthalenyl group. Alternatively, R^1 is selected from the group consisting of methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0100] In some embodiments, R^1 is selected from 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and 2,6-diisopropyl-4-methylphenyl.

[0101] In some embodiments, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or one or more of R^2 and R^3 or R^3 and R^4 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings. In at least one embodiment, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^2, R^3, and R^4 is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0102] In some embodiments, each R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, substituted or unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and a C_1-C_{40} heteroatom-containing group. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. In some embodiments, R^{11} is a C_5-C_{30} cycloalkyl, or C_5-C_{30} substituted cycloalkyl, such as cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, fluorenyl, 9-methylfluorenyl, adamantanyl, or substituted adamantanyl. In some embodiments, R^{11} can be C_1-C_{10} alkyl, such as *tert*-butyl,

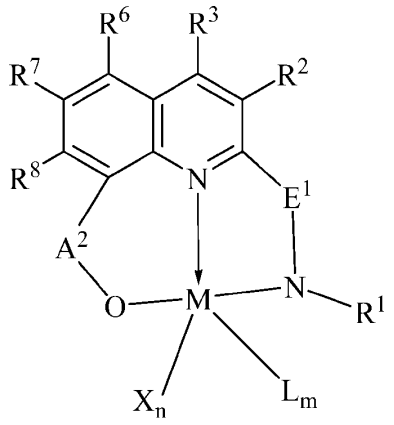
tert-pentyl, and *tert*-octyl (2,4,4-trimethylpent-2-yl), or R^{11} can be a heteroatom-containing group such as trimethylsilyl, carbazol-9-yl or substituted carbazol-9-yl. Alternatively, R^{11} can be aryl or substituted aryl, such as defined for R^1. In some embodiments, R^{13} is a C_1-C_{20} hydrocarbyl such as for example methyl, *tert*-butyl, n-octyl and the like.

[0103] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, substituted adamantanyl, carbazol-9-yl, substituted carbazol-9-yl, fluoren-9-yl, substituted fluoren-9-yl, phenyl, and substituted phenyl.

[0104] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, 3-methyladamantan-1-yl, 3,5-dimethyladamantan-1-yl, carbazol-9-yl 2,7-di-tert-butylcarbazol-9-yl, fluoren-9-yl, 9-methylfluoren-9-yl, phenyl, 3,5-di-tert-butylphenyl, 3,5-di-isopropylphenyl, and 3,5-dimethylphenyl.

[0105] In some embodiments, R^{13} is selected from methyl or *tert*-butyl.

[0106] In some embodiments, a catalyst can be represented by Formula (**IV**):



(**IV**)

wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

A^2 is selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl group;

E^1 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and substituted or unsubstituted silylcarbyl;

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;

R^1 is selected from the group consisting of C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing groups;

each R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, substituted or unsubstituted C_1-C_{40} heteroatom-containing group;

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

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

[0107] In at least one embodiment, the catalyst compounds represented by Formula **(IV)** features one seven-membered and one five-membered metallocycle rings. The seven-membered metallocycle ring contain the atoms from the metal M, a phenolate oxygen, two atoms of the aryl or substituted aryl group A^2, and three atoms from the bridging Lewis base fused with a hydrocarbyl or substituted hydrocarbyl group. The five-membered metallocycle ring contains the atoms from the metal M, a nitrogen, an atom from the hydrocarbyl or substituted hydrocarbyl group E^1, and two atoms from the bridging Lewis base.

[0108] In some embodiments, the metal M is a group 4 metal, such as zirconium or hafnium.

[0109] In at least one embodiment, each L of the catalysts represented by Formula **(IV)** can be independently selected from the group consisting of ethers, amines, phosphines, thioethers, esters, Et_2O, MeO^tBu, Et_3N, $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide. In at least one embodiment, m of the catalysts represented by Formula **(IV)** is 0. In at least one embodiment, each X of the catalysts represented by Formula **(IV)** can be independently selected from the group consisting of methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate, dimethylamido, diethylamido, dipropylamido, and diisopropylamido, such as chloro, such as methyl. In at least one embodiment, n of the catalysts represented by Formula **(IV)** is 2.

[0110] In some embodiments, X is selected from methyl, or benzyl, n is 2, and m is zero.

[0111] In some embodiments, E^1 can be selected from the group consisting of $C(R^{15})(R^{16})$ and $Si(R^{15})(R^{16})$. Each of R^{15} and R^{16} may be independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or R^{15} and R^{16} may be joined to form one or more C_3-C_{20} alkyl groups, hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

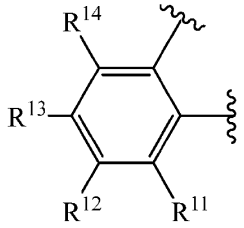
[0112] E^1 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, and is most preferably CH_2.

[0113] In at least one embodiment, R^1 is selected from a substituted or unsubstituted C_6-C_{40} aryl, such as a phenyl group, methylphenyl group, a dimethylphenyl group, a trimethylphenyl group, a tetramethylphenyl group, a pentamethylphenyl group, an ethylphenyl group, a diethylphenyl group, a triethylphenyl group, an isopropylphenyl group, a diisopropylphenyl group, a triisopropylphenyl group, a *tert*-butylphenyl group, a di-*tert*-butylphenyl group, a tri-*tert*-butylphenyl group, a methylisopropylphenyl group, a methyl-*tert*-butlyphenyl group, an ethylisopropylphenyl group, an ethyl-*tert*-butylphenyl group, a methylnaphthalenyl group, an ethylnaphthalenyl group, an isopropylnaphthalenyl group, and a *tert*-butylnaphthalenyl group. Alternatively, R^1 is selected from the group consisting of methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0114] In some embodiments, R^1 is selected from 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and 2,6-diisopropyl-4-methylphenyl.

[0115] In some embodiments, each of R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted heteroatom-containing group, or one or more of R^6 and R^7 or R^7 and R^8 or R^2 and R^3 or R^3 and R^6 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings. In at least one embodiment, each of R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0116] In some embodiment, A^2 of Formula (**IV**) is represented by the formula:



wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group. In at least one embodiment, each of R^{11},

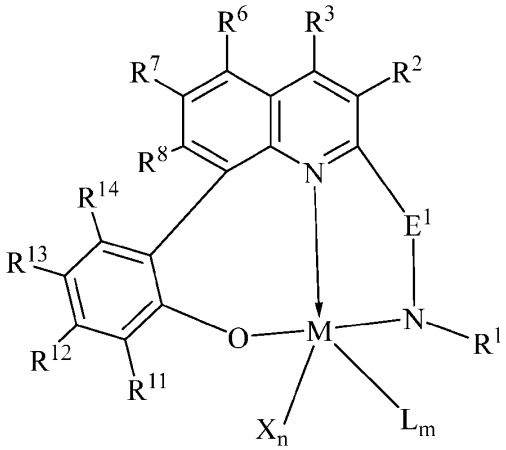
R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. In some embodiments, R^{11} is a C_5-C_{30} cycloalkyl, or C_5-C_{30} substituted cycloalkyl, such as cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, fluorenyl, 9-methylfluorenyl, adamantanyl, or substituted adamantanyl. In some embodiments, R^{11} can be C_1-C_{10} alkyl, such as *tert*-butyl, *tert*-pentyl, and *tert*-octyl (2,4,4-trimethylpent-2-yl), or R^{11} can be a heteroatom-containing group such as trimethylsilyl, carbazol-9-yl or substituted carbazol-9-yl. Alternatively, R^{11} can be aryl or substituted aryl, such as defined for R^1. In some embodiments, R^{13} is a C_1-C_{20} hydrocarbyl such as for example methyl, *tert*-butyl, n-octyl and the like.

[0117] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, substituted adamantanyl, carbazol-9-yl, substituted carbazol-9-yl, phenyl, or substituted phenyl.

[0118] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, 3-methyladamantan-1-yl, 3,5-dimethyladamantan-1-yl, carbazol-9-yl 2,7-di-tert-butylcarbazol-9-yl, fluoren-9-yl, 9-methylfluoren-9-yl, phenyl, 3,5-di-tert-butylphenyl, 3,5-di-isopropylphenyl, 3,5-dimethylphenyl.

[0119] In some embodiments, R^{13} is selected from methyl or *tert*-butyl.

[0120] In some embodiments, a catalyst can be represented by Formula (**V**):



(**V**)

wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

E^1 is selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, and substituted or unsubstituted silylcarbyl;

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;

R^1 is selected from the group consisting of C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing groups;

each R^2, R^3, R^6, R^7, R^8, R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group;

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

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

[0121] In at least one embodiment, the catalyst compounds represented by Formula (**V**) features one seven-membered and one five-membered metallocycle rings. The seven-membered metallocycle ring contain the atoms from the metal M, a phenolate oxygen, two atoms of the aryl group, and three atoms from the bridging Lewis base fused with a hydrocarbyl or substituted hydrocarbyl group. The five-membered metallocycle ring contains the atoms from the metal M, a nitrogen, an atom from the hydrocarbyl or substituted hydrocarbyl group E^1, and two atoms from the bridging Lewis base.

[0122] In some embodiments, the metal M is a group 4 metal, such as zirconium or hafnium.

[0123] In at least one embodiment, each L of the catalysts represented by Formula (**V**) can be independently selected from the group consisting of ethers, amines, phosphines, thioethers, esters, Et_2O, MeO^tBu, Et_3N, $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide. In at least one embodiment, m of the catalysts represented by Formula (**V**) is 0. In at least one embodiment, each X the catalysts represented by Formula (**V**) can be independently selected from the group consisting of methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate, dimethylamido, diethylamido, dipropylamido, and diisopropylamido, such as chloro, such as methyl. In at least one embodiment, n of the catalysts represented by Formula (**V**) is 2.

[0124] In some embodiments, X is selected from methyl, or benzyl, n is 2, and m is zero.

[0125] In some embodiments, E^1 can be selected from the group consisting of $C(R^{15})(R^{16})$ and $Si(R^{15})(R^{16})$. Each of R^{15} and R^{16} may be independently selected from the group consisting

of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and substituted or unsubstituted C_1-C_{40} heteroatom-containing group, or R^{15} and R^{16} may be joined to form one or more C_3-C_{20} alkyl groups, hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0126] E^1 is selected from CH_2, CMe_2, CEt_2, CHMe, CHEt, CPh_2, CHPh, $SiMe_2$, $SiEt_2$, $SiPh_2$, SiMePh, and is most preferably CH_2.

[0127] In at least one embodiment, R^1 is selected from a substituted or unsubstituted C_6-C_{40} aryl, such as a phenyl group, methylphenyl group, a dimethylphenyl group, a trimethylphenyl group, a tetramethylphenyl group, a pentamethylphenyl group, an ethylphenyl group, a diethylphenyl group, a triethylphenyl group, an isopropylphenyl group, a diisopropylphenyl group, a triisopropylphenyl group, a *tert*-butylphenyl group, a di-*tert*-butylphenyl group, a tri-*tert*-butylphenyl group, a methylisopropylphenyl group, a methyl-*tert*-butlyphenyl group, an ethylisopropylphenyl group, an ethyl-*tert*-butylphenyl group, a methylnaphthalenyl group, an ethylnaphthalenyl group, an isopropylnaphthalenyl group, and a *tert*-butylnaphthalenyl group. Alternatively, R^1 is selected from the group consisting of methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0128] In some embodiments, R^1 is selected from 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and 2,6-diisopropyl-4-methylphenyl.

[0129] In some embodiments, each of R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, and substituted or unsubstituted heteroatom-containing group, or one or more of R^6 and R^7 or R^7 and R^8 or R^2 and R^3 or R^3 and R^6 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings. In at least one embodiment, each of R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^2, R^3, R^6, R^7, and R^8 is independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.

[0130] In some embodiments, each R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and a substituted or unsubstituted heteroatom-containing group. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen and C_1-C_{10} alkyl. In at least one embodiment, each of R^{11}, R^{12}, R^{13}, and R^{14} is

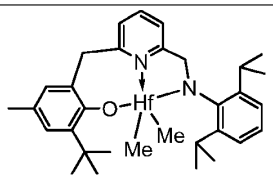
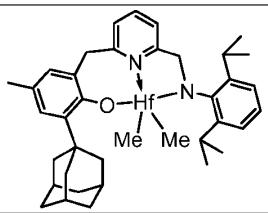
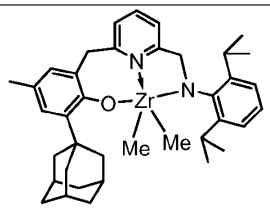
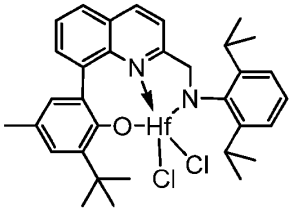
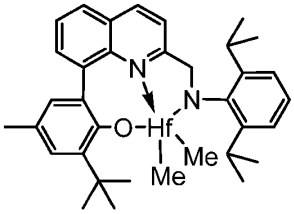
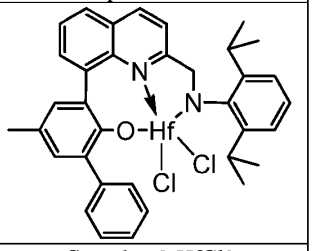
independently selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. In some embodiments, R^{11} is a C_1-C_{20} hydrocarbyl or substituted hydrocarbyl, such as 9-methylfluorenyl. In some embodiments, R^{11} is a C_5-C_{30} cycloalkyl, or C_5-C_{30} substituted cycloalkyl, such as cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, fluorenyl, 9-methylfluorenyl, adamantanyl, or substituted adamantanyl. In some embodiments, R^{11} can be C_1-C_{10} alkyl, such as *tert*-butyl, *tert*-pentyl, and *tert*-octyl (2,4,4-trimethylpent-2-yl), or R^{11} can be a heteroatom-containing group such as trimethylsilyl, carbazol-9-yl or substituted carbazol-9-yl. Alternatively, R^{11} can be aryl or substituted aryl, such as defined for R^1. In some embodiments, R^{13} is a C_1-C_{20} hydrocarbyl such as for example methyl, *tert*-butyl, n-octyl and the like.

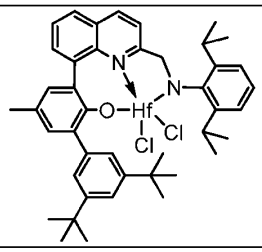
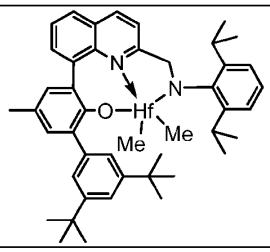
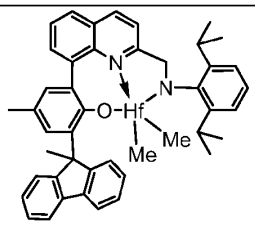
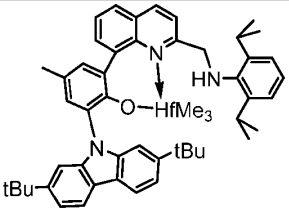
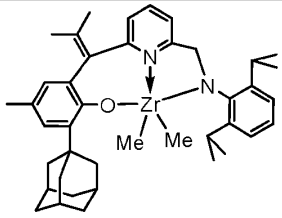
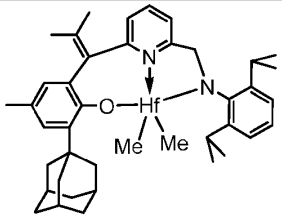
[0131] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, substituted adamantanyl, carbazol-9-yl, substituted carbazol-9-yl, fluoren-9-yl, substituted fluoren-9-yl, phenyl, or substituted phenyl.

[0132] In some embodiments, R^{11} is selected from *tert*-butyl, adamantanyl, 3-methyladamantan-1-yl, 3,5-dimethyladamantan-1-yl, carbazol-9-yl 2,7-di-tert-butylcarbazol-9-yl, fluoren-9-yl, 9-methylfluoren-9-yl, phenyl, 3,5-di-tert-butylphenyl, 3,5-di-isopropylphenyl, or 3,5-dimethylphenyl.

[0133] In some embodiments, R^{13} is selected from methyl or *tert*-butyl.

[0134] In one or more embodiments, a catalyst is selected from the group:

		
Complex 6-HfMe2	Complex 7-HfMe2	Complex 7-ZrMe2
		
Complex 1-HfCl2	Complex 1-HfMe2	Complex 2-HfCl2

		
Complex 3-HfCl2	Complex 3-HfMe2	Complex 4HfMe2
		
Complex 5-HfMe3 comparative	Complex 8-ZrMe2	Complex 8-HfMe2

Catalyst Systems

[0135] The terms "cocatalyst" and "activator" are used herein interchangeably.

[0136] The catalyst systems described herein may comprise a catalyst complex as described above and an activator such as alumoxane or a non-coordinating anion and may be formed by combining the catalyst components described herein with activators in any manner known from the literature including optionally combining the catalyst and the activator with a support, such as silica. The catalyst systems may also be added to or generated in solution polymerization or bulk polymerization (in the monomer). Catalyst systems of the present disclosure may have one or more activators and one, two or more catalyst compounds. Activators are defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral metal compound to a catalytically active metal compound cation. Non limiting activators, for example, may include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Suitable activators may include alumoxane compounds, modified alumoxane compounds, and ionizing anion precursor compounds that abstract a reactive, a-bound, metal ligand making the metal compound cationic and providing a charge-balancing non-coordinating or weakly coordinating anion, *e.g.*, a non-coordinating anion.

[0137] In at least one embodiment, a catalyst system includes one or more catalyst compounds represented by Formula **(I)**, **(II)**, **(III)**, **(IV)**, and **(V)** as described above, and an

activator compound. Activator compounds can include, but are not limited to, alumoxane catalyst and ionizing/non-coordinating anion activators.

Alumoxane Acitvators

[0138] Alumoxane activators are utilized as activators in the catalyst systems described herein. Alumoxanes are generally oligomeric compounds containing -Al(Ra")-O- subunits, where *Ra"'* 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 suitable 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 U.S. Pat. No. 5,041,584, which is incorporated by reference herein). Another useful alumoxane is solid polymethylaluminoxane as described in U.S. Pat. Nos. 9,340,630, 8,404,880, and 8,975,209, which are incorporated by reference herein.

[0139] When the activator is an alumoxane (modified or unmodified), at least one embodiment selects the maximum amount of activator at up to a 5,000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum activator-to-catalyst-compound can be a 1:1 molar ratio. Alternate ranges may include from about 1:1 to about 500:1, such as from about 1:1 to about 200:1, such as from about 1:1 to about 100:1, such as from about 1:1 to about 50:1.

[0140] In an alternate embodiment, little or no alumoxane is used in the polymerization processes described herein. For example, alumoxane can be present at zero mol %, alternately the alumoxane can be present at a molar ratio of aluminum to catalyst compound transition metal less than about 500:1, such as less than about 300:1, such as less than about 100:1, such as less than about 1:1.

Ionizing/Non-Coordinating Anion Activators

[0141] The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to a cation or which is only weakly coordinated to a cation thereby remaining sufficiently labile to be displaced by a Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to

cause it to form a neutral transition metal compound and a neutral byproduct from the anion. Non-coordinating anions useful in accordance with the present disclosure are those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization. Ionizing activators useful herein typically comprise an NCA, particularly a compatible NCA.

[0142] In some embodiments, the activator is an ionizing activator, neutral or ionic. In some embodiments of the present disclosure, neutral or ionic activators can be used alone or in combination with alumoxane or modified alumoxane activators.

[0143] In some embodiments, the catalyst systems of the present disclosure can include at least one non-coordinating anion (NCA) activator. In at least one embodiment, boron containing NCA activators can be used, wherein the boron containing NCA activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein: Z is (L-H) or a reducible Lewis acid; L is a Lewis base; H is hydrogen; (L-H) is a Bronsted acid; A^{d-} is a boron containing non coordinating anion having the charge d-; d is 1, 2, or 3.

[0144] The cation component, Z_d + may include Bronsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl, from the bulky ligand transition metal catalyst precursor, resulting in a cationic transition metal species.

[0145] The activating cation Z_d + may also be a moiety such as silver, tropylium, carbeniums, ferroceniums and mixtures, such as carbeniums and ferroceniums. Z_d+ can be triphenyl carbenium. Reducible Lewis acids can be a triaryl carbenium (where the aryl can be substituted or unsubstituted, such as those represented by the formula: (Ar_3C+), where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl), such as the reducible Lewis acids "Z" may include those represented by the formula: (Ph_3C), where Ph is a substituted or unsubstituted phenyl, such as substituted with C_1 to C_{40} hydrocarbyls or substituted a C_1 to C_{40} hydrocarbyls, such as C_1 to C_{20} alkyls or aromatics or substituted C_1 to C_{20} alkyls or aromatics, such as Z is a triphenylcarbenium. When Z_d+ is the activating cation $(L\text{-}H)_d$+, it can be a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, such as ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo

N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, dioctadecylmethylamine, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers, tetrahydrothiophene, and mixtures thereof.

[0146] The anion component A^{d-} includes those having the formula $[M^{k+}Q_n]^{d-}$ where k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (such as 1, 2, 3, or 4); n-k=d; M is an element selected from Group 13 of the Periodic Table of the Elements, such as boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Each Q can be a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, such as each Q is a fluorinated aryl group, and such as each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

[0147] Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst are the compounds described as (and particularly those specifically listed as) activators in U.S. Pat. No. 8,658,556, which is incorporated by reference herein.

[0148] The ionic stoichiometric activator Z_d^+ (A^{d-}) can be one or more of N,N-dimethylanilinium tetrakis(perfluorophenyl) borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl) borate, dioctadecylmethylammonium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium tetra(perfluorophenyl)borate.

[0149] Alternately, the activator compounds are represented by Formula (**AI**):

$$[R^1R^2R^3EH]_d^+[M^{k+}Q_n]^{d-} \qquad \textbf{(AI)}$$

wherein:

E is nitrogen or phosphorous, preferably nitrogen;

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

each of R^1, R^2, and R^3 is independently H, optionally substituted C_1-C_{40} alkyl (such as branched or linear alkyl), or optionally substituted C_6-C_{50} aryl (alternately each of R^1, R^2, and

R^3 is independently unsubstituted or substituted with at least one of halide, C_6-C_{50} aryl, C_7-C_{35} arylalkyl, C_7-C_{35} alkylaryl and, in the case of the C_6-C_{50} aryl, C_1-C_{50} alkyl); wherein R^1, 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 37 or more carbon atoms, such as 40 or more carbon atoms, such as 45 or more carbon atoms), preferably at least one of R^1, R^2, and R^3 is a C_3 to C_{40} hydrocarbyl, (such as a C_3-C_{40} alkyl, alternately such as a C_7-C_{40} alkyl);

M is an element selected from group 13 of the Periodic Table of the Elements, such as B or Al, and

each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical, such as a fluorinated aryl group, such as a fluoro-phenyl or fluoro-naphthyl, such as perfluorophenyl or perfluoronaphthyl.

[0150] In some embodiments of Formula (**AI**), each of R^1, R^2, and R^3 are independently selected from a substituted linear alkyl, a substituted branched alkyl, a substituted arylalkyl, a substituted silyl group, a substituted alkoxy group, a halogen, a halogen containing group, and combinations thereof.

[0151] In some embodiments, substituted linear alkyls can include, but a not limited to methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, n-henicosyl, n-docosyl, n-tricosyl, n-tetracosyl, n-pentacosyl, n-hexacosyl, n-heptacosyl, n-octacosyl, n-nonacosyl, n-triacontyl, and any isomer thereof.

[0152] In some embodiments, a substituted branched alkyl can include, but is not limited to, alkylbutyl, alkyl-pentyl, alkyl-hexyl, alkyl-heptyl, alkyl-octyl, alkyl-nonyl, alkyl-decyl, alkyl-undecyl, alkyl-dodecyl, alkyl-tridecyl, alkyl-butadecyl, alkylpentadecyl, alkyl-hexadecyl, alkyl-heptadecyl, alkyloctadecyl, alkyl-nonadecyl, alkyl-eicosyl, and isomers thereof. In some embodiments, the substituted branched alkyl is a multi-alkyl analog, such as dialkyl-butyl, dialkyl-pentyl, dialkyl-hexyl, dialkyl-heptyl, dialkyl-octyl, dialkylnonyl, dialkyl-decyl, dialkyl-undecyl, dialkyl-dodecyl, dialkyl-tridecyl, dialkyl-butadecyl, dialkyl-pentadecyl, dialkyl-hexadecyl, dialkyl-heptadecyl, dialkyl-octadecyl, dialkyl-nonadecyl, dialkyl-icosyl, trialkyl-butyl, trialkyl-pentyl, trialkyl-hexyl, trialkyl-heptyl, trialkyloctyl, trialkyl-nonyl, trialkyl-decyl, trialkyl-undecyl, trialkyl-dodecyl, trialkyl-tridecyl, trialkyl-

butadecyl, trialkyl-pentadecy I, trialkyl-hexadecy I, trialky 1-heptadecyl, trialkyl-octadecyl, trialkyl-nonadecyl, trialkyl-icosyl, and isomers thereof. In some embodiments, substituted branched alkyl is independently a C_1 to C_{40} linear, branched or cyclic alkyl group, such as C_2 to C_{30} linear, branched or cyclic alkyl group, such as C_3 to C_{20} linear, branched or cyclic alkyl group. In some embodiments, the alkyl group of the substituted branched alkyl is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, henicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, tricontyl, and isomers thereof.

[0153] In some embodiments, a substituted arylalkyl include methylphenyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, dodecylphenyl, tridecylphenyl, tetradecylphenyl, pentadecylphenyl, hexadecylphenyl, heptadecylphenyl, octadecylphenyl, nonadecylphenyl, icosylphenyl, henicosylphenyl, docosylphenyl, tricosylphenyl, tetracosylphenyl, pentacosylphenyl, hexacosylphenyl, heptacosylphenyl, octacosylphenyl, nonacosylphenyl, tricontylphenyl, 3,5,5-trimethylhexylphenyl, dioctylphenyl, 3,3,5-trimethylhexylphenyl, 2,2,3,3,4 pentamethypentylylphenyl, and isomers thereof.

[0154] In some embodiments, a substituted silyl group include a trialkylsilyl group, wherein each alkyl is independently a substituted C_1 to C_{20} alkyl, such as trimeth ylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, trihexylsilyl, triheptylsilyl, trioctylsilyl, trinonylsilyl, tridecylsilyl, triundecylsilyl, tridodecylsilyl, tritridecylsilyl, tri-tetradecylsilyl, tri-pentadecylsilyl, trihexadecylsilyl, tri-heptadecylsilyl, tri-octadecylsilyl, tri-nonadecylsilyl, tri-icosylsilyl, and isomers thereof.

[0155] In some embodiments, a substituted alkoxy group can be represented by the Formula -OR*, where R* includes a substituted C_1 to C_{20} alkyl or aryl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, phenyl, naphthyl, anthracenyl, and combinations thereof. In some embodiments, R* can includes an alkylphenyl group, such as methyl phenyl, propyl phenyl, and isomers thereof.

[0156] In some embodiments, a halogen includes Br and Cl. In some embodiments, a halogen containing group includes bromomethyl and bromophenyl.

[0157] In some embodiments, the NCA can include one or more of:
N,N-di(hydrogenated tallow)methylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],

N-methyl-4-hexadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-tetradecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-dodecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-decyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-octyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-hexyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-butyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-octadecyl-N-decylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-N-dodecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-N-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-N-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
N-ethyl-4-nonadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-N,N-dioctadecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-N,N-dihexadecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-N,N-ditetradecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-N,N-didodecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-N,N-didecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-N,N-dioctylammonium [tetrakis(perfluorophenyl)borate],
N-ethyl-N,N-dioctadecylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(octadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(hexadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(tetradecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(dodecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-N-hexadecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-N-hexadecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-N-tetradecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-N-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-hexadecyl-N-tetradecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-hexadecyl-N-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-hexadecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-tetradecyl-N-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-tetradecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-dodecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],

N-methyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-N-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-N-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-N-dodecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-N-decylanilinium [tetrakis(perfluorophenyl)borate], and
N-methyl-N-octylanilinium [tetrakis(perfluorophenyl)borate].

NCA Activators

[0158] In some embodiments, the activator is selected from one or more of a triaryl carbenium compounds including triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

[0159] In another embodiment, the activator is selected from one or more of trialkylammonium tetrakis(pentafluorophenyl)borate, N,N-dialkylanilinium tetrakis(pentafluorophenyl)borate, dioctadecylmethylammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trialkylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dialkylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trialkylammonium tetrakis(perfluoronaphthyl)borate, N,N-dialkylanilinium tetrakis(perfluoronaphthyl) borate, trialkylammonium tetrakis(perfluorobiphenyl)borate, N,N-dialkylanilinium tetrakis(perfluorobiphenyl)borate, trialkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, N-methyl-4-nonadecyl-Noctadecylanilinium tetrakis(perfluoronaphthalen-2-yl)borate, N-methy 1-4-nonadecy 1-N-octadecylanilinium tetrakis(perfluorophenyl)borate.

[0160] Suitable activator-to-catalyst ratio for catalyst systems having NCA activators, an activator-to-catalyst ratio may be about a 1:1 molar ratio. In some embodiments, the activator-to-catalyst ratio ranges from about 0.1: 1 to about 100: 1, such as from about 0.5:1 to about 200:1, such as from about 1:1 to about 500:1, such as about 1:1 to about 1000:1. In some embodiments, the activator-to-catalyst ratio is from about 0.5: 1 to about 10:1, such as about 1:1 to about 5:1.

[0161] In some embodiments, any one or more catalyst compounds, one or more alumoxanes, one or more NCA, and one or more activators may be combined in any amount or ratio to form a catalyst system to produce a desired result, such as, but not limited to, a polymer having a desired architecture, molecular weight, physical properties, thermal properties, and combinations thereof.

Optional Scavengers and Cocatalyst

[0162] In some embodiments, catalyst systems can include scavengers and/or coactivators. In some embodiments, aluminum alkyl and alumoxane compounds can be utilized as scavengers and/or coactivators, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, trin-octylaluminum, diisobutylaluminum hydride, methylalumoxane (MAO), modified methylalumoxane (MMAO), MMAO-3A, diethyl zinc, and combinations thereof.

Optional Support Materials

[0163] In some embodiments, the catalyst system may include an inert support material. The supported material can be a porous support material, such as talc and inorganic oxides. Other support materials include zeolites, clays, organoclays, other organic or inorganic support materials, and combinations thereof.

[0164] In some embodiments, the support material can be an inorganic oxide in a finely divided form. Suitable inorganic oxide materials for use in catalyst systems include groups 2, 4, 13, and 14 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides can be employed either alone or in combination with the silica or alumina include magnesia, titania, zirconia, and combinations thereof. Other suitable support materials can include finely divided functionalized polyolefins, such as finely divided polyethylene. Examples of suitable supports include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and combinations thereof. In some embodiments, combinations of these support materials may be used, such as silica-chromium, silica-alumina, and silica-titania. In at least one embodiment, the support material is selected from Al_2O_3, ZrO_2, SiO_2, SiO_2/Al_2O_3, SiO_2/TiO_2, silica clay, silicon oxide/clay, and combinations thereof.

[0165] In some embodiments, the support material has a surface area in the range of from about 10 m^2/g to about 700 m^2/g, a pore volume in the range of from about 0.1 cm^3/g to about 4.0 cm^3/g, and an average particle size in the range of from about 5 μm to about 500 μm. The surface area of the support material can be in the range of from about 50 m^2/g to about 500 m^2/g, pore volume of from about 0.5 cm^3/g to about 3.5 cm^3/g, and average particle size of from about 10 μm to about 200 μm. For example, the surface area of the support material is in the

range is from about 100 m^2/g to about 400 m^2/g, pore volume from about 0.8 cm^3/g to about 3.0 cm^3/g and average particle size is from about 5 μm to about 100 μm. In some embodiments, the average pore size is in the range of about 10 Å to about 1000 Å, such as about 50 Å to about 500 Å, and such as about 75 Å to about 350 Å. In at least one embodiment, the support material is a high surface area, amorphous silica having a surface area of about 300 m^2/gm and a pore volume of about 1.65 cm^3/gm.

[0166] The support material should be dry, that is, free of absorbed water. In some embodiments, drying of the support material can is conducted by heating or calcining at about 100°C to about 1,000°C, such 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. The support material is dried for a time of about 1 minute to about 100 hours, such as from about 12 hours to about 72 hours, such as from about 24 hours to about 60 hours. The calcined support material must have at least some reactive hydroxyl (OH) groups to produce supported catalyst systems. The calcined support material is then contacted with at least one polymerization catalyst comprising at least one catalyst compound and an activator.

[0167] The support material, having reactive surface groups, is slurried in a non-polar solvent and then contacted with a solution of a catalyst compound and an activator. In at least one embodiment, the slurry of the support material is first contacted with the activator for a period of time in the range of about 0.5 hour to about 24 hours, such as about 2 hours to about 16 hours, such as about 4 hours to about 8 hours. The solution of the catalyst compound is then contacted with the isolated support/activator. In at least one embodiment, the supported catalyst system is generated *in situ*. In some embodiments, the slurry of the support material is first contacted with the catalyst compound for a period of time in the range of about 0.5 hour to about 24 hours, such as about 2 hours to about 16 hours, such as about 4 hours to about 8 hours. The slurry of the supported catalyst compound is then contacted with the activator solution.

[0168] The mixture of the catalyst, activator, and support is heated to a temperature ranging from about 0°C to about 70°C, such as from about 23°C to about 60°C, such as at about room temperature. The components of the mixture are allowed to be in contact for about 0.5 hours to about 24 hours, such as about 2 hours to about 16 hours, such as about 4 hours to about 8 hours.

[0169] Suitable non-polar solvents are materials in which all of the reactants used herein, *e.g.*, the activator and the catalyst compound, are at least partially soluble and which are liquid at reaction temperatures. Non-polar solvents can be alkanes, such as isopentane, hexane,

n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene, and ethylbenzene, may also be employed.

Polymerization Processes

[0170] The polymerization process disclosed herein relate to processes where monomer and/or comonomer, are introduced with a catalyst system, the catalyst system including an activator and one or more catalyst compound(s). The catalyst compound and activator may be combined in any order. The catalyst compound and activator may be combined prior to contacting with the monomer. Alternatively, the catalyst compound and activator may be introduced into the polymerization reactor separately, wherein they subsequently react to form the active catalyst.

[0171] In some embodiments, monomers 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 at least one embodiment, the monomer includes ethylene and an optional comonomer comprising one or more C_3 to C_{40} olefins, such as C_4 to C_{20} olefins, such as C_6 to C_{12} olefins, such as 1-octene. The C_3 to C_{40} olefin monomers may be linear, branched, or cyclic. The C_3 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 includes propylene and an optional comonomer 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.

[0172] In some embodiments, the monomer and optional comonomers include one or more of ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbomadiene, substituted derivatives thereof, and isomers thereof, such as hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, ethylidenenorbornene, vinylnorbomene, norbornene, norbomadiene, and their respective homologs and derivatives, such as norbornene, norbomadiene, and dicyclopentadiene.

[0173] The polymerization disclosed herein may be conducted via any suitable polymerization technique, such as suspension, homogenous, bulk, solution, slurry, and/or gas phase polymerization processes. Such processes can be run in a batch, semi-batch, or continuous mode. In some embodiments, bulk homogeneous process is used, wherein no solvent or diluent is present or added in the reaction medium. In some embodiments, a slurry process is used. As used herein, the term "slurry polymerization process" means a polymerization process performed in a hydrocarbon solvent where a supported catalyst is employed, and monomers are polymerized on the supported catalyst particles at a temperature that is below the melting point of the polymer produced.

[0174] In some embodiments, the polymerization process implements any one or more suitable diluents and solvents, which can be non-coordinating, inert liquids including straight and branched chain hydrocarbons, cyclic and alicyclic hydrocarbons, and aromatic and alkylsubstituted aromatic compounds. In some embodiments, suitable solvents may also include one or more liquid olefins which may act as monomers and/or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In at least one embodiment, aliphatic hydrocarbon solvents are used as the solvent, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof, cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In another embodiment, the solvent is not aromatic, such as 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. In some embodiments, straight and branched chain hydrocarbons can include, but are not limited to, any one or more of isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and combinations thereof. In some embodiments, cyclic and acyclic hydrocarbons can include, but are not limited to, any one or more of cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, perhalogenated hydrocarbons, perfluorinated C_4 to C_{10} alkanes, chlorobenzene, and combinations thereof. In some embodiments, aromatic and alkylsubstituted aromatic compounds can include, but are not limited to, any one or more of benzene, toluene, mesitylene, xylene, and combinations thereof.

[0175] In at least one embodiment, the feed concentration of the monomers and comonomers for the polymerization is 60 vol% solvent or less, such as 40 vol% or less, such as 20 vol% or less, based on the total volume of the feedstream. In at least one embodiment, the polymerization is run in a bulk process.

[0176] Polymerizations can be run at any temperature and/or pressure suitable to obtain the desired polymers. In some embodiments, the temperature is in the range of about 0°C to about 300°C, such as about 20°C to about 200°C, such as about 35°C to about 160°C, such as about 80°C to about 160°C, such as about 90°C to about 140°C. In some embodiments, the pressure is in the range of about 0.1 MPa to about 25 MPa, such as about 0.45 MPa to about 6 MPa, or about 0.5 MPa to about 4 MPa.

[0177] In some embodiments, a suitable polymerization can have a run time of about 300 minutes or less, such as about 5 minutes to 250 minutes, such as about 10 minutes to 120 minutes, such as about 20 minutes to 90 minutes, such as about 30 minutes to 60 minutes. In a continuous process, the run time may be considered as the average residence time of the reactor.

[0178] In at least one embodiment, hydrogen is present in the polymerization reactor at a partial pressure of about 0.001 psig to about 50 psig (about 0.007 kPa to about 345 kPa), such as about 0.01 psig to about 25 psig (about 0.07 kPa to about 172 kPa), such as from about 0.1 psig to about 10 psig (about 0.7 kPa to about 70 kPa).

[0179] In at least one embodiment, little to no alumoxane is used in the polymerization process. In some embodiments, the alumoxane can be present at zero mol%. In some embodiments, the alumoxane can be present at a molar ratio of aluminum to transition metal less than about 500:1, such as less than about 300:1, such as less than about 100:1, such as less than about 1:1.

[0180] In at least one embodiment, the polymerization is conducted at temperatures ranging from about 0°C to about 300°C, such as about 25°C to about 250°C, such as about 80°C to 160°C, such as about 100°C to about 140°C. In at least one embodiment, the polymerization is conducted at a pressure range of about atmospheric pressure to about 10 MPa, such as 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 4 MPa. In some embodiments, the polymerization is conducted in one or more aliphatic, cyclic, and alicyclic hydrocarbon solvents including isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In some embodiments, aromatics are present in the solvent at less than about 1 wt%, such as less than about 0.5 wt%, such as at about 0 wt%, based upon the weight of the solvents. In some embodiments, the catalyst system used in the polymerization comprises less than about 0.5 mol% alumoxane, such as about 0 mol%. In some embodiments, the alumoxane is present in the catalyst system at a molar ratio of aluminum to transition metal less than about 500:1,

such as less than about 300:1, such as less than about 100:1, such as less than about 1:1. In some embodiments, the polymerization occurs in one reaction zone. In some embodiments, scavengers are present in the catalyst system at a molar ratio of scavenger metal to transition metal of less than about 100:1, such as less than about 50:1, such as less than about 15:1, such as less than about 10:1. In some embodiments, hydrogen is present in the polymerization reactor at a partial pressure range of about 0.001 psig to about 50 psig (about 0.007 kPa to about 345 kPa), such as about 0.01 psig to about 25 psig (about 0.07 kPa to about 172 kPa), such as about 0.1 psig to about 10 psig (about 0.7 kPa to about 70 kPa). In at least one embodiment, the catalyst system used in the polymerization includes 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 stirred-tank reactor or a loop reactor. When multiple reactors are used in a continuous polymerization process, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in a batch polymerization process, each polymerization stage is considered as a separate polymerization zone. In at least one embodiment, the polymerization occurs in one reaction zone.

[0181] In at least one embodiment, the present disclosure provides a process for the production of an ethylene-based polymer, wherein ethylene is polymerized by contacting the ethylene with the catalyst system in one or more continuous stirred tank reactors or loop reactors at a reactor pressure of about 0.05 MPa to about 1,500 MPa and a reactor temperature of about 30°C to about 230°C. In some embodiments, the one or more continuous stirred tank reactors or loop reactors are in series, in parallel, or a combination of the two. In at least one embodiment, hydrogen is present in the polymerization reactor at a partial pressure range of about 5 psig to about 300 psig, such as about 10 psig to about 250 psig, such as about 20 psig to about 200 psig, such as about 30 psig to about 150 psig, such as about 50 psig to 100 psig, such as about 75 psig. In at least one embodiment, the activity of the catalyst is at least about 1,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$, such as about 1,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$ to about 10,000,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$, such as about 1,500 $gP \cdot mmolcat^{-1} \cdot h^{-1}$ to about 8,000,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$, such as about 1,800 $gP \cdot mmolcat^{-1} \cdot h^{-1}$ to about 1,000,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$. In at least one embodiment, the activity of the catalyst is about 10,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$ to about 8,000,000 $gP \cdot mmolcat^{-1} \cdot h^{-1}$.

[0182] In another embodiment, the present disclosure provides a process for the production of propylene based polymer comprising: polymerizing propylene by contacting the propylene with the catalyst system of the present disclosure described above in one or more continuous stirred tank reactors or loop reactors, in series or in parallel, at a reactor pressure of from

0.5 MPa to 1,500 MPa and a reactor temperature of from 30°C to 230°C to form a propylene based polymer. In at least one embodiment, hydrogen is present in the polymerization reactor at a partial pressure from about 10 psig to about 300 psig, such as from about 20 psig to about 250 psig, such as from about 30 psig to about 200 psig, such as from about 40 psig to about 150 psig, such as from about 50 psig to about 100 psig (*e.g.*, 75 psig). In at least one embodiment, the activity of the catalyst is at least 1,000 $gP.mmolcat^{-1}.h^{-1}$, such as from 1,000 $gP.mmolcat^{-1}.h^{-1}$ to about 1,000,000 $gP.mmolcat^{-1}.h^{-1}$, such as from 2,000 $gP.mmolcat^{-1}.h^{-1}$ to about 3,000 $gP.mmolcat^{-1}.h^{-1}$, alternatively from 10,000 $gP.mmolcat^{-1}.h^{-1}$ to about 750,000 $gP.mmolcat^{-1}.h^{-1}$, such as from 50,000 $gP.mmolcat^{-1}.h^{-1}$ to about 500,000 $gP.mmolcat^{-1}.h^{-1}$, such as from 100,000 $gP.mmolcat^{-1}.h^{-1}$ to about 250,000 $gP.mmolcat^{-1}.h^{-1}$, alternatively from about 1,000,000 $gP.mmolcat^{-1}.h^{-1}$ to about 6,000,000 $gP.mmolcat^{-1}.h^{-1}$, such as from about 2,000,000 $gP.mmolcat^{-1}.h^{-1}$ to about 4,000,000 $gP.mmolcat^{-1}.h^{-1}$.

[0183] In another embodiment, the present disclosure provides a process for the production of an ethylene alpha-olefin copolymer comprising: polymerizing ethylene and at least one C_3-C_{20} alpha-olefin by contacting the ethylene and the at least one C_3-C_{20} alpha-olefin with a catalyst system described above in one or more continuous stirred tank reactors or loop reactors, in series or in parallel, at a reactor pressure of from 0.05 MPa to 1,500 MPa and a reactor temperature of from 30°C to 230°C to form an ethylene alpha-olefin copolymer. In at least one embodiment, hydrogen is present in the polymerization reactor at a partial pressure of from about 10 psig to about 300 psig, such as from about 20 psig to about 250 psig, such as from about 30 psig to about 200 psig, such as from about 40 psig to about 150 psig, such as from about 50 psig to about 100 psig (*e.g.*, 75 psig), alternatively from about 150 psig to about 300 psig (*e.g.*, 200 psig). In at least one embodiment, the activity of the catalyst is at least 1,000 $gP.mmolcat^{-1}.h^{-1}$, such as from about 1,000 $gP.mmolcat^{-1}.h^{-1}$ to about 10,000,000 $gP.mmolcat^{-1}.h^{-1}$, such as from about 1,500 $gP.mmolcat^{-1}.h^{-1}$ to about 8,000,000 $gP.mmolcat^{-1}.h^{-1}$, such as from about 1,800 $gP.mmolcat^{-1}.h^{-1}$ to about 1,000,000 $gP.mmolcat^{-1}.h^{-1}$, alternatively from about 10,000 $gP.mmolcat^{-1}.h^{-1}$ to about 8,000,000 $gP.mmolcat^{-1}.h^{-1}$.

[0184] In another embodiment, the present disclosure provides a process for the production of a propylene alpha-olefin copolymer comprising: polymerizing propylene and at least one ethylene and or at least one C_4-C_{20} alpha-olefin by contacting the propylene and the at least one ethylene and or at least one C_3-C_{20} alpha-olefin with a catalyst system described above in one or more continuous stirred tank reactors or loop reactors, in series or in parallel, at a reactor

pressure of from 0.05 MPa to 1,500 MPa and a reactor temperature of from 30°C to 230°C to form an ethylene alpha-olefin copolymer. In at least one embodiment, hydrogen is present in the polymerization reactor at a partial pressure of from about 10 psig to about 300 psig, such as from about 20 psig to about 250 psig, such as from about 30 psig to about 200 psig, such as from about 40 psig to about 150 psig, such as from about 50 psig to about 100 psig (*e.g.*, 75 psig), alternatively from about 150 psig to about 300 psig (*e.g.*, 200 psig). In at least one embodiment, the activity of the catalyst is at least 1,000 gP.mmolcat^{-1}.h^{-1}, such as from about 1,000 gP.mmolcat^{-1}.h^{-1} to about 10,000,000 gP.mmolcat^{-1}.h^{-1}, such as from about 1,500 gP.mmolcat^{-1}.h^{-1} to about 8,000,000 gP.mmolcat^{-1}.h^{-1}, such as from about 1,800 gP.mmolcat^{-1}.h^{-1} to about 1,000,000 gP.mmolcat^{-1}.h^{-1}, alternatively from about 10,000 gP.mmolcat^{-1}.h^{-1} to about 8,000,000 gP.mmolcat^{-1}.h^{-1}.

[0185] In at least one embodiment, the conversion of olefin monomer is at least about 10%, based upon polymer yield and the weight of the monomer entering the reaction zone, such as about 20% or more, such as about 30% or more, such as about 50% or more, such as about 80% or more.

[0186] In at least one embodiment, little or no alumoxane is used in the process to produce the polymers. In some embodiments, the alumoxane is present at a molar ratio of aluminum to transition metal less than about 500:1, such as less than about 300:1, such as less than about 100:1, such as less than about 1:1.

[0187] In at least one embodiment, little or no scavenger is used in the process to produce the ethylene polymer. In some embodiments, the scavenger is present at a molar ratio of scavenger metal to transition metal of less than about 100:1, such as less than about 50:1, such as less than about 15:1, such as less than about 10:1.

[0188] Other additives may also be used in the polymerization, such as one or more scavengers, hydrogen, aluminum alkyls, or chain transfer agents. In at least one embodiment, an additive includes an alkylalumoxanes, diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof. In at least one embodiment, the alkylalumoxane is represented by the formula AlR_3 or ZnR_2, wherein 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.

Solution Polymerization

[0189] In at least one embodiment, the polymerization process with catalyst compounds of the present disclosure is a solution polymerization process.

[0190] A solution polymerization is a polymerization process in which the polymer is dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are not turbid. Solution polymerizations may involve polymerization in a continuous reactor in which the polymer formed, the starting monomer, and catalyst materials supplied are agitated to reduce or avoid concentration gradients. In some embodiments, the monomer acts as a diluent or solvent. In some embodiments, a hydrocarbon is used as a diluent or solvent. Suitable processes can operate at a temperature range of about 0°C to about 250°C, such as about 50°C to about 170°C, such as about 80°C. to about 150°C, such as about 100°C to about 140°C, and/or at pressures of about 0.1 MPa to about 200 MPa, such as about 0.1 MPa to about 120 MPa, such as about 2 MPa to about 30 MPa. Temperature control in the reactor is obtained by balancing the heat of polymerization with reactor cooling, whereby reactor cooling implements reactor jackets or cooling coils to cool the contents of the reactor, auto refrigeration, pre-chilled feeds, vaporization of liquid medium, or combinations thereof. Adiabatic reactors with pre-chilled feeds can also be used. The purity, type, and amount of solvent can be optimized for the maximum catalyst productivity for a particular type of polymerization. In some embodiments, the solvent is introduced as a catalyst carrier. In some embodiments, the solvent can be introduced as a gas phase or a liquid phase depending on the pressure and temperature. Advantageously, the solvent can be kept in the liquid phase and introduced as a liquid. Solvent can be introduced in the feed to the polymerization reactors.

[0191] In some embodiments, the polymerization process is a solution polymerization process that may be performed in a batch wise fashion or in a continuous process. Suitable reactors may include tank, loop, and tube designs. In at least one embodiment, the process is performed in a continuous fashion wherein dual loop reactors in a series configuration are used. In at least one embodiment, the process is performed in a continuous fashion using one or more dual continuous stirred-tank reactors (CSTRs) in a series configuration, wherein the process can be performed in a continuous fashion using a tube reactor. In another embodiment, the process is performed in a continuous fashion and wherein a one loop reactor and one CSTR are used in a series configuration. The process can also be performed in a batch wise fashion wherein single stirred tank reactor can be used.

Polyolefin products

[0192] Polymers of the present disclosure may be formed via any one or more processes disclosed herein. In some embodiments, the polymers formed include homopolymers of

polyethylene and/or polypropylene. In some embodiments, the polymers formed include copolymers of ethylene or propylene, wherein each respective monomer is copolymerized with one or more of C_3-C_{20} alpha-olefin.

[0193] In at least one embodiment, polyethylene homopolymers have a weight average molecular weight (Mw) of about 50,000 g/mol to about 1,500,000 g/mol, such as about 80,000 g/mol to about 1,300,000 g/mol, such as about 100,000 g/mol to about 1,200,000 g/mol. In at least one embodiment, polyethylene homopolymers formed using any one or more catalyst system include a melting temperature (Tm) of about 129°C to about 137°C, such as about 131°C to about 136°C, such as about 132°C to about 135°C. In at least one embodiment, polyethylene homopolymers formed using any one or more catalyst system include a polydispersity index (PDI) of about 1.4 to about 25.0, such as about 1.5 to about 20.0, such as about 1.6 to about 18.0, such as about 1.7 to about 15.0, such as about 1.8 to about 10.0, such as about 1.9 to about 5.0, such as about 2.0 to about 3.0.

[0194] In some embodiments, polyethylene copolymers are formed using different catalyst systems. Polyethylene copolymers can have a Mw of about 20,000 g/mol to about 1,500,000 g/mol, such as about 30,000 g/mol to about 1,200,000 g/mol, such as about 40,000 g/mol to about 1,000,000 g/mol. In at least one embodiment, polyethylene copolymers can have a PDI of about 1.2 to about 35.0, such as about 1.4 to about 10, such as about 1.8 to about 9, such as about 1.9 to about 6, such as about 2 to about 2.5. In at least one embodiment, polyethylene copolymers can have a Tm of about 65°C to about 130°C, such as about 67°C to about 127°C, such as about 107.5°C.

[0195] In at least one embodiment, polypropylene homopolymers have a Mw of about 2,000 g/mol to about 600,000 g/mol, such as about 2,500 g/mol to about 500,000 g/mol, such as about 30,000 g/mol to about 500,000 g/mol, such as about 60,000 g/mol to about 300,000 g/mol. In at least one embodiment, polypropylene homopolymers have a PDI of about 1.40 to about 3.0, such as about 1.5 to about 2.5, such as about 1.6 to about 2.3, such as about 1.7 to about 2.0. In at least one embodiment, polypropylene homopolymers have a Tm of about 100°C to about 150°C, such as about 109°C to about 147°C.

Blends

[0196] In another embodiment, the polymer (such as the polyethylene or polypropylene) produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate,

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

[0197] In at least one embodiment, the polymer (such as the polyethylene or polypropylene) is present in the above blends, at from 10 wt% to 99 wt%, based upon the weight of the polymers in the blend, such as 20 wt% to 95 wt%, such as at least 30 wt% to 90 wt%, such as at least 40 wt% to 90 wt%, such as at least 50 wt% to 90 wt%, such as at least 60 wt% to 90 wt%, such as at least 70 to 90 wt%.

[0198] The blends described above may be produced by mixing the polymers of the present disclosure with one or more polymers (as described above), by connecting reactors together in series to make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

[0199] The blends may be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (*e.g.*, hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (*e.g.*, IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc.

Films

[0200] Any of the foregoing polymers, such as the foregoing polypropylenes or blends thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films. These films may be formed by any number of well-known extrusion or coextrusion techniques, such as a blown bubble film processing technique, wherein the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially oriented, or biaxially oriented to the same or different extents. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. The uniaxially orientation can be accomplished using typical cold drawing or hot drawing methods. Biaxial orientation can be accomplished using tenter frame equipment or a double bubble processes and may occur before or after the individual layers are brought together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene then optionally the combination could be oriented even further. For example, the films can be oriented in the Machine Direction (MD) at a ratio of up to 15, such as from about 5 to about 7, and in the Transverse Direction (TD) at a ratio of up to 15, such as from about 7 to about 9. However, in another embodiment the film is oriented to the same extent in both the MD and TD directions.

[0201] The films may vary in thickness depending on the intended application; however, films of a thickness from 1 μm to 50 μm can be suitable. Films intended for packaging can be from 10 μm to 50 μm thick. The thickness of the sealing layer can be from 0.2 μm to 50 μm. There may be a sealing layer on both the inner and outer surfaces of the film, or the sealing layer may be present on only the inner or the outer surface.

[0202] In another embodiment, one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, flame treatment, or microwave. In at least one embodiment, one or both of the surface layers is modified by corona treatment.

Waxes

[0203] Polyolefin waxes, such as polyethylene waxes, having low molecular weight of about 250 g/mol to about 5,000 g/mol, for example, can be prepared in a solution polymerization process using the Lewis base catalysts. The production of polyolefin waxes

may be performed at a temperature of from about 50°C to about 220°C, such as from about 100°C to about 200°C, such as from about 120°C to about 160°C. The production of polyolefin waxes may be performed at a reactor pressure of from about 0.5 MPa to about 25 MPa, such as from about 0.7 MPa to about 6 MPa. The production of polyolefin waxes may be performed in the presence of added hydrogen at a partial pressure of from 0 psig to about 100 psig, such as from 0 psig to about 40 psig, such as 0 psig.

EXPERIMENTAL

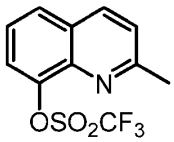
Pre-Catalyst Synthesis

General information

[0204] All reactions with compounds sensitive to oxygen and moisture were conducted in atmosphere of argon in a glove box or using Schlenk technique. 2-Bromo-4-methyl-6-phenylphenol [US 2004/014950], 2-bromo-4-methyl-6-(3,5-di-*tert*-butylphenyl)phenol [JP 2015/193612], 1-bromo-3-(*tert*-butyl)-2-(methoxymethoxy)-5-methylbenzene, 1-(3-bromo-2-(methoxymethoxy)-5-methylphenyl)adamantane, 2-(2-(methoxymethoxy)-5-methyl-3-(9-methyl-9-fluorenyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [US 11,214,634], 2-(2-allyloxy-3-(*tert*-butyl)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [WO 2021/048030], 2,7-di-tert-butyl-9-(2-(methoxymethoxy)-5-methylphenyl)-9*H*-carbazole [WO 2018/122693], bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane [*Org. Lett.*, **2014**, *16*, 6342] were prepared as described in the literature. 2,2'-(2-Methylprop-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was prepared from 1,1-dibromo-2-methylprop-1-ene, *n*BuLi in THF-Et_2O, and bis(pinacolato)diboron using a method described by Hata and coworkers [*Angew. Chem. Int. Ed.*, **2001**, *40*, 790]. All other reagents are available from commercial chemical suppliers.

Preparation of the ligands

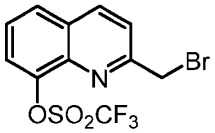
[0205] **2-Methylquinolin-8-yl trifluromethanesulfonate**



To a solution of 2-methylquinolinol-8 (10.0 g, 62.9 mmol) and pyridine (9.9 g, 126 mmol) in dry dichloromethane (150 mL), a solution of triflic anhydride (21.3 g, 75.4 mmol) in 20 mL of dry dichloromethane was added dropwise at 0°C. The mixture was warmed to room temperature and stirred for 1 hour. After that, the mixture was washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to yield 18.1 g

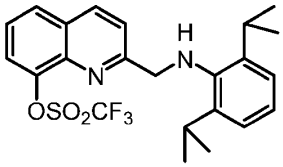
(99%) of the product as a white crystalline powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.5 Hz, 1H), 7.77 (dd, J = 8.1 Hz, J = 1.1 Hz, 1H), 7.56 (dd, J = 7.6 Hz, J = 1.1 Hz, 1H), 7.46 (dd, J = 8.1 Hz, J = 7.6 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 2.78 (s, 3H).

[0206] 2-(Bromomethyl)quinolin-8-yl trifluoromethanesulfonate



A mixture of 2-methylquinolin-8-yl trifluromethanesulfonate (18.1 g, 62.2 mmol), N-bromosuccinimide (NBS, 18.8 g, 106 mmol), and azobisisobutyronitrile (AIBN, 1.07 g, 6.53 mmol) in 200 mL of dry CCl_4 was heated to reflux for 36 hours in an argon atmosphere. The reaction mixture was cooled to room temperature, filtered and the filtrate was evaporated under reduced pressure. The product was isolated from the residue by column chromatography (silica gel 60, 40–63 um, eluent: hexane/dichloromethane = 7/3, vol.) Yield: 7.50 g (31%) of the product as a white crystalline powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.56 (dd, J = 7.9 Hz, J = 7.1 Hz, 1H), 4.73 (s, 2H).

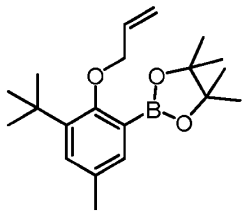
[0207] 2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl trifluoromethanesulfonate



To a solution of 2,6-diisopropylaniline (3.3 g, 18.4 mmol) in THF (100 mL) a solution of nBuLi in hexane (2.5 M, 6.44 mL, 16.12 mmol) was added dropwise at 0°C. The reaction mixture was stirred for 30 minutes at this temperature, and cooled to –78°C, and a solution of 2-(bromomethyl)quinolin-8-yl trifluromethanesulfonate (5.7 g, 15.35 mmol) in THF (20 ml) was added dropwise. The mixture was allowed to warm slowly to room temperature, poured into 300 ml of water, and the product was extracted with 3×100 ml of dichloromethane. The combined organic phase was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The product was isolated by column chromatography (silica gel 60, 40–60 um, eluent: hexane/EtOAc = 10/1, vol.). Yield: 4.9 g (68%) of the product as a white crystalline powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55 (dd, J = 8.3 Hz, J = 7.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H),

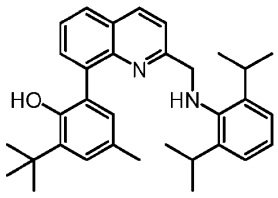
7.10-7.15 (m, 3H), 4.53 (br. s, 1H), 4.43 (s, 2H), 3.50 (sept, J = 6.8 Hz, 2H), 1.25 (d, J = 6.8 Hz, 12H).

[0208] 2-(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



To a solution of 2-(allyloxy)-1-bromo-3-(*tert*-butyl)-5-methylbenzene (24.6 g, 86.7 mmol) in anhydrous THF (500 mL) a solution of *n*BuLi in hexanes (2.45 M, 35.4 mL, 86.7 mmol) was added dropwise at –78°C. The reaction mixture was stirred at this temperature for 1 hour. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19.3 g, 104 mmol) was added in one portion, and the mixture was stirred overnight at room temperature. Next, water (200 mL) was added, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (2×100 mL). The combined organic extract was dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. Recrystallization of the residue from methanol gave 20.4 g (72%) of the product as a yellowish crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 1H), 7.22 (m, 1H), 6.17 (m, 1H), 5.43 (m, 1H), 5.25 (m, 1H), 4.45 (m, 2H), 2.29 (s, 3H), 1.38 (s, 9H), 1.35 (s, 12H).

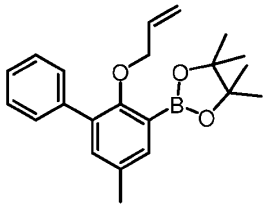
[0209] 2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-*tert*-butylphenol



A mixture of 2-(2-allyloxy-3-(*tert*-butyl)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.31 g, 3.97 mmol), 2-(((2,6-diisopropylphenyl)amino)methyl)quinolin-8-yl trifluromethanesulfonate (1.76 g, 3.78 mmol), Cs_2CO_3 (3.1 g, 9.44 mmol), water (20 mL), dioxane (35 mL), $Pd(PPh_3)_4$ (0.220 g, 0.189 mmol) was stirred for 10 hours at 105°C. Then, the reaction mixture was poured into 200 mL of water, the product was extracted with 3×100 ml of dichloromethane, the combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Column chromatography on silica gel 60 (40–63 um,

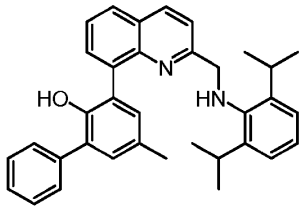
eluent: hexane/EtOAc/Et_3N = 100/10/1, vol.) afforded 920 mg (51%) of the product as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 9.80 (br s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.84-7.87 (m, 2H), 7.65-7.68 (m, 1H), 8.59 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.05-7.12 (m, 4H), 4.40 (s, 2H), 3.85 (br s, 1H), 3.26 (sept, J = 6.8 Hz, 2H), 2.37 (s, 3H), 1.46 (s, 9H), 1.15 (d, J = 6.8 Hz, 12H).

[0210] 2-(2-Allyloxy-3-phenyl-5-methylphenyl)4,4,5,5-tetramethyl-1,3,2-dioxaborolane



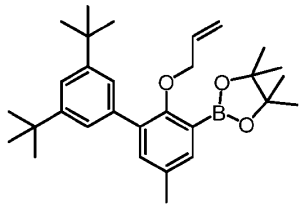
A mixture of 2-bromo-4-methyl-6-phenylphenol (4.0 g, 15.2 mmol), allyl bromide (2.76 g, 22.8 mmol), anhydrous K_2CO_3 (4.2 g, 30.4 mmol) in 50 ml of acetone was stirred for 10 hours at 50°C. The reaction mixture was poured into 300 mL of water, the product was extracted with 3×100 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The resulting 2-(allyloxy)-1-bromo-3-phenyl-5-methylbenzene (4.60 g) was used without further purification. To a solution of the above obtained 2-(allyloxy)-1-bromo-3-phenyl-5-methylbenzene (4.60 g, 15.18 mmol) in 100 ml THF a 2.5 M solution of *n*BuLi in hexane (6.42 ml, 16.04 mmol) was added dropwise at −78°C. The reaction mixture was stirred for 30 minutes at this temperature. Then, 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (3.69 g, 19.9 mmol) was added in one portion and the reaction mixture was warmed to ambient temperature. The reaction mixture was then poured into 300 mL of water, the product was extracted with 3×100 mL of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Yield: 5.25 g (99%) of the product as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.2 Hz, 2H), 7.49 (s, 1H), 7.34-7.39 (m, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.24 (s, 1H), 5.74-5.86 (m, 1H), 4.97-5.06 (m, 2H), 3.99 (d, J = 5.8 Hz, 2H), 2.34 (s, 3H), 1.35 (s, 12H).

[0211] 2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-phenylphenol



A mixture of 2-(2-allyloxy-5-methyl-3-phenylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.79 g, 5.92 mmol), 2-(((2,6-diisopropylphenyl)amino)methyl)quinolin-8-yl trifluromethanesulfonate (2.30 g, 4.94 mmol), Cs_2CO_3 (4.02 g, 12.34 mmol), water (10 mL), dioxane (20 mL), $Pd(PPh_3)_4$ (0.285 g, 0.247 mmol) was stirred for 10 hours at 105°C. Then, the reaction mixture was poured into 100 mL of water, the product was extracted with 3×30 ml of dichloromethane, the combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Column chromatography on silica gel 60 (40–63 um, eluent: hexane/EtOAc/Et_3N = 100/10/1, vol.) afforded 607 mg (25%) of the product as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 9.72 (br s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.7 Hz, 2H), 7.67-7.71 (m, 1H), 7.62-7.65 (m, 2H), 7.60 (d, J = 8.4 Hz, 1H), 7.32-7.36 (m, 2H), 7.26-7.30 (m, 2H), 7.21 (d, J = 2.1 Hz, 1H), 7.02-7.10 (m, 3H), 4.37 (s, 2H), 3.4 (br s, 1H), 3.23 (sept, J = 6.9 Hz, 2H), 2.41 (s, 3H), 1.10 (d, J = 6.9 Hz, 12H).

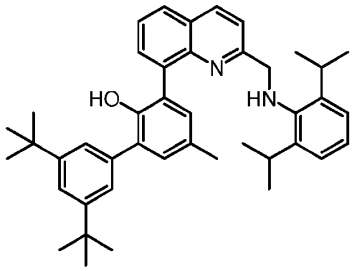
[0212] 2-(2-Allyloxy-3-(3,5-di-*tert*-butylphenyl)-5-methylphenyl)4,4,5,5-tetramethyl-1,3,2-dioxaborolane



A mixture of 2-bromo-4-methyl-6-(3,5-di-*tert*-butylphenyl)phenol (4.0 g, 10.7 mmol), allyl bromide (1.94 g, 16.0 mmol), anhydrous K_2CO_3 (4.2 g, 30.4 mmol) in 50 ml of acetone was stirred for 10 hours at 50°C. The reaction mixture was poured into 300 mL of water, the product was extracted with 3×100 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The resulting 2-(allyloxy)-1-bromo-3-(3,5-di-*tert*-butylphenyl)-5-methylbenzene (4.40 g) was used without further purification. To a solution of the above obtained 2-(allyloxy)-1-bromo-3-(3,5-di-*tert*-butylphenyl)-5-methylbenzene (4.40 g, 10.6 mmol) in 100 mL of THF a 2.5 M solution of BuLi

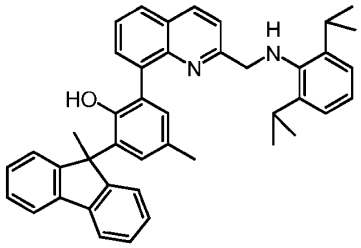
in hexane (4.50 ml, 11.25 mmol) was added dropwise at –78°C. The reaction mixture was stirred for 30 minutes at this temperature. Then, 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (2.59 g, 13.93 mmol) was added in one portion and the reaction mixture was warmed to room temperature. The reaction mixture was then poured into 300 mL of water, and the product was extracted with 3×100 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Yield: 4.85 g (99%) of the product as a white crystalline powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 2.0 Hz, 1H), 7.39-7.41 (m, 2H), 7.35-7.38 (m, 1H), 7.26 (s, 1H), 5.76-5.86 (m, 1H), 4.96-5.06 (m, 2H), 3.99 (d, J = 5.8 Hz, 2H), 2.35 (s, 3H), 1.36 (s, 12H) 1.34 (s, 18H).

[0213] 2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-(3,5-di-*tert*-butylphenyl)phenol



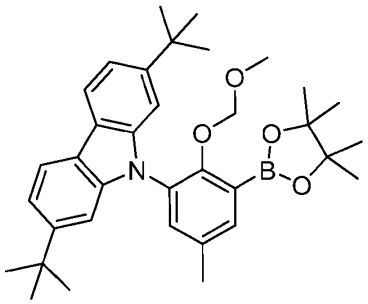
A mixture of 2-(2-allyloxy-5-methyl-3-(3,5-di-*tert*-butylphenyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.70 g, 1.51 mmol), 2-(((2,6-diisopropylphenyl)amino)methyl)quinolin-8-yl trifluromethanesulfonate (0.50 g, 1.07 mmol), Cs_2CO_3 (1.03 g, 3.15 mmol), water (5 mL), dioxane (10 mL), $Pd(PPh_3)_4$ (0.070 g, 0.061 mmol) was stirred for 10 hours at 105°C. Then, the reaction mixture was poured into 100 mL of water, the product was extracted with 3×20 ml of dichloromethane, the combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Column chromatography on silica gel 60 (40–63 um, eluent: hexane/EtOAc/Et_3N = 100/10/1, vol.) afforded 401 mg (61%) of the product as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.87-7.93 (m, 2H), 7.66-7.70 (m, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 1.8 Hz, 2H), 7.97 (t, J = 1.8 Hz, 1H), 7.27 (d, J = 1.9 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 7.00-7.07 (m, 3H), 4.36 (s, 2H), 3.97 (br s, 1H), 3.20 (sept, J = 6.8 Hz, 2H), 2.42 (s, 3H), 1.31 (s, 18H), 1.07 (d, J = 6.8 Hz, 12H).

[0214] 2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-(9-methyl-9-fluorenyl)phenol



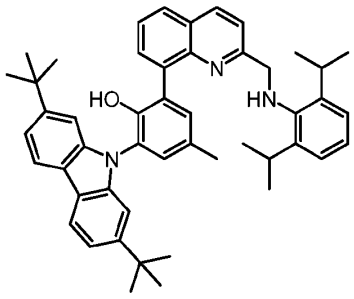
A mixture of 2-(2-(methoxymethoxy)-5-methyl-3-(9-methyl-9-fluorenyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.35 g, 5.14 mmol), 2-(((2,6-diisopropylphenyl)amino)methyl)quinolin-8-yl trifluromethanesulfonate (2.0 g, 4.29 mmol), Cs_2CO_3 (3.5 g, 10.71 mmol), water (10 mL), dioxane (16 mL), and $Pd(PPh_3)_4$ (0.25 g, 0.214 mmol) was stirred for 10 hours at 105°C. Then, the reaction mixture was poured into 100 mL of water, and the product was extracted with 3×20 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was dissolved in a mixture of 40 ml of THF and 40 ml of MeOH, and 2.2 ml of 12M HCl was added to the resulting solution. The mixture was stirred at 60°C for 10 hours, cooled to room temperature, poured into 300 mL of 3% aqueous solution of $NaHCO_3$, and the product was extracted with 3×100 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Column chromatography on silica gel 60 (40–60 um, eluent: hexane/EtOAc/Et_3N = 100/10/1, vol.) afforded 2.2 g (85%) of the product as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.76 (dd, J = 7.3 Hz, J = 1.4 Hz, 1H), 7.73 (dd, J = 8.5 Hz, J = 1.4 Hz, 1H), 7.61-7.65 (m, 2H), 7.59 (s, 1H), 7.52-7.56 (m, 2H), 7.23-7.26 (m, 2H), 7.13-7.17 (m, 4H), 6.99-7.07 (m, 4H), 3.85 (s, 2H), 3.06 (sept, J = 6.8 Hz, 2H), 2.46 (s, 3H), 1.85 (s, 3H), 1.15 (d, J = 6.8 Hz, 12H).

[0215] 2-(2-(Methoxymethoxy)-5-methyl-3-(2,7-di-*tert*-butylcarbazol-9-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



2,7-Di-tert-butyl-9-(2-(methoxymethoxy)-5-methylphenyl)carbazole was dissolved in dry diethyl ether (500 mL) and *n*BuLi (2.5 M in hexanes, 13.0 mL, 32.0 mmol) was added dropwise to the solution at 0°C. After that, the cooling bath was removed, and the resulting mixture was stirred at room temperature overnight. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.80 mL, 7.54 g, 41.0 mmol) was added dropwise to the mixture at -80°C and the resulting mixture was allowed to warm to room temperature and stirred at this temperature overnight. To the mixture, water (1000 mL) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3×100 ml); the combined organic extracts were washed with brine, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane/EtOAc = 20/1, vol.). Yield: 6.70 g (45%, 85% purity) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 2H), 7.76-7.73 (m, 1H), 7.32-7.27 (m, 3H), 7.12-7.08 (m, 2H), 4.66 (s, 2H), 2.48 (s, 3H), 2.41 (s, 3H), 1.41 (s, 12H), 1.37 (s, 18H).

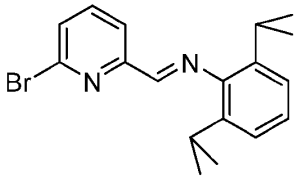
[0216] 2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-(2,7-di-*tert*-butylcarbazol-9-yl)phenol



A mixture of 2-(2-(methoxymethoxy)-5-methyl-3-(2,7-di-*tert*-butylcarbazol-9-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.86 g, 5.14 mmol), 2-(((2,6-diisopropylphenyl)amino)methyl)quinolin-8-yl trifluromethanesulfonate (2.00 g, 4.29 mmol),

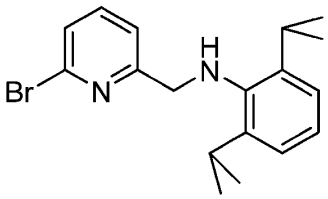
Cs_2CO_3 (3.50 g, 10.71 mmol), water (10 mL), dioxane (16 mL), $Pd(PPh_3)_4$ (0.25 g, 0.214 mmol) were stirred for 10 hours at 105°C. Then, the reaction mixture was poured into 100 mL of water, the product was extracted with 3×20 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvent evaporated was in vacuum. The residue was dissolved in a mixture of 40 mL of THF and 40 mL of MeOH, and 2.2 mL of 12M HCl was added to the resulting solution. The mixture was stirred at 60°C for 10 hours, cooled to room temperature, and poured into 300 mL of 3% aqueous $NaHCO_3$. The product was extracted with 3×100 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Column chromatography on silica gel 60 (40–63 um, eluent: hexane/EtOAc/Et_3N = 100/10/1, vol.) afforded 2.0 g (67%) of the product as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 10.20 (s, 1H), 8.32 (d, J = 8.5 Hz, 1H), 8.02 (dd, J = 7.3 Hz, J = 1.3 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.92 (dd, J = 8.2 Hz, J = 1.3 Hz, 1H), 7.69-7.75 (m, 2H), 7.44 (dd, J = 2.2 Hz, J = 0.6 Hz, 1H), 7.34 (dd, J = 2.2 Hz, J= 0.6 Hz, 1H), 7.26 (d, J = 1.7 Hz, 1H), 7.24 (d, J = 1.7 Hz, 1H), 7.21-7.23 (m, 2H), 6.98-7.02 (m, 3H), 4.27 (s, 2H), 3.54 (br s, 1H), 3.08 (sept, J = 6.9 Hz, 2H), 2.46 (s, 3H), 1.27 (s, 18H), 0.99 (d, J1 = 6.9 Hz, 12H).

[0217] ***N*-((6-Bromopyridin-2-yl)methylene)-2,6-diisopropylaniline**



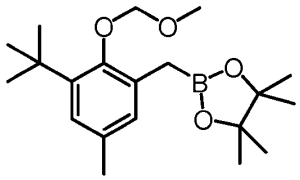
A mixture of 85.0 g (457 mmol) of 6-bromopyridine-2-carbaldehyde and 80.9 g (457 mmol) of 2,6-diisopropylaniline in 1000 mL of ethanol was heated to reflux under argon atmosphere for 8 hours. The obtained solution was evaporated to dryness, and the resulting solid was recrystallized from 200 ml of methanol. Yield: 113.5 g (72%) of the product as a yellow crystalline solid. ^1H NMR ($CDCl_3$): δ 8.24-8.26 (m, 2H), 7.68-7.72 (m, 1H), 7.59-7.61 (m, 1H), 7.10-7.18 (m, 3H), 2.91 (sept, J = 6.8 Hz, 2H), 1.16 (d, J = 6.8 Hz, 12H).

[0218] ***N*-((6-Bromopyridin-2-yl)methyl)-2,6-diisopropylaniline**



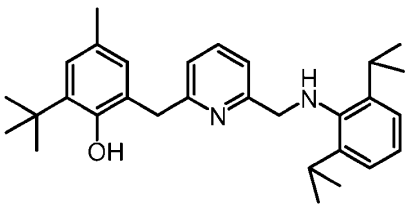
Under argon atmosphere, a mixture of 113.5 g (329 mmol) of *N*-((6-bromopyridin-2-yl)methylene)-2,6-diisopropylaniline, 33.2 g (526 mmol) of $NaBH_3CN$, 9 mL of glacial acetic acid and 1000 mL of methanol was heated to reflux for 12 hours. The mixture was cooled to room temperature, poured into 1000 mL of water, and then extracted with 3×200 mL of ethyl acetate. The combined extract was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane/EtOAc = 10/1, vol.). Yield: 104 g (91%) of the product as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.51-7.55 (m, 1H), 7.41-7.43 (m, 1H), 7.31-7.33 (m, 1H), 7.08-7.15 (m, 3H), 4.21 (s, 2H), 3.96 (br s, 1H), 3.36 (sept, J = 6.8 Hz, 2H), 1.26 (d, J = 6.8 Hz, 12H).

[0219] 2-(3-(*tert*-Butyl)-2-(methoxymethoxy)-5-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



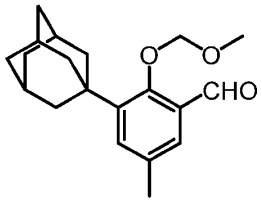
To a solution of 770 mg (2.88 mmol) of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane, 500 mg (1.44 mmol) of 1-bromo-3-(*tert*-butyl)-2-(methoxymethoxy)-5-methylbenzene and 74 mg (0.144 mmol) of $Pd(P^tBu_3)_2$ in 15 mL of dioxane, 0.360 mL of 8N aqueous KOH (2.88 mmol) was added dropwise at room temperature. The resulting mixture was stirred at this temperature overnight, and then poured into 30 mL of water. The crude product was extracted with 3×20 mL of dichloromethane. The combined organic extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure to near dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um; eluent: hexane/dichloromethane = 10/1, vol.). Yield 307 mg (61%) of the product as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.94 (d, J = 1.8 Hz, 1H), 6.86 (d, J = 1.8 Hz, 1H), 4.98 (s, 2H), 3.64 (s, 3H), 2.26 (s, 3H), 2.25 (s, 2H), 1.40 (s, 9H), 1.25 (s, 12H).

[0220] 2-(*tert*-Butyl)-6-(((6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methyl)-4-methylphenol



To a solution of 500 mg (1.44 mmol) of 2-(3-(*tert*-butyl)-2-(methoxymethoxy)-5-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 600 mg (1.72 mmol) of *N*-((6-bromopyridin-2-yl)methyl)-2,6-diisopropylaniline in 8 mL of dioxane, 1.41 g (4.31 mmol) of cesium carbonate, 40 mg (0.08 mmol) of $Pd(P^tBu_3)$, and 2 mL of water were subsequently added. The mixture was stirred for 12 hours at 95°C, cooled to room temperature and diluted with 50 ml of water. To the obtained mixture, 50 ml of diethyl ether was added, the organic layer was separated and washed with brine. The resulting solution was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. To the residue, 10 mL of THF, 10 mL of methanol and 0.7 mL of 12 N HCl were subsequently added. The mixture was stirred overnight at 60°C, then, poured into 30 mL of water, and aqueous $NaHCO_3$ was added until pH≈7. The obtained mixture was extracted with dichloromethane (3×20 mL), the combined organic extract was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane/EtOAc/Et_3N = 100/10/1, vol.). Yield: 510 mg (79%) of the product as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 11.3 (br s, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 7.11-7.13 (m, 3H), 6.99 (d, J = 1.9 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H), 4.13 (s, 2H), 4.09 (s, 2H), 3.28 (sept, J = 6.8 Hz, 2H), 2.26 (s, 3H), 1.44 (s, 9H), 1.22 (d, J = 6.8 Hz, 12H).

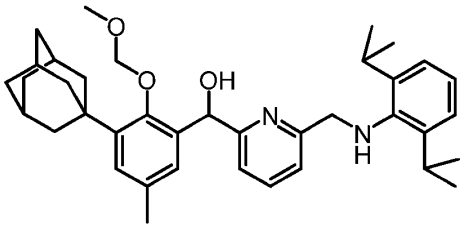
[0221] 3-(Adamantan-1-yl)-2-(methoxymethoxy)-5-methylbenzaldehyde



To a solution of 10.0 g (27.5 mmol) of 1-(3-bromo-2-(methoxymethoxy)-5-methylphenyl)adamantane in 250 mL of THF 11.5 mL of *n*BuLi (28.8 mmol, 2.5M in hexanes) was added dropwise at -78°C. The resulting suspension was stirred at this temperature for 1 hour, then 3.01 g (41.0 mmol) of N,N-dimethylformamide (DMF) was added in one portion. The resulting mixture was warmed to -10°C and quenched with 100 mL of 2N aqueous citric acid. The obtained mixture was extracted with 150 mL of dichloromethane, the organic extract was washed with 100 mL of water and 100 mL of brine, dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. The residue was triturated with 20 mL of n-pentane, the precipitate thus obtained was filtered off on a glass frit, washed with 2×10 ml of n-pentane and dried in vacuum. Yield: 7.10 g (83%) of the product as a light-yellow crystalline solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 10.19 (s, 1H), 7.51 (d, J = 2.2 Hz, 1H), 7.35 (d, J = 2.2 Hz,

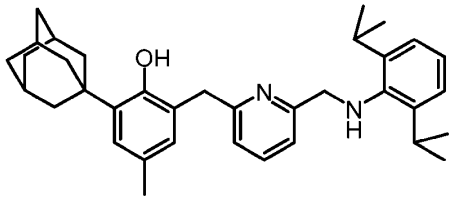
1H), 5.02 (s, 2H), 3.65 (s, 3H), 2.34 (s, 3H), 2.08-2.13 (m, 9H), 1.79 (br s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5, 158.3, 143.4, 134.2, 133.6, 130.6, 126.9, 102.6, 57.6, 41.5, 37.1, 36.8, 28.9, 20.9.

[0222] (3-(Adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methanol



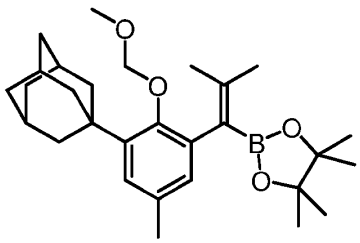
To a solution of 2.00 g (5.75 mmol) of *N*-((6-bromopyridin-2-yl)methyl)-2,6-diisopropylaniline in 24 mL of hexane-toluene mixture (2:1, vol.) 2.3 mL of *n*BuLi (5.75 mmol, 2.5M in hexanes) was added dropwise at -45°C. The resulting mixture was warmed to -10°C, stirred at this temperature for 5 minutes, cooled to -60°C, and 20 mL of diethyl ether was added, then, cooled to -90°C, and 6.72 mL of *t*BuLi (12.1 mmol, 1.8M in pentane) was added dropwise. The resulting suspension was warmed to -75°C, and a solution of 2.35 g (7.40 mmol) of 3-(adamantan-1-yl)-2-(methoxymethoxy)-5-methylbenzaldehyde in 5 mL of toluene was added in one portion. The mixture was warmed to -10°C and quenched with 150 mL of water. To the obtained two-phase mixture 150 mL of dichloromethane was added, the organic layer was separated, washed with 100 mL of water and 100 mL of brine, dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. Volatile impurities were distilled off using Kugelrohr apparatus (0.1 mbar, 150°C). The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane/EtOAc = 10/1, vol.). Yield: 2.22 g (66%) of the product as a light-yellow viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (t, J = 7.7 Hz, 1H), 7.12-7.25 (m, 5H), 7.06 (d, J = 1.8 Hz, 1H), 6.77 (d, J = 1.8 Hz, 1H), 6.30 (d, J = 3.2 Hz, 1H), 5.40 (d, J = 3.4 Hz, 1H), 5.27 (d, J = 5.3 Hz, 1H, AB), 5.20 (d, J = 5.3 Hz, 1H, AB), 4.25 (s, 2H), 4.09 (br.s, 1H), 3.71 (s, 3H), 3.39 (sept, J = 6.9 Hz, 1H), 2.21 (s, 3H), 2.08-2.20 (m, 9H), 1.82 (br.s, 6H), 1.28 (d, J = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.7, 156.3, 152.7, 142.73, 142.67, 142.1, 137.0, 136.6, 133.2, 127.6, 127.0, 123.5, 123.2, 120.1, 119.9, 101.1, 68.4, 57.1, 56.1, 41.4, 37.0, 36.6, 28.8, 27.5, 23.9, 23.81, 23.79, 20.8.

[0223] 2-(Adamantan-1-yl)-6-((6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methyl)-4-methylphenol



To a mixture of 30 mL of acetic acid and 7 ml of conc. HI 1.01 g (1.72 mmol) of (3-(adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methanol was added in one portion. The resulting suspension was heated to 95°C until complete dissolution of the starting material (ca. 20 minutes). The resulting solution was cooled to room temperature and poured into 500 mL of aqueous solution of $NaHCO_3$ (70 g) and Na_2SO_3 (6 g). To the obtained two-phase mixture, 150 ml of diethyl ether was added, the organic layer was separated and washed with 100 mL of water and 100 mL of brine, dried over Na_2SO_4, and passed through a short pad of silica gel, and the filtrate was evaporated under reduced pressure. The residue was triturated with 55 mL of methanol-dichloromethane mixture (10:1 vol.). From this mixture, dichloromethane was carefully evaporated under reduced pressure. The precipitate obtained was filtered off on a glass frit, washed with 2×5 mL of methanol and dried in vacuum. Yield: 590 mg (66%) of the product as a white crystalline powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.11 (s, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.12-7.14 (s, 3H), 6.95 (d, J = 1.8 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 4.18 (s, 2H), 4.08 (s, 2H), 3.42 (br.s, 1H), 3.23 (sept, J = 6.9 Hz, 1H), 2.27 (s, 3H), 2.19 (br.s, 6H), 2.06 (br.s, 3H), 1.72-1.84 (m, 6H), 1.21 (d, J = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.3, 158.5, 152.9, 142.9, 142.1, 139.0, 138.7, 128.5, 128.3, 127.5, 126.4, 124.3, 123.6, 121.0, 119.9, 56.7, 41.5, 40.6, 37.1, 37.0, 29.1, 27.7, 24.2, 20.8.

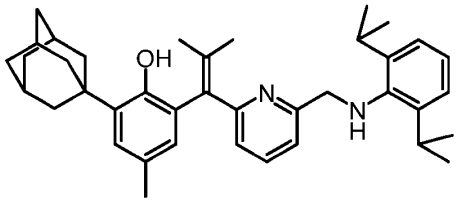
[0224] 2-(1-(3-(Adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-2-methylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



To a solution of 3.98 g (9.65 mmol) of (3-iodo-2-(methoxymethoxy)-5-methylphenyl)adamantane, 3.12 g (10.2 mmol) of 2,2'-(2-methylprop-1-ene-1,1-

diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 352 mg (0.48 mmol) of (1,1'-bis(diphenylphosphino)ferrocene)$PdCl_2$ in 200 mL of THF, 9.7 mL of aqueous KOH (29 mmol, 3M) was added dropwise at room temperature. This mixture was stirred at room temperature overnight and poured into 200 mL of water. To the obtained two-phase mixture, 150 mL of dichloromethane was added, the organic layer was separated, washed with 100 ml of water and 100 ml of brine, was dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was taken up in 150 mL of n-hexane, the obtained mixture was filtered (G4), and the filtrate was evaporated under reduced pressure to give 4.66 g (quant., 96% purity) of the product as a red viscous oil, which was used in the next step without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.94 (d, J = 2.0 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 5.04 (d, J = 4.7 Hz, 1H, AB), 4.68 (d, J = 4.7 Hz, 1H, AB), 3.58 (s, 3H), 2.27 (s, 3H), 2.14 (br.s, 6H), 2.08 (br.s, 3H), 2.07 (s, 3H), 1.77 (br.s, 6H), 1.72 (s, 3H), 1.26 (s, 12H).

[0225] 2-(Adamantan-1-yl)-6-(1-(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)-2-methylprop-1-en-1-yl)-4-methylphenol

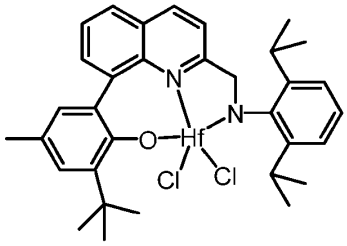


To a solution of 3.00 g (6.44 mmol) of 2-(1-(3-(adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-2-methylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 1.86 g (5.36 mmol) of *N*-((6-bromopyridin-2-yl)methyl)-2,6-diisopropylaniline and 240 mg (0.33 mmol) of (1,1'-bis(diphenylphosphino)ferrocene)$PdCl_2$ in 45 mL of 1,4-dioxane, 7.5 mL of aqueous KOH (22.5 mmol, 3M) was added dropwise at room temperature. This mixture was stirred at room temperature overnight and poured into 200 mL of water. To the obtained two-phase mixture, 150 mL of dichloromethane was added, the organic layer was separated, washed with 100 mL of water and 100 mL of brine, dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: dichloromethane). The solvent was evaporated under reduced pressure and the residue was dissolved in 80 mL of THF-methanol mixture (1:1, vol.), to which 2 mL of conc. HCl was added. The resulting solution was stirred at 60°C overnight and poured into 150 mL of water. To the obtained two-phase mixture, 150 mL of dichloromethane was added, the organic layer was separated, washed with 100 mL of water and 100 mL of brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was crystallized from n-pentane,

the crystals obtained were filtered off on a glass frit (G4), washed with 2×10 of n-pentane and dried in vacuum to give 1.71 g (57%) of the product as white crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.58 (s, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.08-7.13 (m, 3H), 6.95 (s, 1H), 6.74 (s, 1H), 3.48 (br.s, 1H), 3.21 (sept, J = 6.8 Hz, 2H), 2.25 (s, 3H), 2.11-2.24 (m, 6H), 2.04 (br.s, 3H), 1.84 (s, 3H), 1.74-1.82 (m, 6H), 1.70 (s, 3H), 1.20 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.8 Hz, 6H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.6, 157.7, 151.1, 142.5, 138.3, 137.3, 136.0, 133.4, 130.0, 128.1, 127.6, 126.1, 123.8, 123.2, 122.1, 119.5, 56.4, 40.2, 36.8, 36.6, 28.8, 27.3, 23.9, 23.8, 21.6, 21.2, 20.4.

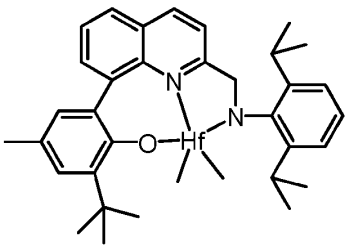
Preparation of the transition metal complexes

[0226] Complex 1-$HfCl_2$



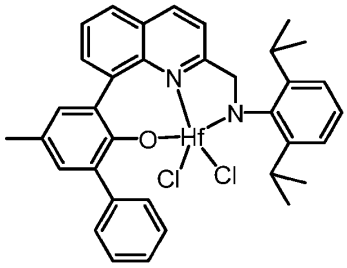
2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-*tert*-butylphenol (747 mg, 1.55 mmol) was dissolved in toluene (70 mL) and $Hf(NMe_2)_4$ (551 mg, 1.55 mmol) was subsequently added. The reaction mixture was stirred at 100°C overnight. The volatiles were then evaporated in vacuum, the residue was dissolved in toluene (70 mL) and Me_2SiCl_2 (1.0 mL, 7.75 mmol) was subsequently added. The reaction mixture was stirred at 55°C overnight, then, the volatiles were evaporated under reduced pressure. Recrystallization of the residue from toluene/hexane mixture gave 904 mg (80%) of complex **1-$HfCl_2$** as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.54 (d, J = 8.3 Hz, 1H), 8.02 (dd, $J1$ = 7.8 Hz, $J2$ = 1.6 Hz, 1H), 7.88 (m, 1H), 7.81 (m, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.29 (m, 1H), 7.18 (s, 3H), 6.63 (br.s, 1H), 5.18 (br.s, 2H), 3.46 (m, 2H), 2.30 (s, 3H), 1.56 (s, 9H), 1.25 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H).

[0227] Complex 1-$HfMe_2$



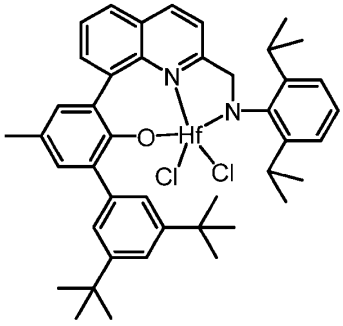
Complex **1-HfCl$_2$** (500 mg, 0.7 mmol) was dissolved in dry dichloromethane (50 mL) and solution of MeMgBr in diethyl ether (500 μL, 2.9 M) was added to the solution at room temperature. The mixture was stirred at room temperature overnight. The volatiles were evaporated under reduced pressure, the residue was extracted with hot hexane, and the extract was filtered through a short pad of diatomaceous earth. The filtrate was evaporated, and the residue was dried in vacuum to give complex **1-HfMe$_2$** (300 mg, 62%) as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.43 (d, J = 8.4 Hz, 1H), 7.94 (m, 1H), 7.82 (m, 1H), 7.73 (m, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.29 (m, 1H), 7.15-7.24 (m, 3H), 6.62 (m, 1H), 5.78 (m, 1H), 4.44 (m, 1H), 3.84 (m, 1H), 3.63 (m, 1H), 2.31 (s, 3H), 1.62 (s, 9H), 1.19-1.35 (m, 12H), -0.26 (s, 3H), -0.90 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2), 166.4, 156.8, 149.0, 146.7, 146.0, 145.8, 141.8, 138.1, 138.0, 136.3, 133.4, 131.3, 129.1, 128.4, 127.8, 127.7, 125.5, 124.4, 123.9, 119.6, 67.0, 56.2, 44.8, 35.3, 30.6, 28.1, 27.5, 26.2, 24.8, 24.5, 20.9.

[0228] Complex 2-HfCl$_2$



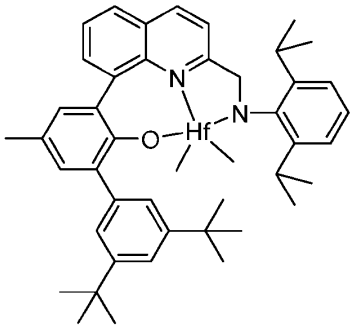
2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-phenylphenol (607 mg, 1.2 mmol) was dissolved in toluene (50 mL) and Hf(NMe$_2$)$_4$ (430 mg, 1.2 mmol) was subsequently added. The reaction mixture was stirred at 100°C overnight. The volatiles were then evaporated under reduced pressure, the residue was dissolved in toluene (50 mL) and Me_2SiCl_2 (0.8 mL, 6.0 mmol) was subsequently added. The reaction mixture was stirred at 55°C overnight, the volatiles were evaporated under reduced pressure, and the residue was recrystallized from toluene/hexane mixture to give complex **2-HfCl$_2$** (300 mg, 33%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.90 (m, 1H), 7.81 (m, 1H), 7.71 (d, J = 7.3 Hz, 2H), 7.56 (s, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.28-7.33 (m, 3H), 7.19-7.26 (m, 2H), 7.10-7.13 (m, 2H), 5.27 (m, 2H), 3.48 (m, 2H), 2.50 (s, 3H), 1.22 (d, J = 6.5 Hz, 6H), 1.14 (d, J = 5.4 Hz, 6H).

[0229] **Complex 3-$HfCl_2$**



2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-(3,5-di-*tert*-butylphenyl)phenol (380 mg, 0.62 mmol) was dissolved in toluene (50 mL) and $Hf(NMe_2)_4$ (220 mg, 0.62 mmol) was subsequently added. The reaction mixture was stirred at 100°C overnight. The volatiles were then evaporated under reduced pressure, the residue was dissolved in toluene (50 mL), and Me_2SiCl_2 (0.4 mL, 3.1 mmol) was subsequently added. The reaction mixture was stirred at 55°C overnight, then, the volatiles were evaporated under reduced pressure, and the residue was recrystallized from toluene/hexane mixture to give complex **3-$HfCl_2$** (200 mg, 37%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 8.5 Hz, 1H), 7.98 (m, 1H), 7.88 (m, 1H), 7.79 (m, 1H), 7.45 (m, 4H), 7.31 (m, 1H), 7.24-7.27 (m, 1H), 7.19 (m, 1H), 7.10 (m, 2H), 3.46 (br.s, 2H), 2.47 (s, 3H), 1.30 (s, 18H), 1.20 (d, J = 6.8 Hz, 6H), 1.13 (d, J = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 149.6, 149.3, 144.2, 141.5, 137.7, 136.7, 136.2, 135.1, 134.7, 129.0, 128.8, 128.2, 127.8, 125.9, 125.3, 124.1, 123.8, 121.6, 118.7, 66.3, 34.8, 31.5, 27.8, 25.3, 24.8, 22.6, 21.0, 14.1.

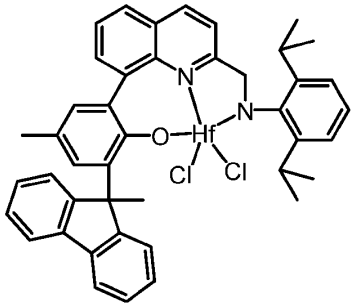
[0230] **Complex 3-$HfMe_2$**



Complex **3-$HfCl_2$** (100 mg, 0.12 mmol) was dissolved in dry dichloromethane, and solution of MeMgBr in diethyl ether (88 µL, 2.9 M) was added to the solution at room temperature. The resulting mixture was stirred at room temperature overnight. Then, the volatiles were evaporated under reduced pressure, the residue was extracted with hot hexane, and the extract

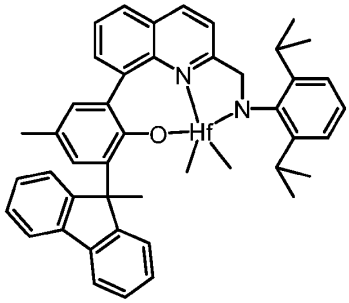
was filtered through a short pad of diatomaceous earth. The filtrate was evaporated, and the residue was dried in vacuum to give complex **3-HfMe$_2$** (82 mg, 56%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 1.7 Hz, 2H), 7.68 (dd, $J1$ = 7.2 Hz, $J2$ = 1.6 Hz, 1H), 7.64 (m, 1H), 7.59 (t, J = 1.8 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.30 (m, 1H), 7.21 (m, 3H), 7.10 (m, 1H), 6.83 (d, J = 2.1 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 5.30 (m, 1H), 5.06 (m, 1H), 4.17 (m, 1H), 3.51 (m, 1H), 2.31 (s, 3H), 1.49 (m, 3H), 1.48 (s, 18H), 1.34 (m, 6H), 1.17 (m, 3H), -0.12 (s, 3H), -0.23 (s, 3H).

[0231] Complex 4-HfCl$_2$



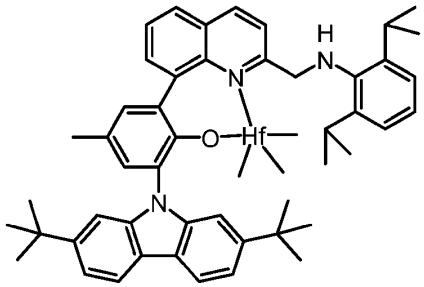
2-(2-(((2,6-Diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-(9-methyl-9-fluorenyl)phenol (1.0 g, 1.66 mmol) was dissolved in toluene (100 mL) and Hf(NMe$_2$)$_4$ (589 mg, 1.66 mmol) was subsequently added. The reaction mixture was stirred at 100°C overnight. The volatiles were then evaporated under reduced pressure, the residue was dissolved in toluene (100 mL) and Me_2SiCl_2 (1.0 mL, 8.3 mmol) was subsequently added. The reaction mixture was stirred at 55°C overnight, then, the volatiles were evaporated under reduced pressure, and the residue was recrystallized from toluene/hexane mixture to give complex **4-HfCl$_2$** (650 mg, 46%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 8.4 Hz, 1H), 7.98 (m, 1H), 7.70–7.76 (m, 3H), 7.53–7.69 (m, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.27–7.35 (m, 2H), 7.15–7.24 (m, 6H), 6.99 (br.s, 1H), 6.48 (d, J = 1.9 Hz, 1H), 5.31 (br.s, 2H), 3.71 (br.s, 2H), 2.35 (s, 3H), 2.03 (s, 3H), 1.34 (d, J = 6.8 Hz, 6H), 1.28 (d, J = 6.8 Hz, 6H).

[0232] **Complex 4-HfMe$_2$**



Complex **4-HfCl$_2$** (500 mg, 0.59 mmol) was dissolved in dry dichloromethane (50 mL), and solution of MeMgBr in diethyl ether (0.51 mL, 2.9 M) was added to the solution at room temperature. The resulting mixture was stirred at room temperature overnight. Then, the volatiles were evaporated under reduced pressure, the residue was extracted with toluene and filtered through a short pad of diatomaceous earth. The filtrate was evaporated under reduced pressure, and the residue was recrystallized from toluene/hexane mixture to give complex 4m (200 mg, 43%) as yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.3 Hz, 2H), 7.91 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.83 (dd, J = 7.2 Hz, J = 1.3 Hz, 1H), 7.75 (br.s, 1H), 7.71 (m, 1H), 7.60 (br.s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.44 (br.s, 2H), 7.31 (br.s, 2H), 7.28 (m, 1H), 7.18-7.22 (m, 3H), 6.65 (d, J = 1.9 Hz, 1H), 6.59 (d, J = 1.9 Hz, 1H), 5.86 (m, 1H), 4.49 (m, 1H), 3.81 (sept, J = 6.8 Hz, 2H), 2.47 (s, 3H), 2.02 (s, 3H), 1.23-1.31 (m, 12H), -0.17 (s, 3H), -0.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 157.6, 154.8, 148.2, 146.4, 145.1, 141.1, 137.8, 136.0, 134.5, 132.6, 131.9, 130.8, 129.0, 128.7, 128.2, 128.0, 127.4, 127.0, 125.2, 125.1, 124.1, 123.6, 120.1, 119.7, 119.0, 66.7, 57.3, 56.3, 45.2, 27.8, 27.6, 27.2, 25.9, 24.5, 20.4.

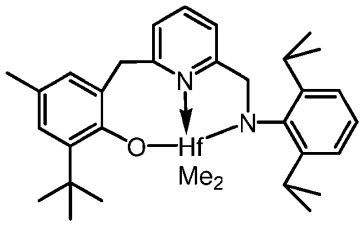
[0233] **Complex 5-HfMe$_3$**



A solution MeMgBr in diethyl ether (3.4 mL, 2.9 M) and a solution of 2-(2-(((2,6-diisopropylphenyl)amino)methyl)quinolin-8-yl)-4-methyl-6-(2,7-di-*tert*-butylcarbazol-9-yl)phenol (750 mg, 1.07 mmol) in toluene (20 mL) were subsequently added to a suspension

of $HfCl_4$ (349 mg, 1.07 mmol) in toluene (50 ml) at room temperature. The reaction mixture was stirred at room temperature overnight. Then, hexane (50 ml) was added to the mixture and the resulting suspension was filtered through a short pad of diatomaceous earth. The filtrate where evaporated under reduced pressure, and the residue was dissolved in toluene and filtered through a short pad of diatomaceous earth. The filtrate was evaporated under reduced pressure, and the residue was recrystallized from toluene/hexane mixture to give complex **5-HfMe$_3$** (510 mg, 52%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6): δ 8.08 (d, J = 8.1 Hz, 2H), 7.92 (s, 2H), 7.65 (dd, J = 7.0 Hz, J = 1.6 Hz, 1H), 7.46 (d, J = 1.8 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.37 (br.s, 2H), 7.14-7.23 (m, 2H), 7.01 (m, 3H), 6.77 (d, J = 1.9 Hz, 1H), 6.54 (d, J = 8.3 Hz, 1H), 5.26 (m, 1H), 4.50 (m, 1H), 3.87 (m, 1H), 3.19 (m, 1H), 2.19 (s, 3H), 1.10-1.51 (m, 30H), 0.49 (br.s, 3H), -0.42 (br.s, 3H), -0.83 (br.s, 3H).

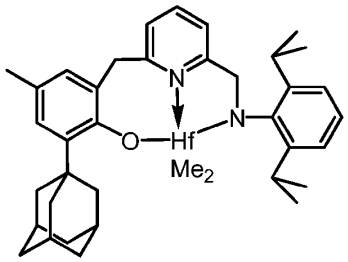
[0234] Complex 6-HfMe$_2$



To a suspension of 576 mg (1.80 mmol) of $HfCl_4$ in 50 ml of dry toluene, 3.02 ml (8.10 mmol, 2.7 M) of MeMgBr in diethyl ether was added in one portion at room temperature. The resulting mixture was stirred for 10 minutes, and a solution of 800 mg (1.00 mmol) of 2-(*tert*-butyl)-6-((6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methyl)-4-methylphenol in 10 ml of dry toluene was added dropwise for 5 minutes. The reaction mixture was stirred overnight at room temperature and then the solvents were evaporated under reduced pressure to near dryness. The solid residue was extracted with 2×20 ml of hot toluene, the combined extract was filtered through a short pad of diatomaceous earth, and the filtrate was evaporated under reduced pressure. The resulting solid was washed with 10×2 ml of *n*-pentane and dried in vacuum. Yield: 610 mg (49%) of complex **6-HfMe$_2$** as a white solid. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.25-7.33 (m, 3H), 7.19 (d, J = 2.1 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 6.65 (t, J = 7.6 Hz, 1H), 6.44 (d, J = 7.6 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H), 4.82-4.94 (m, 2H, AB), 4.54 (d, J = 13.1 Hz, 1H, AB), 4.36 (sept, J = 6.9 Hz, 1H), 3.46 (sept, J = 6.9 Hz, 1H), 3.23 (d, J = 13.1 Hz, 1H, AB), 2.29 (s, 3H), 1.62 (d, J = 6.9 Hz, 3H), 1.61 (s, 9H), 1.36 (d, J = 6.9 Hz, 6H), 1.28 (d, J = 6.9 Hz, 3H), 0.74 (s, 3H), 0.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.1, 159.5, 158.3, 149.0, 145.3, 144.8, 139.5, 137.8, 128.7, 127.7, 127.5, 127.0,

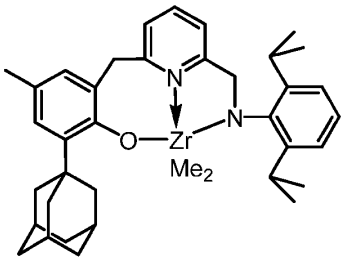
125.0, 123.9, 123.8, 122.2, 118.9, 67.7, 55.0, 47.4, 40.0, 34.7, 29.8, 29.7, 27.7, 27.5, 26.9, 26.3, 25.2, 24.3, 20.84, 20.82.

[0235] Complex 7-$HfMe_2$



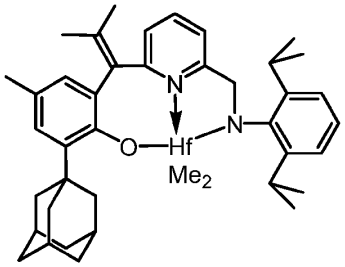
To a suspension of 153 mg (0.48 mmol) of $HfCl_4$ in 50 mL of dry toluene 0.695 mL (2.02 mmol, 2.9 M) of MeMgBr in diethyl ether was added in one portion at room temperature. The resulting mixture was stirred for 10 minutes, and a solution of 250 mg (0.48 mmol) of 2-(adamantan-1-yl)-6-((6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methyl)-4-methylphenol in 10 mL of dry toluene was added dropwise for 5 minutes. The reaction mixture was stirred overnight at room temperature and then the solvents were evaporated under reduced pressure. The residue was extracted with 2×20 ml of hot toluene, the combined extract was filtered through a short pad of diatomaceous earth, and the filtrate was evaporated under reduced pressure. The residue was washed with 10×2 ml of n-pentane and dried in vacuum. Yield: 252 mg (72%) of complex **7-$HfMe_2$** as a white solid. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.24-7.33 (m, 3H), 7.18 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 1.9 Hz, 1H), 6.68 (t, J = 7.8 Hz, 1H), 6.45 (d, J = 7.2 Hz, 1H), 6.15 (d, J = 7.2 Hz, 1H), 4.83-4.96 (m, 2H, AB), 4.54 (d, J = 13.2 Hz, 1H, AB), 4.39 (sept, J = 6.9 Hz, 1H), 3.47 (sept, J = 6.9 Hz, 1H), 3.24 (d, J = 13.2 Hz, 1H, AB), 2.42-2.51 (m, 3H), 2.32-2.38 (m, 3H), 2.34 (s, 3H), 2.15 (br.s, 3H), 1.92-2.00 (m, 3H), 1.71-1.80 (m, 3H), 1.62 (d, J = 6.9 Hz, 3H), 1.40 (d, J = 6.9 Hz, 3H), 1.34 (d, J = 6.9 Hz, 3H), 1.28 (d, J = 6.9 Hz, 3H), 0.76 (s, 3H), 0.44 (s, 3H). ^{13}C NMR (C_6D_6, 100 MHz): δ 163.2, 160.0, 159.9, 150.0, 145.9, 145.1, 139.6, 139.0, 129.7, 129.2, 128.9, 128.5, 128.3, 126.1, 124.8, 124.7, 122.0, 118.7, 68.6, 57.5, 48.3, 41.5, 40.6, 38.0, 37.7, 29.9, 28.7, 28.3, 27.6, 27.3, 25.7, 25.2, 21.5.

[0236] **Complex 7-$ZrMe_2$**



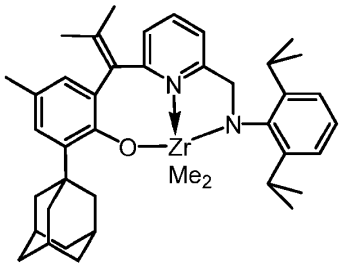
To a suspension of 112 mg (0.48 mmol) of $ZrCl_4$ in 50 mL of dry toluene 0.695 mL (2.02 mmol, 2.9 M) of MeMgBr in diethyl ether was added in one portion at room temperature. The resulting mixture was stirred for 10 minutes, and a solution of 250 mg (0.48 mmol) of 2-(adamantan-1-yl)-6-((6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)methyl)-4-methylphenol in 10 mL of dry toluene was added dropwise for 5 minutes. The reaction mixture was stirred overnight at room temperature and then evaporated under reduced pressure. The residue was extracted with 2×20 ml of hot toluene, the combined extract was filtered through a short pad of diatomaceous earth, and the filtrate was evaporated in vacuum. The residue was washed with 10×2 ml of n-pentane and dried in vacuum. Yield: 233 mg (76%) of complex **7-$ZrMe_2$** as a white solid. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.21-7.33 (m, 3H), 7.16 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 1.9 Hz, 1H), 6.68 (t, J = 7.7 Hz, 1H), 6.47 (d, J = 7.5 Hz, 1H), 6.16 (d, J = 7.5 Hz, 1H), 4.68-4.84 (m, 2H, AB), 4.50 (d, J = 13.3 Hz, 1H, AB), 4.47 (sept, J = 6.9 Hz, 1H), 3.39 (sept, J = 6.9 Hz, 1H), 3.26 (d, J = 13.3 Hz, 1H, AB), 2.46-2.51 (m, 3H), 2.32-2.39 (m, 3H), 2.33 (s, 3H), 2.14 (br.s, 3H), 1.92-2.00 (m, 3H), 1.73-1.80 (m, 3H), 1.64 (d, J = 6.9 Hz, 3H), 1.38 (d, J = 6.9 Hz, 3H), 1.35 (d, J = 6.9 Hz, 3H), 1.27 (d, J = 6.9 Hz, 3H), 0.92 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (C_6D_6, 100 MHz): δ 162.7, 159.9, 159.4, 150.0, 145.4, 144.7, 139.5, 138.4, 129.7, 129.3, 128.9, 128.5, 128.3, 126.2, 126.0, 124.8, 121.8, 118.6, 68.4, 49.3, 41.5, 41.0, 39.4, 38.0, 37.6, 30.0, 28.8, 28.4, 27.5, 27.2, 25.7, 25.1, 21.5.

[0237] **Complex 8-$HfMe_2$**



To a suspension of 290 mg (0.62 mmol) of $HfCl_4$ in 50 mL of dry toluene, 0.760 mL (2.80 mmol, 3.7 M) of MeMgBr in diethyl ether was added in one portion at room temperature. The resulting mixture was stirred for 10 minutes, and a solution of 350 mg (0.48 mmol) of 2-(adamantan-1-yl)-6-(1-(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)-2-methylprop-1-en-1-yl)-4-methylphenol in 10 mL of dry toluene was added dropwise for 1 minute. The reaction mixture was stirred overnight at room temperature and the solvents were evaporated under reduced pressure. The residue was extracted with 2×20 ml of hot toluene, the combined extract was filtered through a short pad of diatomaceous earth, and the filtrate was evaporated under reduced pressure. The residue was washed with 10×2 ml of n-pentane and dried in vacuum to give 395 mg (83%) of complex **8-HfMe$_2$** as a beige solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.86 (t, J = 7.7 Hz, 1H), 7.12-7.30 (m, 5H), 7.04 (d, J = 1.9 Hz, 1H), 6.85 (d, J = 1.9 Hz, 1H), 5.07 (d, J = 20.6 Hz, 1H, AB), 4.94 (d, J = 20.6 Hz, 1H, AB), 4.19 (sept, J = 6.9 Hz, 1H), 3.18 (sept, J = 6.9 Hz, 1H), 2.27 (s, 3H), 2.20-2.29 (m, 3H), 2.10-2.16 (m, 3H), 2.02 (br.s, 3H), 1.79-1.85 (m, 3H), 1.64-1.75 (m, 3H), 1.70 (s, 3H), 1.57 (s, 3H), 1.41 (d, J = 6.9 Hz, 3H), 1.30 (d, J = 6.9 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.9 Hz, 3H), 0.11 (s, 3H), -0.31 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 164.0, 160.5, 159.2, 151.0, 146.0, 145.4, 140.1, 138.8, 138.7, 132.8, 131.6, 129.0, 128.7, 128.2, 125.1, 124.23, 124.18, 123.3, 119.5, 68.3, 55.4, 48.6, 41.2, 37.7, 37.5, 29.8, 28.2, 27.9, 27.2, 27.0, 25.2, 24.8, 21.9, 21.6.

[0238] Complex 8-ZrMe$_2$



To a suspension of 145 mg (0.62 mmol) of $ZrCl_4$ in 50 mL of dry toluene 0.760 mL (2.80 mmol, 3.7 M) of MeMgBr in diethyl ether was added in one portion at room temperature. The resulting mixture was stirred for 10 minutes, and a solution of 350 mg (0.48 mmol) of 2-(adamantan-1-yl)-6-(1-(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)-2-methylprop-1-en-1-yl)-4-methylphenol in 10 mL of dry toluene was added dropwise for 1 minute. The reaction mixture was stirred overnight at room temperature and the solvents were evaporated under reduced pressure. The residue was extracted with 2×20 ml of hot toluene, the combined extract was filtered through a short pad of diatomaceous earth, and the filtrate was evaporated under reduced pressure. The residue was washed with 10×2 ml of n-pentane

and dried in vacuum to give 370 mg (87%) of complex **8-ZrMe$_2$** as a beige solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.84 (t, J = 7.7 Hz, 1H), 7.10-7.28 (m, 5H), 7.04 (d, J = 1.9 Hz, 1H), 6.85 (d, J = 1.9 Hz, 1H), 4.96 (d, J = 20.8 Hz, 1H, AB), 4.82 (d, J = 20.8 Hz, 1H, AB), 4.29 (sept, J = 6.9 Hz, 1H), 3.12 (sept, J = 6.9 Hz, 1H), 2.23-2.31 (m, 3H), 2.27 (s, 3H), 2.11-2.20 (m, 3H), 2.03 (br.s, 3H), 1.80-1.87 (m, 3H), 1.66-1.73 (m, 3H), 1.71 (s, 3H), 1.55 (s, 3H), 1.43 (d, J = 6.9 Hz, 3H), 1.31 (d, J = 6.9 Hz, 3H), 1.13 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.9 Hz, 3H), 0.29 (s, 3H), -0.10 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 163.5, 160.4, 158.6, 151.3, 145.4, 144.9, 140.0, 138.6, 138.2, 133.1, 132.0, 129.1, 128.1, 127.8, 125.1, 124.3, 124.2, 123.0, 119.4, 68.1, 47.4, 41.3, 39.3, 37.8, 37.5, 29.8, 28.2, 28.0, 27.1, 27.0, 25.2, 24.7, 21.8, 21.6.

Polymerization Examples

[0239] Solutions of the pre-catalysts were made using toluene (ExxonMobil Chemical—anhydrous, stored under N_2) (98%). Pre-catalyst solutions were typically 0.5 mmol/L.

[0240] Solvents, polymerization grade toluene and/or isohexanes were supplied by ExxonMobil Chemical Co. and are purified by passing through a series of columns: two 500 cc Oxyclear cylinders in series from Labclear (Oakland, Calif.), followed by two 500 cc columns in series packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and two 500 cc columns in series packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company).

[0241] 1-octene (C_8; 98%, Aldrich Chemical Company) was dried by stirring over NaK overnight followed by filtration through basic alumina (Aldrich Chemical Company, Brockman Basic 1).

[0242] Polymerization grade ethylene (C_2) was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, Calif.) followed by a 500 cc column packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and a 500 cc column packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company).

[0243] Polymerization grade propylene (C_3) was used and further purified by passing it through a series of columns: 2250 cc Oxiclear cylinder from Labclear followed by a 2250 cc column packed with 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then two 500 cc columns in series packed with 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then a 500 cc column packed with Selexsorb CD (BASF), and finally a 500 cc column packed with Selexsorb COS (BASF).

[0244] Activation of the pre-catalysts was either by methylalumoxane (MAO, 10 wt% in toluene, Albemarle Corp.; Act ID = M), or dimethylanilinium tetrakis(perfluorophenyl)borate

(Boulder Scientific or Albemarle Corp; Act ID = D). MAO was used as a 0.5 wt% or 1.0 wt% in toluene solution. Micromoles of MAO reported in the experimental section are based on the micromoles of aluminum in MAO. The formula weight of MAO is 58.0 grams/mole. Dimethylanilinium tetrakis(perfluorophenyl)borate was typically used as a 0.5 mmol/L solution in toluene.

[0245] For polymerization runs using dimethylanilinium tetrakis(perfluorophenyl)borate, tri-n-octylaluminum (TnOAl, Neat, AkzoNobel) was also used as a scavenger prior to introduction of the activator and pre-catalyst into the reactor. TnOAl was typically used as a 5 mmol/L solution in toluene.

Reactor Description and Preparation:

[0246] Polymerizations were conducted in an inert atmosphere (N2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor = 23.5 mL for C_2 and C_2/C_8; 22.5 mL for C_3 runs), septum inlets, regulated supply of nitrogen, ethylene and propylene, and equipped with disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen at 110°C or 115°C for 5 hours and then at 25°C for 5 hours.

Ethylene Polymerization (PE) or Ethylene/1-octene Copolymerization (EO):

[0247] The reactor was prepared as described above, and then purged with ethylene. For MAO (Act ID = M) activated runs, toluene, 1-octene (0.100 mL when used), and activator (MAO) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80°C) and charged with ethylene to process pressure (75 psig=618.5 kPa or 200 psig=1480.3 kPa) while stirring at 800 RPM. The pre-catalyst solution was then added via syringe to the reactor at process conditions. For dimethylanilinium tetrakisperfluorophenylborate (Act ID = D) activated runs, toluene, 1-octene (100 μL when used) and tri(n-octyl)aluminum scavenger (TnOAl, 0.5 μmol) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80°C) and charged with ethylene to process pressure (75 psig=618.5 kPa or 200 psig=1480.3 kPa) while stirring at 800 RPM. The activator solution, followed by the pre-catalyst solution, was injected via syringe to the reactor at process conditions. Ethylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (+/−2 psig). Reactor temperature was monitored and typically maintained within +/−1°C. Polymerizations were halted by addition of approximately 50 psi compressed dry air gas mixture to the autoclave for approximately 30 seconds. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been

added (maximum quench value in psid) or for a maximum of 30 minutes polymerization time. Afterwards, the reactors were cooled and vented. Polymers were isolated after the solvent was removed in-*vacuo*. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr). Ethylene homopolymerization runs and ethylene/1-octene copolymerization runs are summarized in Table 1.

Propylene Polymerization (PP):

[0248] The reactor was prepared as described above, then heated to 40°C, and then purged with propylene gas at atmospheric pressure. For MAO activated runs, toluene or isohexane, MAO, and liquid propylene (1.0 mL) were added via syringe. The reactor was then heated to process temperature (70°C or 100°C) while stirring at 800 RPM. The pre-catalyst solution was added via syringe with the reactor at process conditions. For dimethylanilinium tetrakisperfluorophenylborate activated runs, toluene or isohexanes, liquid propylene (1.0 mL) and tri(n-octyl)aluminum scavenger (TnOAl, 0.5 μmol) were added via syringe. The reactor was then brought to process temperature (70°C or 100°C) while stirring at 800 RPM. The activator solution, followed by the pre-catalyst solution, were injected via syringe to the reactor at process conditions. Reactor temperature was monitored and typically maintained within +/−1°C. Polymerizations were halted by addition of approximately 50 psi compressed dry air gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of 8 psid (maximum quench value) or for a maximum of 30 minutes. The reactors were cooled and vented. The polymers were isolated after the solvent was removed in-*vacuo*. The actual quench time (s) is reported as quench time(s). Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr). Propylene homopolymerization examples are reported in Table 2.

Polymer Characterization

[0249] For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich) containing 2,6-di-tert-butyl-4-methylphenol (BHT, 99% from Aldrich) at 165°C in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was between 0.1 to 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples were cooled to 135°C for testing.

[0250] High temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as described in U.S. Patents 6,491,816; 6,491,823; 6,475,391;

6,461,515; 6,436,292; 6,406,632; 6,175,409; 6,454,947; 6,260,407; and 6,294,388; each of which is incorporated herein by reference. Molecular weights (weight average molecular weight (Mw) and number average molecular weight (Mn)) and molecular weight distribution (MWD = Mw/Mn), which is also sometimes referred to as the polydispersity (PDI) of the polymer, were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with evaporative light scattering detector (ELSD) and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 5000 and 3,390,000). Alternatively, samples were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with dual wavelength infrared detector and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 580 and 3,039,000). Samples (250 μL of a polymer solution in TCB were injected into the system) were run at an eluent flow rate of 2.0 mL/minute (135°C sample temperatures, 165°C oven/columns) using three Polymer Laboratories: PLgel 10μm Mixed-B 300 x 7.5mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch® software available from Symyx Technologies or Automation Studio software available from Freeslate. The molecular weights obtained are relative to linear polystyrene standards. Molecular weight data is reported in Tables 1 and 2 under the headings Mn, Mw, Mz and PDI as defined above.

[0251] Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220°C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/minute and then cooled at a rate of 50°C/minute. Melting points were collected during the heating period. The results are reported in the Tables 1 and 2 under the heading, Tm (°C)

[0252] Samples for infrared analysis were prepared by depositing the stabilized polymer solution onto a silanized wafer (Part number S10860, Symyx). By this method, approximately between 0.12 and 0.24 mg of polymer is deposited on the wafer cell. The samples were subsequently analyzed on a Brucker Equinox 55 FTIR spectrometer equipped with Pikes' MappIR specular reflectance sample accessory. Spectra, covering a spectral range of 5000 cm^{-1} to 500 cm^{-1}, were collected at a 2 cm^{-1} resolution with 32 scans.

[0253] For ethylene-1-octene copolymers, the wt% octene in the copolymer was determined via measurement of the methyl deformation band at ~1375 cm^{-1}. The peak height of this band was normalized by the combination and overtone band at ~4321 cm^{-1}, which corrects for path length differences. The normalized peak height was correlated to individual

calibration curves from ^{1}H NMR data to predict the wt% octene content within a concentration range of ~2 wt% to 35 wt% for octene. Typically, R^2 correlations of 0.98 or greater are achieved. These numbers are reported in Table 1 under the heading C_8 wt%).

[0254] Polymerization results are collected in Tables 1 and 2 below. "Ex#" stands for example number. Under the Ex# column heading, the following abbreviations are defined: PE = polyethylene, EO = ethylene-1-octene copolymer, PP = polypropylene, CPE = comparative polyethylene, CEO = comparative ethylene-1-octene copolymer, CPP = comparative polypropylene. Examples starting with a "C" as in CPP and CPE are comparative examples. "Cat ID" identifies the pre-catalyst used in the experiment. Corresponding numbers identifying the pre-catalyst (also referred to as pre-catalyst, complex or compound) are located in the synthetic experimental section. "Cat (μmol)" is the amount of pre-catalyst added to the reactor. For all experiments using dimethylanilinium tetrakis(perfluorophenyl)borate (Act ID = D), the molar ratio of activator/pre-catalyst was 1.1. For all experiments using MAO (Act ID = M) as the activator, a 500 Al/M molar ratio was used unless noted otherwise. T(°C) is the polymerization temperature which was typically maintained within +/- 1°C. "Yield" is polymer yield, and is not corrected for catalyst residue. "Quench time (s)" is the actual duration of the polymerization run in seconds. "Quench Value (psid)" for ethylene based polymerization runs is the set maximum amount of ethylene uptake (conversion) for the experiment. If a polymerization quench time is less than the maximum time set, then the polymerization ran until the set maximum value of ethylene uptake was reached. For propylene homopolymerization runs, quench value indicates the maximum set pressure loss (conversion) of propylene (for PP runs) during the polymerization. Activity is reported at grams polymer per mmol of catalyst per hour.

Table 1. Ethylene homopolymerizations and ethylene/1-octene copolymerization examples

[0255] General reaction conditions: Total solvent volume including catalyst and activator diluents was 5.0 ml toluene for ethylene homopolymerizations and 4.9 ml toluene for ethylene-octene copolymerizations with 0.1 mL 1-octene (shown in table in microliters (uL)); 25 nmol pre-catalyst and 500 equiv. Act ID M or 1.1 equiv. Act ID D; 80°C polymerization temperature; 75 or 200 psi of ethylene with uptake; Quench Value was set at 20 psid ethylene uptake when 75 psi of ethylene was used and at 15 psid ethylene uptake when 200 psi of ethylene was used, or for a maximum time of 30 minutes. *Indicates that the FTIR value reported is outside the calibration range.

Table 1

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
PE-1	Complex 1-HfCl2	M	0	75	1801	0.0232	1,855	37,407	218,072	3,623,184	5.83		133.3
PE-2	Complex 1-HfCl2	M	0	75	1800	0.0233	1,864	52,901	770,400	4,729,889	14.6		133.9
PE-3	Complex 1-HfCl2	M	0	75	1801	0.0188	1,503	40,660	521,914	5,595,676	12.8		133.4
EO-1	Complex 1-HfCl2	M	100	75	1801	0.0152	1,215	46,086	382,665	4,529,573	8.30	5.7	122.0
EO-2	Complex 1-HfCl2	M	100	75	1800	0.0283	2,264	39,540	185,918	5,178,666	4.70	3.4*	126.2
EO-3	Complex 1-HfCl2	M	100	75	1312	0.0295	3,238	36,497	345,822	5,395,443	9.48	5.1	122.6
EO-4	Complex 1-HfCl2	M	100	200	430	0.0219	7,334	93,119	662,735	6,596,104	7.12	3.4*	127.1
EO-5	Complex 1-HfCl2	M	100	200	551	0.0260	6,795	118,460	856,756	3,973,931	7.23	3.7*	126.9
EO-6	Complex 1-HfCl2	M	100	200	516	0.0245	6,837	98,669	643,810	5,256,631	6.52	3.4*	126.8
PE-4	Complex 2-HfCl2	M	0	75	1800	0.0270	2,160	40,615	529,665	5,683,829	13.0		132.7
PE-5	Complex 2-HfCl2	M	0	75	1800	0.0287	2,296	34,800	311,845	3,391,162	8.96		132.8
PE-6	Complex 2-HfCl2	M	0	75	1800	0.0269	2,152	38,859	463,319	4,661,171	11.9		132.7
EO-7	Complex 2-HfCl2	M	100	75	1801	0.0113	903	7,681	249,796	5,982,820	32.5	9.4	123.1
EO-8	Complex 2-HfCl2	M	100	75	1800	0.0202	1,616	8,913	184,286	4,355,358	20.7	9.8	122.6
EO-9	Complex 2-HfCl2	M	100	75	1800	0.0285	2,280	9,029	87,573	2,011,429	9.70	8.3	122.7
EO-10	Complex 2-HfCl2	M	100	200	682	0.0269	5,680	26,957	619,360	4,953,296	23.0	4.3	126.1
EO-11	Complex 2-HfCl2	M	100	200	422	0.0187	6,381	23,795	598,153	4,711,471	25.1	4.1	126.5
EO-12	Complex 2-HfCl2	M	100	200	713	0.0311	6,281	29,661	611,524	4,951,581	20.6	4.1	126.1
PE-7	Complex 3-HfCl2	M	0	75	771	0.0376	7,023	53,237	149,992	662,944	2.82		133.6
PE-8	Complex 3-HfCl2	M	0	75	878	0.0388	6,364	50,203	151,076	747,297	3.01		133.3
PE-9	Complex 3-HfCl2	M	0	75	844	0.0387	6,603	52,182	152,771	739,726	2.93		

Table 1 – *(Cont.)*

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
EO-13	Complex 3-HfCl2	M	100	75	569	0.0285	7,213	25,407	41,122	75,436	1.62	8.9	114.2
EO-14	Complex 3-HfCl2	M	100	75	631	0.0350	7,987	26,359	41,349	73,514	1.57	7.9	116.6
EO-15	Complex 3-HfCl2	M	100	75	628	0.0353	8,094	27,938	43,039	77,350	1.54	7.2	116.2
EO-16	Complex 3-HfCl2	M	100	200	239	0.0339	20,425	49,655	426,236	3,927,520	8.58	4.1	124.9
EO-17	Complex 3-HfCl2	M	100	200	290	0.0382	18,968	50,381	441,782	5,397,303	8.77	4.1	124.4
EO-18	Complex 3-HfCl2	M	100	200	348	0.0471	19,490	61,005	377,648	3,601,432	6.19	4.4	125.1
PE-10	Complex 3-HfMe2	D	0	75	39	0.0672	248,123	84,698	138,705	277,401	1.64		135.7
PE-11	Complex 3-HfMe2	D	0	75	38	0.0702	266,021	89,878	157,026	387,542	1.75		135.8
PE-12	Complex 3-HfMe2	D	0	75	40	0.0681	245,160	81,861	157,801	460,119	1.93		135.7
PE-13	Complex 3-HfMe2	M	0	75	273	0.0428	22,576	74,891	573,390	4,152,887	7.66		134.4
PE-14	Complex 3-HfMe2	M	0	75	352	0.0466	19,064	93,058	534,599	3,556,277	5.74		134.3
PE-15	Complex 3-HfMe2	M	0	75	338	0.0466	19,853	76,601	464,451	2,878,995	6.06		134.3
EO-19	Complex 3-HfMe2	D	100	75	137	0.0296	31,112	30,360	58,681	153,243	1.93	6.4	119.4
EO-20	Complex 3-HfMe2	D	100	75	39	0.0684	252,554	25,897	48,075	110,660	1.86	9.4	115.4
EO-21	Complex 3-HfMe2	D	100	75	46	0.0615	192,522	30,513	54,805	139,710	1.80	7.4	116.4
EO-22	Complex 3-HfMe2	M	100	75	321	0.0406	18,213	28,250	45,191	85,657	1.60	10.0	113.9
EO-23	Complex 3-HfMe2	M	100	75	309	0.0373	17,383	27,954	44,891	81,647	1.61	8.7	113.6
EO-24	Complex 3-HfMe2	M	100	75	329	0.0429	18,777	32,882	48,718	87,742	1.48	9.1	114.6
EO-25	Complex 3-HfMe2	D	100	200	20	0.1099	791,280	45,877	80,084	178,993	1.75	3.4*	124.5
EO-26	Complex 3-HfMe2	D	100	200	29	0.0864	429,021	48,276	89,456	215,768	1.85	3.4*	125.1
EO-27	Complex 3-HfMe2	D	100	200	20	0.1115	802,800	43,342	81,083	187,750	1.87	3.7*	124.6
EO-28	Complex 3-HfMe2	M	100	200	155	0.0566	52,583	59,752	353,091	3,608,154	5.91	4.4	124.4

Table 1 – *(Cont.)*

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
EO-29	Complex 3-HfMe2	M	100	200	137	0.0646	67,901	62,999	414,969	5,291,963	6.59	4.7	124.6
EO-30	Complex 3-HfMe2	M	100	200	131	0.0621	68,263	67,890	314,681	2,922,398	4.64	5.0	124.6
PE-16	Complex 1-HfMe2	M	0	75	538	0.0386	10,332	66,563	123,944	357,129	1.86		134.3
PE-17	Complex 1-HfMe2	M	0	75	403	0.0366	13,078	60,436	102,802	225,138	1.70		134.3
PE-18	Complex 1-HfMe2	M	0	75	421	0.0413	14,126	61,838	109,655	239,144	1.77		134.4
EO-31	Complex 1-HfMe2	M	100	75	296	0.0387	18,827	72,699	125,778	265,531	1.73	5.8	119.8
EO-32	Complex 1-HfMe2	M	100	75	269	0.0380	20,342	73,165	127,041	250,805	1.74	5.2	119.7
EO-33	Complex 1-HfMe2	M	100	75	357	0.0363	14,642	64,519	106,635	212,397	1.65	5.3	119.8
EO-34	Complex 1-HfMe2	M	100	200	125	0.0431	49,651	137,565	214,289	425,702	1.56	2.6*	126.3
EO-35	Complex 1-HfMe2	M	100	200	109	0.0369	48,749	141,816	227,648	476,532	1.61	3.1*	126.1
EO-36	Complex 1-HfMe2	M	100	200	134	0.0530	56,955	140,418	240,794	574,571	1.71	2.8*	126.6
PE-19	Complex 6-HfMe2	D	0	75	96	0.0551	82,650	380,782	688,176	1,817,338	1.81		136.3
PE-20	Complex 6-HfMe2	D	0	75	92	0.0514	80,452	346,406	624,372	1,325,931	1.80		136.6
PE-21	Complex 6-HfMe2	D	0	75	99	0.0516	75,055	350,388	627,550	1,360,100	1.79		136.6
PE-22	Complex 6-HfMe2	M	0	75	1423	0.0304	3,076	51,257	778,790	4,575,204	15.2		133.8
PE-23	Complex 6-HfMe2	M	0	75	1602	0.0326	2,930	65,326	1,013,279	6,196,270	15.5		133.9
PE-24	Complex 6-HfMe2	M	0	75	1570	0.0322	2,953	56,557	1,026,015	5,702,171	18.1		134.1
EO-37	Complex 6-HfMe2	D	100	75	115	0.0524	65,614	266,115	417,666	828,155	1.57	16.6	87.8
EO-38	Complex 6-HfMe2	D	100	75	121	0.0493	58,671	224,596	382,264	781,921	1.70	18.3	88.5
EO-39	Complex 6-HfMe2	D	100	75	117	0.0564	69,415	209,875	368,155	765,206	1.75	16.6	87.4
EO-40	Complex 6-HfMe2	M	100	75	1801	0.0056	448						
EO-41	Complex 6-HfMe2	M	100	75	1801	0.0167	1,335	26,871	55,791	176,185	2.08	16.7	98.3
EO-42	Complex 6-HfMe2	M	100	75	1801	0.0145	1,159	21,421	57,873	215,596	2.70	11.5	98.5

Table 1 – *(Cont.)*

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
EO-43	Complex 6-HfMe2	D	100	200	62	0.0493	114,503	372,644	668,881	1,519,845	1.79	9.0	108.8
EO-44	Complex 6-HfMe2	D	100	200	63	0.0719	164,343	343,368	630,193	1,386,400	1.84	10.8	107.4
EO-45	Complex 6-HfMe2	D	100	200	61	0.0760	179,410	345,115	632,348	1,401,999	1.83	8.7	107.5
EO-46	Complex 6-HfMe2	M	100	200	575	0.0109	2,730	47,910	122,869	590,264	2.56	5.1	123.6
EO-47	Complex 6-HfMe2	M	100	200	1473	0.0314	3,070	59,768	111,501	292,865	1.87	7.1	120.8
EO-48	Complex 6-HfMe2	M	100	200	1081	0.0198	2,638	44,601	118,077	501,216	2.65	5.9	122.1
PE-25	Complex 7-HfMe2	D	0	75	83	0.0685	118,843	269,356	502,158	1,026,836	1.86		133.3
PE-26	Complex 7-HfMe2	D	0	75	96	0.0786	117,900	296,272	535,836	1,122,522	1.81		135.7
PE-27	Complex 7-HfMe2	D	0	75	146	0.0830	81,863	317,436	577,595	1,214,189	1.82		135.5
EO-49	Complex 7-HfMe2	D	100	75	75	0.0799	153,408	190,362	346,274	730,598	1.82	31.1	67.7
EO-50	Complex 7-HfMc2	D	100	75	81	0.0846	150,400	195,468	352,182	698,917	1.80	27.9	69.1
EO-51	Complex 7-HfMe2	D	100	75	78	0.0812	149,908	203,708	367,628	766,601	1.80	29.8	74.5
EO-52	Complex 7-HfMe2	D	100	200	124	0.1795	208,452	278,406	545,666	1,183,470	1.96	20.3	97.1
EO-53	Complex 7-HfMe2	D	100	200	117	0.1831	225,354	306,770	637,867	1,699,900	2.08	16.6	97.4
EO-54	Complex 7-HfMe2	D	100	200	130	0.1782	197,391	309,741	605,855	1,427,239	1.96	16.5	97.3
PE-28	Complex 7-ZrMe2	D	0	75	51	0.0771	217,694	220,279	417,608	946,430	1.90		134.3
PE-29	Complex 7-ZrMe2	D	0	75	51	0.0771	217,694	218,165	436,054	1,107,057	2.00		133.6
PE-30	Complex 7-ZrMe2	D	0	75	55	0.0788	206,313	196,745	430,282	1,062,889	2.19		135.3
EO-55	Complex 7-ZrMe2	D	100	75	51	0.0811	228,988	121,022	239,565	559,479	1.98	24.1	92.2
EO-56	Complex 7-ZrMe2	D	100	75	51	0.0813	229,553	117,116	237,289	548,121	2.03	23.1	92.7
EO-57	Complex 7-ZrMe2	D	100	75	53	0.0804	218,445	138,655	269,165	745,203	1.94	22.3	92.4
EO-58	Complex 7-ZrMe2	D	100	200	40	0.1312	472,320	192,145	394,904	936,757	2.06	10.3	107.7
EO-59	Complex 7-ZrMe2	D	100	200	50	0.1298	373,824	202,402	388,266	874,563	1.92	9.2	108.2

Table 1 – *(Cont.)*

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
EO-60	Complex 7-ZrMe2	D	100	200	40	0.1184	426,240	205,472	397,871	918,730	1.94	9.4	108.5
PE-31	Complex 4-HfMe2	D	0	75	1800	0	0						
PE-32	Complex 4-HfMe2	D	0	75	1801	0	0						
PE-33	Complex 4-HfMe2	D	0	75	1800	0	0						
PE-34	Complex 4-HfMe2	M	0	75	1800	0.0014	112						
PE-35	Complex 4-HfMe2	M	0	75	1801	0.0009	72						
PE-36	Complex 4-HfMe2	M	0	75	1800	0.0013	104						
EO-61	Complex 4-HfMe2	D	100	75	1801	0	0						
EO-62	Complex 4-HfMe2	D	100	75	1801	0	0						
EO-63	Complex 4-HfMe2	D	100	75	1801	0	0						
EO-64	Complex 4-HfMc2	M	100	75	1801	0.0001	8						
EO-65	Complex 4-HfMe2	M	100	75	1800	0.0000	0						
EO-66	Complex 4-HfMe2	M	100	75	1801	0.0007	56						
EO-67	Complex 4-HfMe2	D	100	200	1107	0	0						
EO-68	Complex 4-HfMe2	D	100	200	1801	0	0						
EO-69	Complex 4-HfMe2	D	100	200	1800	0	0						
EO-70	Complex 4-HfMe2	M	100	200	1801	0.0015	120						
EO-71	Complex 4-HfMe2	M	100	200	1223	0.0013	153						
EO-72	Complex 4-HfMe2	M	100	200	1801	0.0016	128						
PE-37	Complex 8-HfMe2	D	0	75	105	0.0762	104,503	299,578	647,045	1,805,284	2.16		135.8
PE-38	Complex 8-HfMe2	D	0	75	86	0.0781	130,772	237,828	681,290	2,237,823	2.86		136.8
PE-39	Complex 8-HfMe2	D	0	75	111	0.0769	99,762	313,278	723,340	2,657,159	2.31		135.3
EO-73	Complex 8-HfMe2	D	100	75	81	0.0971	172,622	175,366	439,175	1,591,609	2.5	14.0	108.1

Table 1 – *(Cont.)*

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
EO-74	Complex 8-HfMe2	D	100	75	62	0.0713	165,600	280,862	560,104	1,445,206	1.99	14.2	113.4
EO-75	Complex 8-HfMe2	D	100	75	76	0.0950	180,000	162,470	382,369	978,597	2.35	13.3	107.1
EO-76	Complex 8-HfMe2	D	100	200	29	0.0893	443,421	408,133	877,006	2,193,634	2.15	7.1	116.9
EO-77	Complex 8-HfMe2	D	100	200	23	0.0968	606,052	431,408	1,007,789	3,644,389	2.34	5.9	116.7
EO-78	Complex 8-HfMe2	D	100	200	52	0.1381	382,431	273,578	747,387	2,122,246	2.73	6.8	115.5
PE-40	Complex 8-ZrMe2	D	0	75	269	0.0698	37,365	452,003	1,201,189	3,771,707	2.66		135.5
PE-41	Complex 8-ZrMe2	D	0	75	156	0.0659	60,831	420,631	1,095,776	3,419,176	2.61		134.5
PE-42	Complex 8-ZrMe2	D	0	75	213	0.0657	44,417	484,927	1,139,523	3,263,228	2.35		135.8
EO-79	Complex 8-ZrMe2	D	100	75	77	0.0790	147,740	238,243	542,351	1,551,983	2.28	12.8	110.4
EO-80	Complex 8-ZrMe2	D	100	75	66	0.0847	184,800	198,322	501,657	1,696,477	2.53	9.3	109.8
EO-81	Complex 8-ZrMe2	D	100	75	66	0.0736	160,582	224,398	514,885	1,447,314	2.29	10.2	109.4
EO-82	Complex 8-ZrMe2	D	100	200	52	0.0960	265,846	294,557	831,267	2,408,627	2.82	4.6	118.7
EO-83	Complex 8-ZrMe2	D	100	200	54	0.0956	254,933	362,983	933,789	2,852,839	2.57	5.0	120.0
EO-84	Complex 8-ZrMe2	D	100	200	71	0.0995	201,803	406,099	928,022	2,951,729	2.29	3.9*	119.3
CPE-1	Complex 5-HfMe3	D	0	75	78	0.0450	83,077	9,573	16,449	33,108	1.72		129.1
CPE-2	Complex 5-HfMe3	D	0	75	61	0.0473	111,659	9,762	17,350	36,467	1.78		128.9
CPE-3	Complex 5-HfMe3	D	0	75	65	0.0442	97,920	8,608	16,697	35,986	1.94		128.7
CPE-4	Complex 5-HfMe3	M	0	75	1103	0.0328	4,282	15,460	40,655	222,962	2.63		131.6
CPE-5	Complex 5-HfMe3	M	0	75	1121	0.0324	4,162	12,080	27,801	111,535	2.3		131.7
CPE-6	Complex 5-HfMe3	M	0	75	1139	0.0345	4,362	11,865	29,969	135,124	2.53		131.6
CEO-1	Complex 5-HfMe3	D	100	75	83	0.0524	90,911	2,279	4,540	10,438	1.99	28.5	94.0
CEO-2	Complex 5-HfMe3	D	100	75	112	0.0430	55,286	2,214	4,575	11,102	2.07	28.4	93.7
CEO-3	Complex 5-HfMe3	D	100	75	103	0.0452	63,192	2,188	5,002	12,638	2.29	27.5	94.0

Table 1 – *(Cont.)*

Ex#	Pre-Catalyst	Act ID	octene (uL)	C_2 (psig)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	C_8 (wt%)	Tm (°C)
CEO-4	Complex 5-HfMe3	M	100	75	1260	0.0360	4,114	2,236	4,668	10,537	2.09	22.3	120.5
CEO-5	Complex 5-HfMe3	M	100	75	1197	0.0336	4,042	2,943	4,981	9,879	1.69	26.0	106.4
CEO-6	Complex 5-HfMe3	M	100	75	1203	0.0351	4,201	2,292	4,623	10,231	2.02	23.5	106.4
CEO-7	Complex 5-HfMe3	D	100	200	40	0.0511	183,960	4,659	8,799	21,671	1.89	23.5	117.6
CEO-8	Complex 5-HfMe3	D	100	200	37	0.0553	215,222	4,900	8,550	18,347	1.74	26.7	117.7
CEO-9	Complex 5-HfMe3	D	100	200	59	0.0368	89,817	4,302	8,212	19,303	1.91	13.2	118.1
CEO-10	Complex 5-HfMe3	M	100	200	364	0.0275	10,879	3,471	8,370	18,228	2.41	12.2	124.7
CEO-11	Complex 5-HfMe3	M	100	200	339	0.0288	12,234	4,812	9,428	22,136	1.96	18.0	117.9
CEO-12	Complex 5-HfMe3	M	100	200	349	0.0292	12,048	4,886	9,280	19,901	1.9	9.0	125.4

Table 2: Propylene polymerization examples

[0256] General reaction conditions: Total solvent volume including catalyst and activator diluents was 4.1 ml solvent; 1.0 ml propylene; pre-catalyst amount and activator amount is listed in the Table; TnOAl (500 nmol) was used when Act ID D was used; polymerization was conducted at 70°C or 100°C as indicated; Quench was set for the psi loss of 8 psid or for a maximum time of 30 minutes.

Table 2

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (uL)	Tol-uene (uL)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
PP-1	Complex 6-HfMe2	D	0.025	3,895	205	70	345	0.0952	39,736	256,958	443,948	904,618	1.73	114.1
PP-2	Complex 6-HfMe2	D	0.025	3,895	205	70	321	0.0930	41,720	264,941	466,790	987,953	1.76	112.6
PP-3	Complex 6-HfMe2	D	0.025	3,895	205	70	408	0.0920	32,471	273,504	472,089	978,581	1.73	113.2
PP-4	Complex 6-HfMe2	D	0.025	3,895	205	100	1801	0.0601	4,805	95,784	176,656	456,281	1.84	109.4
PP-5	Complex 6-HfMe2	D	0.025	3,895	205	100	926	0.0682	10,606	78,684	149,515	332,573	1.90	109.5
PP-6	Complex 6-HfMe2	D	0.025	3,895	205	100	1801	0.0555	4,438	92,466	169,427	365,876	1.83	109.0
PP-7	Complex 6-HfMe2	M	0.040	0	4099	70	1801	0.0146	730	22,529	35,555	69,871	1.58	
PP-8	Complex 6-HfMe2	M	0.040	0	4099	70	1802	0.0134	669	22,749	36,715	78,973	1.61	
PP-9	Complex 6-HfMe2	M	0.040	0	4099	70	1800	0.0110	550	23,500	34,585	63,669	1.47	
PP-10	Complex 6-HfMe2	M	0.040	0	4099	100	1801	0.0140	700	21,934	38,181	82,554	1.74	
PP-11	Complex 6-HfMe2	M	0.040	0	4099	100	1802	0.0126	629	20,154	34,128	68,905	1.69	
PP-12	Complex 6-HfMe2	M	0.040	0	4099	100	1801	0.0132	660	21,638	34,345	66,979	1.59	
PP-13	Complex 7-HfMe2	D	0.040	3,832	268	70	861	0.0747	7,808	119,298	229,117	585,753	1.92	

Table 2 – *(Cont.)*

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (uL)	Tol-uene (uL)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
PP-14	Complex 7-HfMe2	D	0.040	3,832	268	70	873	0.0813	8,381	139,271	263,830	586,383	1.89	
PP-15	Complex 7-HfMe2	D	0.040	3,832	268	70	628	0.0790	11,322	138,429	264,226	619,574	1.91	139.3
PP-16	Complex 7-HfMe2	D	0.040	3,832	268	100	1801	0.0193	964	45,222	93,808	261,220	2.07	140.9
PP-17	Complex 7-HfMe2	D	0.040	3,832	268	100	1801	0.0285	1,424	45,886	106,112	299,120	2.31	141.3
PP-18	Complex 7-HfMe2	D	0.040	3,832	268	100	1801	0.0307	1,534	60,688	106,672	237,485	1.76	140.9
PP-19	Complex 7-ZrMe2	D	0.040	3,832	268	70	1802	0.0376	1,878	72,516	127,344	257,900	1.76	
PP-20	Complex 7-ZrMe2	D	0.040	3,832	268	70	1802	0.0422	2,108	88,450	145,876	284,013	1.65	
PP-21	Complex 7-ZrMe2	D	0.040	3,832	268	70	1800	0.0590	2,950	78,926	145,427	305,742	1.84	
PP-22	Complex 7-ZrMe2	D	0.040	3,832	268	100	1800	0.0054	270					
PP-23	Complex 7-ZrMe2	D	0.040	3,832	268	100	1800	0.0083	415					
PP-24	Complex 7-ZrMe2	D	0.040	3,832	268	100	1801	0.0093	465					
PP-25	Complex 1-HfCl2	M	0.040	0	4099	70	1801	0.0034	170					
PP-26	Complex 1-HfCl2	M	0.040	0	4099	70	1801	0.0030	150					
PP-27	Complex 1-HfCl2	M	0.040	0	4099	70	1800	0.0014	70					

Table 2 – *(Cont.)*

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (uL)	Tol-uene (uL)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
PP-28	Complex 1-HfCl2	M	0.040	0	4099	100	1801	0.0061	305					
PP-29	Complex 1-HfCl2	M	0.040	0	4099	100	1801	0.0043	215					
PP-30	Complex 1-HfCl2	M	0.040	0	4099	100	1801	0.0042	210					
PP-31	Complex 2-HfCl2	M	0.040	0	4099	70	1801	0.0034	170					
PP-32	Complex 2-HfCl2	M	0.040	0	4099	70	1802	0.0031	155					
PP-33	Complex 2-HfCl2	M	0.040	0	4099	70	1800	0.0014	70					
PP-34	Complex 2-HfCl2	M	0.040	0	4099	100	1801	0.0044	220					
PP-35	Complex 2-HfCl2	M	0.040	0	4099	100	1801	0.0034	170					
PP-36	Complex 2-HfCl2	M	0.040	0	4099	100	1800	0.0032	160					
PP-37	Complex 3-HfCl2	M	0.040	0	4099	70	1800	0.0083	415					
PP-38	Complex 3-HfCl2	M	0.040	0	4099	70	1800	0.0081	405					
PP-39	Complex 3-HfCl2	M	0.040	0	4099	70	1800	0.0055	275					
PP-40	Complex 3-HfCl2	M	0.040	0	4099	100	1800	0.0041	205					
PP-41	Complex 3-HfCl2	M	0.040	0	4099	100	1800	0.0041	205					

Table 2 – *(Cont.)*

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (uL)	Tol-uene (uL)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
PP-42	Complex 3-HfCl2	M	0.040	0	4099	100	1801	0.0039	195					
PP-43	Complex 3-HfMe2	D	0.025	3,895	205	70	1802	0.0036	288					
PP-44	Complex 3-HfMe2	D	0.025	3,895	205	70	1801	0.0045	360					
PP-45	Complex 3-HfMe2	D	0.025	3,895	205	70	1800	0.0051	408					
PP-46	Complex 3-HfMe2	D	0.025	3,895	205	100	1801	0.0006	48					
PP-47	Complex 3-HfMe2	D	0.025	3,895	205	100	1800	0.0008	64					
PP-48	Complex 3-HfMe2	D	0.025	3,895	205	100	1800	0.0007	56					
PP-49	Complex 3-HfMe2	M	0.040	0	4099	70	1800	0.0116	580	1,558	2,868	6,693	1.84	
PP-50	Complex 3-HfMe2	M	0.040	0	4099	70	1801	0.0121	605	1,676	3,068	6,757	1.83	
PP-51	Complex 3-HfMe2	M	0.040	0	4099	70	1800	0.0099	495	1,588	3,063	6,956	1.93	
PP-52	Complex 3-HfMe2	M	0.040	0	4099	100	1801	0.0034	170					
PP-53	Complex 3-HfMe2	M	0.040	0	4099	100	1801	0.0033	165					
PP-54	Complex 3-HfMe2	M	0.040	0	4099	100	1801	0.0034	170					
PP-55	Complex 8-HfMe2	D	0.025	3,895	205	70	1801	0.0431	3,446	53,525	94,270	234,618	1.76	147.0

Table 2 – *(Cont.)*

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (uL)	Tol-uene (uL)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
PP-56	Complex 8-HfMe2	D	0.025	3,895	205	70	1801	0.0487	3,894	51,616	91,898	189,828	1.78	131.1
PP-57	Complex 8-HfMe2	D	0.025	3,895	205	70	1801	0.0609	4,869	57,725	99,554	206,247	1.72	144.6
PP-58	Complex 8-HfMe2	D	0.025	3,895	205	100	1800	0.0073	584					
PP-59	Complex 8-HfMe2	D	0.025	3,895	205	100	1801	0.0089	712					
PP-60	Complex 8-HfMe2	D	0.025	3,895	205	100	1800	0.0086	688					
PP-61	Complex 8-ZrMe2	D	0.025	3,895	205	70	1801	0.0201	1,607	32,654	62,573	131,799	1.92	145.0
PP-62	Complex 8-ZrMe2	D	0.025	3,895	205	70	1801	0.0181	1,447	29,526	61,535	145,773	2.08	
PP-63	Complex 8-ZrMe2	D	0.025	3,895	205	70	1801	0.0244	1,951	33,790	61,757	131,261	1.83	
PP-64	Complex 8-ZrMe2	D	0.025	3,895	205	100	1801	0.0022	176					
PP-65	Complex 8-ZrMe2	D	0.025	3,895	205	100	1801	0.0028	224					
PP-66	Complex 8-ZrMe2	D	0.025	3,895	205	100	1801	0.0030	240					
CPP-1	Complex 5-HfMe3	D	0.025	3,895	205	70	1802	0.0009	72					
CPP-2	Complex 5-HfMe3	D	0.025	3,895	205	70	1802	0.0008	64					
CPP-3	Complex 5-HfMe3	D	0.025	3,895	205	70	1800	0.0017	136					

Table 2 – *(Cont.)*

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (uL)	Tol-uene (uL)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
CPP-4	Complex 5-HfMe3	D	0.025	3,895	205	100	1802	0	0					
CPP-5	Complex 5-HfMe3	D	0.025	3,895	205	100	1800	0	0					
CPP-6	Complex 5-HfMe3	D	0.025	3,895	205	100	1801	0.0007	56					
CPP-7	Complex 5-HfMe3	M	0.040	0	4099	70	1801	0.0015	75					
CPP-8	Complex 5-HfMe3	M	0.040	0	4099	70	1801	0.0014	70					
CPP-9	Complex 5-HfMe3	M	0.040	0	4099	70	1800	0.0017	85					
CPP-10	Complex 5-HfMe3	M	0.040	0	4099	100	1800	0.0017	85					
CPP-11	Complex 5-HfMe3	M	0.040	0	4099	100	1801	0.0020	100					
CPP-12	Complex 5-HfMe3	M	0.040	0	4099	100	1800	0.0020	100					

[0257] Overall, catalyst compounds of the present disclosure having phenolate-heterocyclic-amido ligands coordinated to group 4 transition metals can form catalyst compounds having a five-membered ring in addition to a seven-membered ring. Catalyst compounds of the present disclosure can provide high molecular weight polymers at high catalyst activity useful for commercial polymer production.

[0258] 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.

[0259] 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 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.

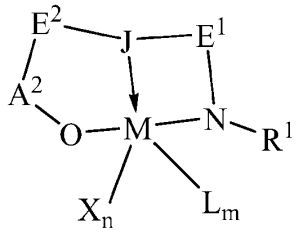
[0260] All documents described herein are incorporated by reference herein, including any priority documents and or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term “comprising” is considered synonymous with the term “including” 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,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

[0261] 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 of the present disclosure.

IN THE CLAIMS

1. A catalyst comprising:

a chemical structure represented by Formula (**I**):



(**I**)

wherein:

M is a group 3, 4, 5 or 6 transition metal or lanthanide metal;

A^2 is selected from the group consisting of unsubstituted aryl, substituted aryl, unsubstituted heteroaryl, and substituted heteroaryl group;

J is a heterocyclic Lewis base;

E^1 is selected from the group consisting of unsubstituted hydrocarbyl, substituted hydrocarbyl, unsubstituted silylcarbyl, and substituted silylcarbyl;

E^2 is selected from the group consisting of unsubstituted hydrocarbyl, substituted hydrocarbyl, unsubstituted silylcarbyl, and substituted silylcarbyl;

J and E^2 are optionally fused to form one or more unsubstituted hydrocarbyl rings, substituted hydrocarbyl rings, unsubstituted heterocyclic rings, or substituted heterocyclic rings;

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 4 or less;

R^1 is selected from the group consisting of unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, unsubstituted C_1-C_{40} heteroatom-containing group, and substituted C_1-C_{40} heteroatom-containing group;

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

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

2. The catalyst of claim 1, wherein L is independently selected from the group consisting of ethers, amines, phosphines, thioethers, and esters.

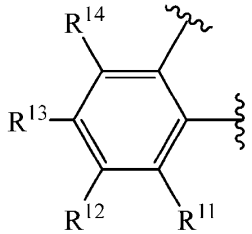
3. The catalyst of claim 2, wherein L is independently selected from Et_2O, MeO^tBu, Et_3N, $PhNMe_2$, $MePh_2N$, tetrahydrofuran, and dimethylsulfide.

4. The catalyst of claim 1, wherein X is independently selected from the group consisting of methyl, benzyl, trimethylsilyl, neopentyl, ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate, dimethylamido, diethylamido, dipropylamido, and diisopropylamido.

5. The catalyst of any of claims 1 to 4, wherein E^1 is selected from the group consisting of $C(R^{15})(R^{16})$ and $Si(R^{15})(R^{16})$, wherein R^{15} and R^{16} are independently selected from the group consisting of hydrogen, C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, and C_1-C_{40} heteroatom-containing group.

6. The catalyst of any of claims 1 to 5, wherein R^1 is selected from the group consisting of methylphenyl, dimethylphenyl, trimethylphenyl, tetramethylphenyl, pentamethylphenyl, ethylphenyl, diethylphenyl, triethylphenyl, isopropylphenyl, diisopropylphenyl, triisopropylphenyl, *tert*-butylphenyl, di-*tert*-butylphenyl, tri-*tert*-butylphenyl, methylisopropylphenyl, methyl-*tert*-butlyphenyl, ethylisopropylphenyl, ethyl-*tert*-butylphenyl, methylnaphthalenyl, ethylnaphthalenyl, isopropylnaphthalenyl, and *tert*-butylnaphthalenyl.

7. The catalyst of any of claims 1 to 6, wherein A^2 is represented by the structure:



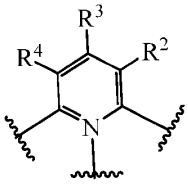
wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, substituted C_1-C_{40} heteroatom-containing group, and unsubstituted C_1-C_{40} heteroatom-containing group.

8. The catalyst of claim 7, wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently selected from the group consisting of hydrogen, substituted C_1-C_{30} hydrocarbyl, and unsubstituted C_1-C_{30} hydrocarbyl.

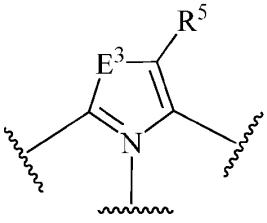
9. The catalyst of claim 7, wherein R^{11} is selected from the group consisting of unsubstituted C_1-C_{30} alkyl, substituted C_1-C_{30} alkyl, unsubstituted C_5-C_{30} cycloalkyl, and substituted C_5-C_{30} cycloalkyl, unsubstituted C_1-C_{30} heteroatom-containing group, substituted C_1-C_{30} heteroatom-containing group, unsubstituted C_6-C_{30} aryl, and substituted C_6-C_{30} aryl.

10. The catalyst of claim 8, wherein R^{13} is unsubstituted C_1-C_{20} hydrocarbyl.

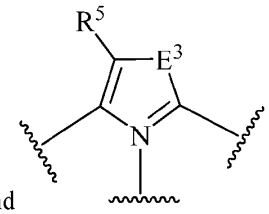
11. The catalyst of any of claims 1 to 10, wherein J is selected from the group consisting of



(IA),



(IB), and



(IC).

wherein E^3 is selected from the group consisting of O, S, and $N(R^{10})$, each of R^2, R^3, R^4, R^5 and R^{10} is independently selected from the group consisting of hydrogen, unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, unsubstituted C_1-C_{30} heteroatom-containing group, substituted C_1-C_{30} heteroatom-containing group, wherein one or more of R^2 and R^3 or R^3 and R^4 may be joined to form one or more hydrocarbyl rings, substituted hydrocarbyl rings, unsubstituted heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms.

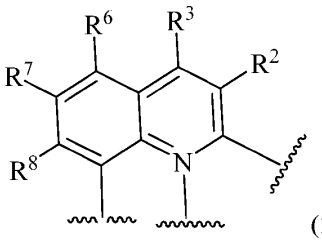
12. The catalyst of claim 11, wherein each R^2, R^3, R^4, and R^5 is independently selected from the group consisting of hydrogen, unsubstituted C_1-C_{40} hydrocarbyl, and substituted C_1-C_{40} hydrocarbyl.

13. The catalyst of claims 1 to 12, wherein E^2 is selected from the group consisting of $C(R^{25})(R^{26})$, $Si(R^{25})(R^{26})$, and $C{=}C(R^{25})(R^{26})$, wherein R^{25} and R^{26} are independently selected from the group consisting of hydrogen, unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, unsubstituted C_1-C_{40} heteroatom-containing group, and substituted C_1-C_{40} heteroatom-containing group, wherein one or more of R^{25} and R^{26} may be joined to

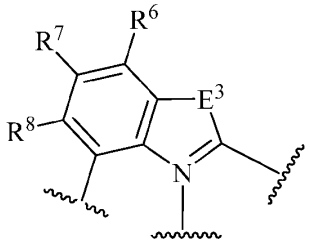
form one or more unsubstituted hydrocarbyl rings, substituted hydrocarbyl rings, unsubstituted heterocyclic rings, or substituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms.

14. The catalyst of any of claims 1 to 13, wherein E^2 is joined to J to form a fused ring structure selected from the group consisting of unsubstituted hydrocarbyl ring, substituted hydrocarbyl ring, unsubstituted heterocyclic ring, and substituted heterocyclic ring.

15. The catalyst of claim 14, wherein the fused ring structure is represented by Formula **(1D)** or **(1E)**:



(1D) or



(1E)

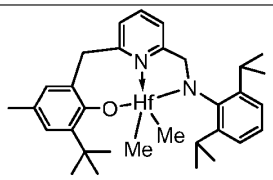
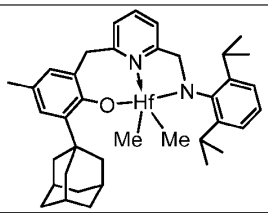
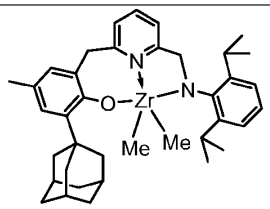
wherein:

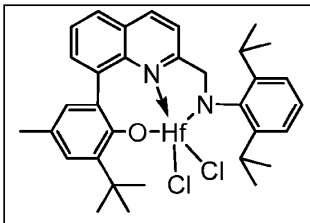
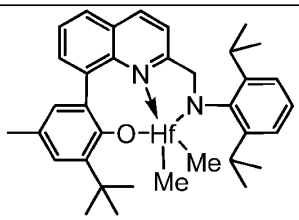
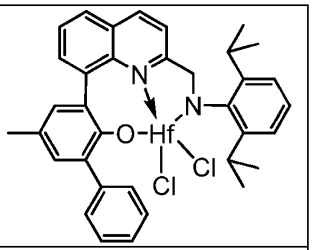
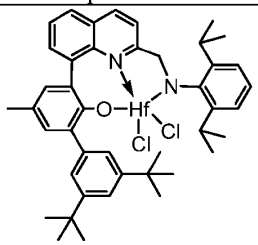
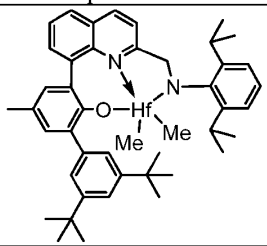
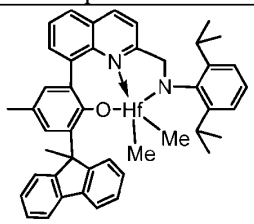
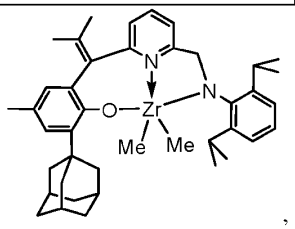
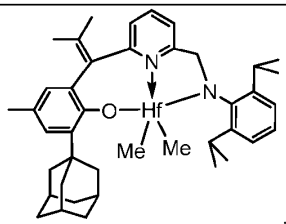
E^3 is selected from the group consisting of O, S, and $N(R^{10})$, wherein each R^2, R^3, R^4, R^5 R^6, R^7, R^8, and R^{10} is selected from the group consisting of hydrogen, unsubstituted C_1-C_{40} hydrocarbyl, substituted C_1-C_{40} hydrocarbyl, a heteroatom, substituted C_1-C_{40} heteroatom-containing group, and substituted C_1-C_{40} heteroatom-containing group.

16. The catalyst of claim 15, wherein each R^2, R^3, R^4, R^5 R^6, R^7, and R^8 is hydrogen.

17. The catalyst of claim 15, wherein one or more of R^2 and R^3, R^3 and R^4, R^6 and R^7, R^7 and R^8, and R^3 and R^6 are fused together to form unsubstituted hydrocarbyl ring or substituted hydrocarbyl ring.

18. The catalyst of claim 1, wherein the catalyst is selected from the group consisting of:

		
Complex 6-HfMe2	Complex 7-HfMe2	Complex 7-ZrMe2

		
Complex 1-HfCl2	Complex 1-HfMe2	Complex 2-HfCl2
		
Complex 3-HfCl2	Complex 3-HfMe2	Complex 4HfMe2
 , and	 .	
Complex 8-ZrMe2	Complex 8-HfMe2	

19. A process for producing polyolefins, the process comprising:

polymerizing one or more C_2-C_{20} alpha-olefin monomers by introducing the one or more C_2-C_{20} alpha-olefin monomers with a catalyst system comprising an activator and the catalyst compound of any of claims 1-18 into a reactor to form a polyolefin polymer.

20. The process of claim 19, wherein the one or more C_2-C_{20} alpha-olefin monomers comprises ethylene.

21. The process of claim 19, wherein the one or more C_2-C_{20} alpha-olefin monomers comprises propylene.

22. The process of claims 19, wherein the one or more C_2-C_{20} alpha-olefin monomers comprises ethylene an a C_3-C_{12} alpha-olefin.